COPPER(II) COMPLEXES OF N-ACYLHYDRAZINE

AND

POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE LIGANDS

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CONTENTS

Page

CHAPTER 1 - INTRODUCTION

CHAPTER 2 - COMPLEXES OF HYDRAZINE-CONTAINING LIGANDS

CHAPTER 3 - MULTIDENTATE LIGANDS CONTAINING HYDRAZINE

CHAPTER 4 - THE STEREOCHEMISTRY AND VISIBLE REGION SPECTRA OF COPPER(II) COMPLEXES

COPPER(II) COMPLEXES OF N-ACYLHYDRAZINE AND POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE LIGANDS.

SUMMARY

The N-acylhydrazine grouping, R.CO.NH.NH_2, as exemplified by N-benzoylhydrazine, N-acetylhydrazine and N-propionylhydrazine can coordinate in the keto form to copper(II), giving rise to bis-chelates of the type L_2CuX_2 ($X = Cl^-$, NO_3^-, ClO_4^-, $\frac{1}{2}SO_4^{2-}$) containing five-membered rings. In addition to these compounds displaying effectively the normal coordination number of four for copper(II), N-benzoylhydrazine complexes of the type L_3CuX_2 and L_4CuX_2 were isolated and some information on the manner in which the ligands are coordinated was obtained from visible and infrared spectroscopy.

The isopropylidene derivatives of the above N-acylhydrazines are also able to form keto complexes. A proton can be removed from these ligands giving rise to neutral bis- complexes. It was found that in these complexes the coordination number of copper(II) could be expanded to five (or six) by the formation of monoaquo and mono- or bis- heterocyclic base adducts. Equilibrium constants for the addition of pyridine, 4-methylpyridine and 2-methylpyridine to bis-(N-isopropylidene-N'- benzoylhydrazino)copper(II) and bis-(N-isopropylidene-N'- propionylhydrazino)copper(II) in benzene solution were measured

spectrophotometrically and indicated that the addition of one molecule of base is mainly responsible for large shifts in the visible region spectra.

The visible region spectra of the above classes of chelate were determined and used as a guide to the stereochemistry of the copper(II) complexes of the series of N,N-diacyldihydrazine ligands, $(CH_2)_n(CONHNH_2)_2$, from n = 0 to 10. As the value of n increases in such a series, the stereochemistry of the chelates formed would be expected to vary from a bis-bidentate polymeric structure through a tridentate to a quadridentate type structure.

Three series of chelates were examined.

(1) Complexes of N,N-diacyldihydrazine ligands coordinated in the keto form. The lower members of the series (n = 0,1) form complexes of the type $LCuX_2.0.5H_2O$ ($X = Cl^-$, $\frac{1}{2}SO_4^{2-}$) from acid solution. Such complexes could have a polymeric structure, but the coordination of anions or water molecules would appear likely, producing monomers. Preparations from neutral solution resulted in the spontaneous liberation of hydrogen ions, producing precipitates of somewhat variable composition but approximating to the formulation $L_2Cu_3X_2.xH_2O$. When n = 2 to 6, $LCuX_2.0.5$(or 1)H_2O complexes were produced and from n = 7 to 10, anhydrous complexes were obtained. For the higher members of the series $L_3Cu_2X_4$ type complexes are apparently more stable.

(2) Complexes of N,N-diisopropylidene-N',N'-diacyldihydrazine ligands coordinated in the keto form. When n = 0, the complex $LCu_2Cl_4.0.5H_2O$ was formed. The remaining members (n = 1 to 10) formed $LCuX_2.0.5$(or 1)H_2O type complexes. Coordination of halide in the fifth or sixth position of copper(II) is a feature of this class of complex and gives rise to a band at approximately 25,000 cm^{-1} which is absent in the perchlorate complexes. A spectrophotometric study of the n = 4 complex indicated that in pure water, acetone is hydrolysed from the molecule, while in nearly pure acetone the coordination of chloride ion has a large perturbing effect on the spectrum.

(3) Complexes of N,N-diisopropylidene-N',N'-diacyldihydrazine ligands coordinated in the enol form.

When n = 0, a polymeric complex LCu was obtained. From n = 2 to 4, $LCu.H_2O$ complexes were formed. The similarity of the visible spectra of the n = 3 and 4 complexes to the anhydrous N-isopropylidene-N'-acylhydrazine complexes indicated that water was not coordinated in the apical positions of the copper(II) ion. When n = 5 or 6, both anhydrous complexes and monohydrates containing apically coordinated water were obtained. A structure in which the ligands are bis-bidentate, forming dimers, would appear to be in best agreement with the spectra of this series of complexes. For the n = 4 complex, the formation of a monopyridinate showing the spectral effects of apically coordinated pyridine would preclude the possibility of a tridentate configuration. Further information on this problem was obtained by examination of the spectra of some complexes of tridentate ligands containing pyridine in the fourth coordination position.

In discussing the effects of solvents on the visible spectrum of bis-(acetylacetonato)copper(II), it was suggested that the changes may best be accounted for by resolution of the spectra into only two Gaussian components. Such a procedure would indicate d_{z^2} to have the highest energy (for positive hole transitions) in a square planar configuration, and to be most affected by apical coordination of solvent molecules.

To the best of my knowledge this thesis contains no material previously published or written by another person, nor any material previously submitted for a degree or diploma in any University, except where due reference is made in the text.

ABBREVIATIONS

N-acylhydrazines

BH	N-benzoylhydrazine
AH	N-acetylhydrazine
PH	N-propionylhydrazine
SALH	N-salicoylhydrazine

Polymethylene-N,N-diacyldihydrazines

OXDH	oxalyldihydrazine
MADH	malonyldihydrazine
SUDH	succinyldihydrazine
GLDH	glutaryldihydrazine
ADDH	adipoyldihydrazine
PMDH	pimeloyldihydrazine
SRDH	suberoyldihydrazine
AZDH	azelaoyldihydrazine
SBDH	sebacoyldihydrazine
DDDM	dodecanedioyldihydrazine

Tridentate ligands.

SALBH	salicylaldehydebenzoylhydrazone
ACACBH	acetylacetonebenzoylhydrazone

IP	designates the isopropylidene derivatives of monoacylhydrazines or the diisopropylidene derivatives of diacyldihydrazines.

CHAPTER 1

INTRODUCTION

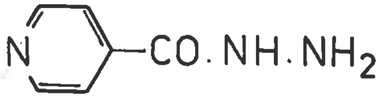
(1.1) HISTORICAL BACKGROUND.

The ability of aliphatic and aromatic N-acylhydrazines, R.CO.NHNH$_2$, to act as bidentate chelating agents has not been widely investigated. From time to time, incidental preparations of complexes of these ligands have appeared in the literature since the first reported synthesis of bis-(N-benzoylhydrazine)copper(II) sulphate dihydrate by Aggarwal, Darbari and Ray[1] in 1929. Jensen and Bak[2] prepared the anhydrous form of this complex and the corresponding N-acetylhydrazine complex. Tris-(N-acetylhydrazine)nickel(II) sulphate was reported by Jensen and Ranke-Madsen[3].

Since these earlier preparations there have been few instances in which complexes of this type have been examined. In this Department we have been interested to carry out a systematic investigation of the complexes of N-acylhydrazines with copper(II)[4,5], cobalt(II)[6] and nickel(II)[7], the results of which will be discussed in Chapter 2 of this thesis.

There are two groups of hydrazine-containing ligands which have, however, been extensively investigated. Firstly, Sacconi and co-workers in the last decade have examined the nickel(II) chelates formed by the condensation products of N-acylhydrazines with a variety of aldehydes and ketones. Many complexes were prepared in which the steric requirements of the acylhydrazones used suggested that they were acting as tridentate and quadridentate ligands. In addition, some complexes have been isolated which are described as binuclear species and others in which the relative positions of the donor atoms in the ligand is such that they cannot all be bonded to a single metal ion. In view of the general insolubility of these latter complexes and the molecular arrangement of the ligands, it is concluded that they can only be polymeric in nature.

The study of N-isonicotinoylhydrazine (I) has provided the second main area of research.



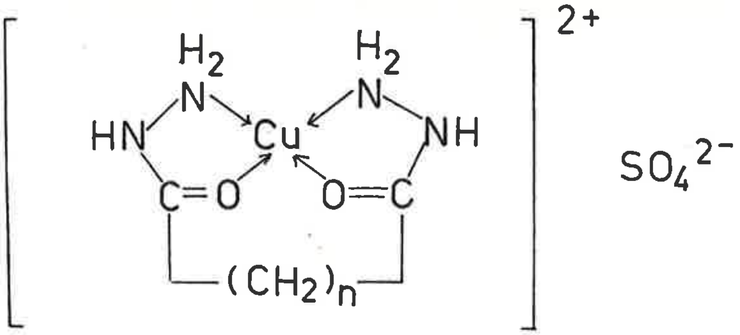
(I)

This compound has been used with considerable success as an anti-tubercular agent for a number of years. The discovery that the addition of copper(II) increased the in vitro tuberculostatic activity tenfold[8] prompted investigation of the coordinating properties of this ligand and related compounds in an endeavour to determine whether chelate formation is important in its mode of action. The results of this research, together with the work of Sacconi, will be reviewed in greater detail in Chapters 2 and 3.

(1.2) COPPER(II) COMPLEXES OF POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE LIGANDS.

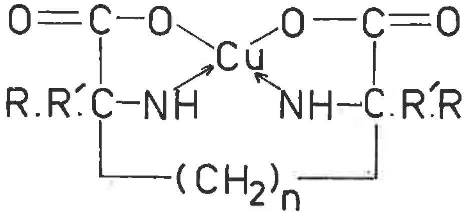
The bidentate acylhydrazine grouping can be attached easily to aliphatic carbon atoms, consequently it is possible to prepare molecules containing two or more such groups. In 1936, Jensen and Bak[2] published a paper which described the preparation of the copper(II) complexes of a series of polymethylene-N,N-diacyldihydrazines, $(CH_2)_n(CONHNH_2)_2$ from n = 0 to 8. The authors reported that this series of ligands gave rise to two distinct classes of complex. The lower members of the series, oxalyldihydrazine* (n = 0) and malonyldihydrazine* (n= 1) produced precipitates with copper(II) sulphate which were insoluble and strongly hydrated and which appeared to have indefinite composition. These precipitates contained between one and two ions of copper per dihydrazide molecule and it was thought doubtful if they were definite compounds. On the other hand, the dihydrazides from n = 2 to n = 8 produced compounds containing copper and dihydrazide in the ratio 1:1. It was proposed that in these latter compounds the dihydrazide molecule would occupy the four coordination positions of the copper ion giving rise to complexes of type (II) in agreement with the fact that the monoacylhydrazines formoyl-, acetyl-, benzoyl- and phenylacetyl-

* Trivial names for the members of this series will be used henceforth.



(II)

produced bis- complexes in which each hydrazide molecule should occupy two coordination positions. Molecular weight determinations on the complexes n = 3 and 4 were attempted by the depression of freezing point of anhydrous formic acid, the only solvent found in which these compounds were readily soluble. However, no decision between a monomeric or dimeric formulation could be made and it was proposed that a monomeric formula was most probable by analogy with complexes of the alkylene-bis-imino acid series (III)[9] and the salicylaldimine complexes (IV) of Pfeiffer et al,[10] which have been found to be monomeric. The dihydrazine ligands differ from these in that the methylene chain must span a much greater distance before a stable quadridentate structure is possible.



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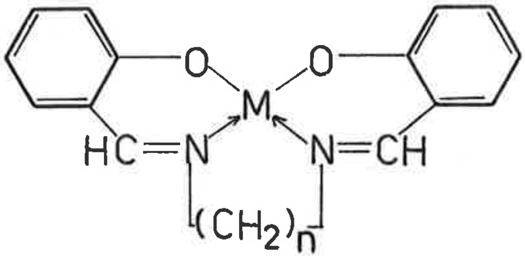

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(1.3) POSSIBLE MODES OF COORDINATION IN POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE COMPLEXES.

As pointed out by Jensen and Bak, it is understandable on steric reasons why the lower members of the dihydrazine series do not form complexes of the same type as the other members. However, it will be realised that the situation is somewhat more complicated than the proposal of these authors.

Examination of models* of the dihydrazide ligands shows that the length of the methylene chain is extremely important in determining the nature of the complexes which may be formed. Figure 1.1 shows diagramatically the manner in which models indicate that the dihydrazide ligands could be coordinated about a metal ion with square planar symmetry such as copper(II). It can be seen that three basic situations arise as the series of ligands is ascended.

Firstly, the lower members ($n = 0$ to 2) should give rise only to polymeric complexes in which the ligand acts as a bis-bidentate chelating agent (figure 1.1-ii). Provided the end groups of such a polymer are both either dihydrazide or copper, the ratio ligand : copper will range from 2 : 1 (or 0.5 : 1 respectively) to 1 : 1 as the number of monomeric units tends to infinity. Relying on normal analytical techniques to determine this ratio, any polymer with more than approximately fifty units (i.e. 50 : 49 or 50 : 51) would effectively analyse for a 1 : 1 ratio. For practical reasons it would be impossible to determine the degree of polymerisation with any certainty in a polymer containing more than about ten units. Co-

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* Models of the complexes were constructed using Leybold atomic models.

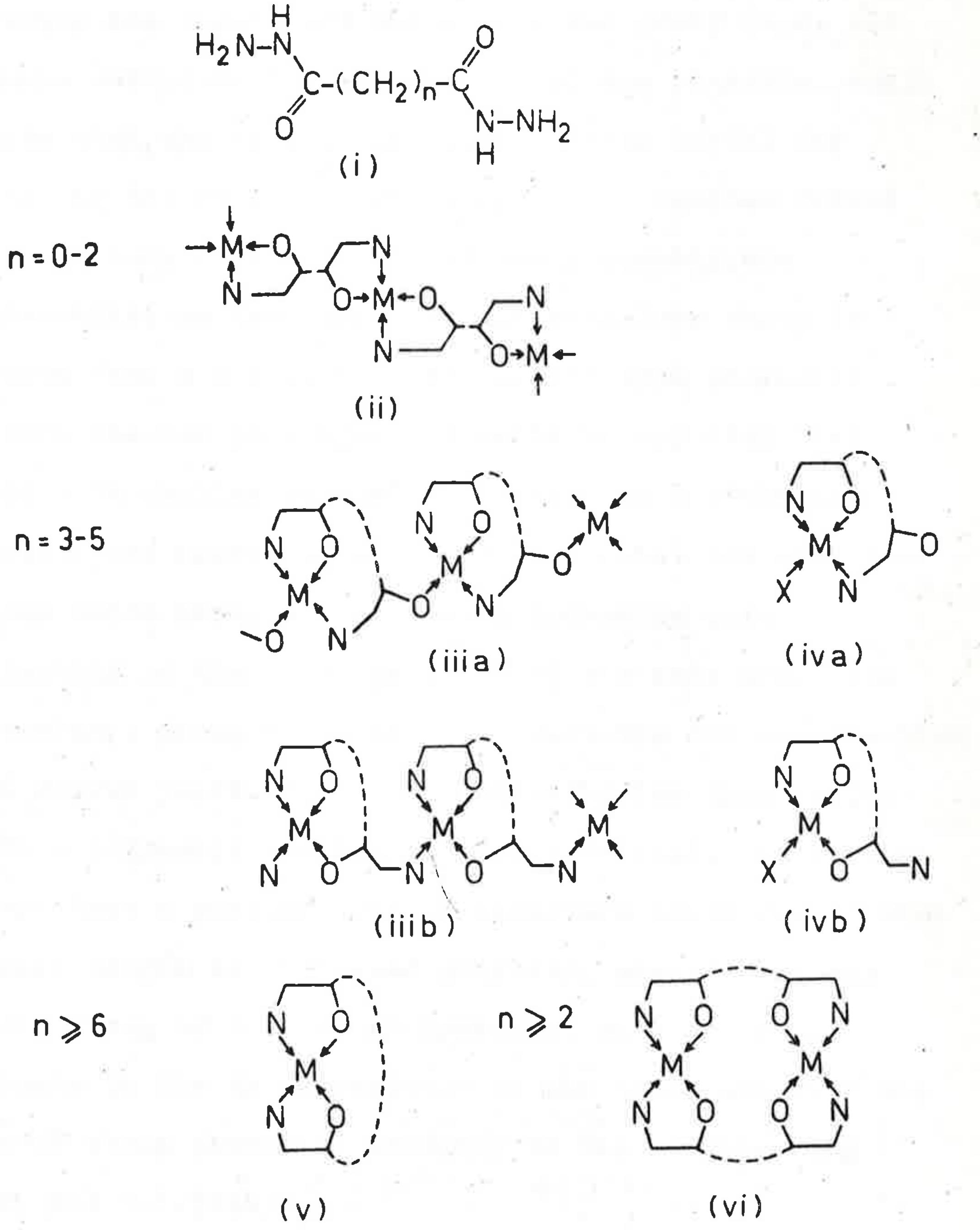

FIGURE 1.1. Possible modes of coordination of the polymethylene-N,N-diacyldihydrazine series of ligands of general formula (i). The polymethylene chain is represented by a dashed line.

precipitation of ligand or metal not incorporated in the polymeric chain, coupled with the fact that polymers containing one ligand and one copper end group (i.e. all oligomers analysing for a 1 : 1 ratio) are possible, would indicate that analysis is not particularly useful for elucidating the nature of any polynuclear complex formed unless its composition is fortuitously unambiguous.

Secondly, as the length of the methylene chain is increased from n = 3 to 5, a tridentate-type polymeric structure becomes possible. It would be expected that ligands with smaller values of n within this group could coordinate one hydrazide grouping to a metal ion with the terminal amino group of the second hydrazide unit coordinating in the third position of the same ion. The free carbonyl group would then be available for coordination in the fourth position of a neighbouring ion thus giving rise to a polymeric complex (figure 1.1-iiia). It is also apparent that a similar type of structure could result when the chain length is increased slightly, except that the carbonyl group of the second hydrazide unit could now coordinate in the third position of the metal ion with the hydrazine group providing bridging to the neighbouring ion (figure 1.1-iiib).

An alternative structure of the complexes formed by this second group of ligands is also possible. Preparations carried out in coordinating solvents or of complexes containing coordinating anions could result in the fourth coordination position being filled by a monodentate group, thus producing a monomeric complex in which the dihydrazide is tridentate and has either a non-coordinated carbonyl (figure 1.1-iva) or amino group (figure 1.1-ivb).

The third group of ligands, from n = 6 upwards, would appear from consideration of the models to be the only ligands which could give rise to quadridentate complexes as proposed by Jensen and Bak. It is apparent that for n = 6 or 7 the restricted length of the methylene chain means that a cis-quadridentate structure (figure 1.1-v) is the most likely possibility, while cis or trans isomers could be formed with ligands in which n = 10 or greater.

There is also the possibility that a bis-bidentate structure (figure 1.1-vi) could be formed from ligands where n is greater than 2. Evidence that a complex of this type is important in the 2,7-diaminosuberic acid - copper(II) system has been presented[11] (see Chapter 3).

(1.4) RESEARCH AIMS.

As a result of the above observations on the molecular models of square planar polymethylene-N,N-diacyldihydrazine complexes, it was decided to reinvestigate the work of Jensen and Bak to determine whether the expected changes in stereochemistry, as the series of ligands was ascended, could be observed and correlated with some property of the complexes. It is realised that models will not allow an accurate prediction of the values of n at which stereochemical changes should occur, but rather serve to illustrate the importance of the length of the methylene chain in determining the type of complex which could be formed. The metal ion chosen was copper(II) in view of the predominant characteristic of this ion to form essentially square planar complexes. Conveniently, copper(II) complexes are quite stable, as indicated by the position of this ion in the Irving-Williams series[12].

The different coordination environments suggested by the molecular models would be expected to affect the electronic transitions of copper(II). Thus it was decided that a study of the visible spectra of the dihydrazide series of complexes might provide a diagnostic tool whereby the stereochemical changes could be observed. It is felt that a review of the spectra and stereochemistry of copper(II) complexes is pertinent and this will be presented in Chapter 4.

Owing to the very slight solubility in most solvents displayed by the sulphate complexes of the dihydrazide series, the study of these compounds in solution was precluded. Hence it was proposed to investigate the complexes containing anions other than sulphate in the hope that they might prove to be sufficiently soluble to allow a conductometric investigation and perhaps be suitable for molecular weight determinations. Consequently, members of the chloride and perchlorate series were examined but in each case presented difficulties other than solubility problems. In the presence of chloride ions, copper(II) tends to catalyse the oxidation of hydrazine from N-acylhydrazine ligands (see Chapter 2) reducing part of the copper(II) present to the copper(I) state, accompanied by the liberation of nitrogen. Thus, although the chloride complexes decompose relatively slowly in the solid state, aqueous solutions of these compounds are stable only for short periods of time.

The perchlorate complexes do show a much increased solubility compared with the sulphate compounds. Despite this, a serious drawback in handling these compounds is their explosive nature. While the higher members of the series explode only when heated and appear to be quite stable to mulling techniques, the adipoyldihydrazine copper(II) perchlorate ($n = 4$) complex proved to be much more sensitive. A quantity of this compound, estimated to be less than one gram, detonated violently when the crystals were being crushed in preparation for drying, resulting in severe damage to the author's hands and necessitating the amputation of four phalanges. In view of the dangerous nature of these compounds it was decided to abandon any further investigation of them.

The various ways in which the mono-N-acylhydrazine grouping is able to coordinated will be discussed in Chapter 2. In addition to coordination of the ligands in the keto form, giving rise to charged complexes, coordination can occur via the enol form of the ligand. This process gives rise to a neutral complex where the effective charge of the metal ion has been neutralised by the ligand. The condensation product of an N-acylhydrazine with acetone is also able to coordinate in both of the above ways. Consequently, it was of interest to determine whether the dihydrazide series of ligands produced the expected changes in stereochemistry when coordinated in these alternative forms. For purposes of comparison, the study of the copper(II) complexes of N-benzoyl-, N-acetyl- and N-propionyl- hydrazines[4,5] was extended to provide more information on the typical complexes formed by the N-acylhydrazine grouping.

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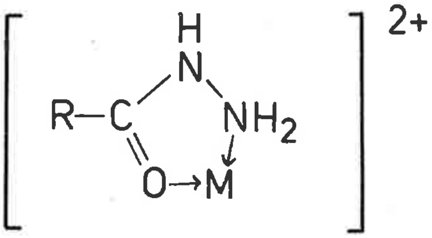
CHAPTER 2

COMPLEXES OF HYDRAZINE-CONTAINING LIGANDS.

(2.1) COMPLEX FORMATION WITH MONOACYLHYDRAZINE LIGANDS.

Earlier work on complexes containing hydrazine itself has been reviewed by Audrieth and Ogg.[1a] The ligand has been shown to be monodentate in solution[2,3], indicating that the formation of three-membered rings with both nitrogen atoms coordinated is unlikely. It is considered probable that in many of its solid complexes, hydrazine acts as a bridging group giving rise to polymeric structures.[4,5] These compounds will not be further discussed since complexes of organic ligands containing hydrazine are of primary interest here.

The earlier preparations of complexes containing N-acylhydrazines have been mentioned in section 1.1. It is apparent from the stoichiometry of these complexes that the ligand is coordinated through the terminal amino nitrogen atom and the carbonyl oxygen atom giving rise to the five-membered chelate ring system (V), containing the



(V)

keto form of the ligands. Some evidence for the keto formulation has been presented by Nagano et al.[6,7] from an infrared study of N-benzoylhydrazinedichlorocopper(II) and N-benzoylhydrazinedichlorocadmium(II).

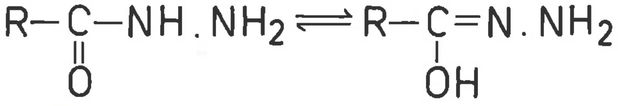
Recently, as part of an investigation into the complexing properties of the N-acylhydrazine grouping, chelates of N-benzoylhydrazine (BH) with cobalt(II), nickel(II) and copper(II) have been synthesised and their visible absorption spectra examined.[8] When prepared from neutral solutions, cationic chelates are formed displaying the typical coordination numbers of the metal ions. The tris-(N-benzoylhydrazine)cobalt(II) and nickel(II) complexes crystallize with water molecules, the number varying with the anion, so that presumably they occupy lattice sites and are not coordinated.

For each of the cations $(BH)_3Co^{2+}$ [8], $(BH)_3Ni^{2+}$ [8] and $(BH)_2Cu^{2+}$ [9], the visible spectra indicate that the ligand is placed between water and ammonia in the spectrochemical series, as expected from the keto formulation. The spectra of the cobalt(II) and nickel(II) compounds show good agreement with band positions predicted from the Orgel diagrams,[10] and magnetic moments are in agreement with an octahedral configuration of these complexes.

Further reports in the literature of the formation of keto complexes with N-acylhydrazines are few. N-salicoylhydrazine has been used for the quantitative determination of palladium, weighed as the insoluble bis-complex dichloride or sulphate.[11]

The possibility of keto-enol tautomerism in N-acylhydrazines has been indicated by a number of authors.[12,13] Probably the best evidence for the existence of the enol form (VI) is that the monosodium salt of N-benzoylhydrazine has been isolated.[14]

Some evidence for this process has also been obtained from a study of the ultraviolet spectra of these compounds in solutions of varying pH,[15] and dissociation constants have been measured.[15,33]



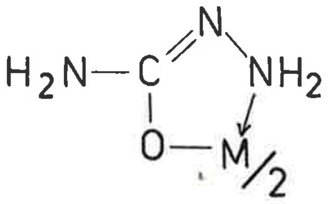
$$R-\underset{\underset{O}{\|}}{C}-NH.NH_2 \rightleftharpoons R-\underset{\underset{OH}{|}}{C}=N.NH_2$$

(VI)

The ligands in this form should give rise to neutral complexes with metals where the number of coordinated ligands is equivalent to the charge on the metal ion. With N-benzoylhydrazine, the complexes $(BH)_3Co$[16] and $(BH)_2Cu$ (this thesis, Chapter 7) have been isolated in an impure state. Both complexes are insoluble and difficult to purify. It is probable that the reducing properties of the ligand are responsible for the difficulty in obtaining pure products (see section 2.2). The complexes of N-isonicotinoylhydrazine appear to belong to this category (section 2.3), where the heterocyclic nitrogen atom may aid in enolisation by acting as a proton acceptor.[21]

Neutral complexes of other hydrazine-containing ligands.

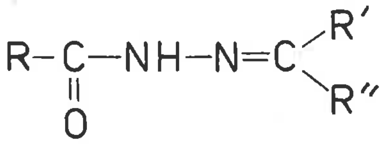
have been reported. Thus, Jensen[17] has investigated many metal complexes of thiosemicarbazide and semicarbazide which form neutral complexes of type (VII) as well as



(VII)

cationic complexes. Chernyaev[18] has isolated neutral complexes of dithiocarbazic acid and related compounds with platinum(II). Hydrazinecarboxylic acid forms neutral nickel(II) complexes.[19]

The condensation products of N-acylhydrazines with aldehydes and ketones (VIII) readily form neutral complexes,



(VIII)

presumably because the enol form is stabilised by the formation of a conjugated system. The sodium salt of N-isopropylidene-N'-acetylhydrazine is easily prepared.[20] Diamantis[21] has reported the isolation of bis-(N-isopropylidene-N'-benzoylhydrazine)copper(II) and the corresponding N-acetylhydrazine complex has been obtained as a monohydrate.[22] Further studies on these complexes are reported in Chapter 7. Both are readily soluble in organic solvents, however the corresponding bis-(N-benzoylhydrazine) complex of cobalt(II) was obtained as an insoluble mono- or possibly dihydrate.[16] This complex forms a crystalline dipyridinate, the visible spectrum and magnetic moment of which indicate an octahedral configuration.[8]

Bis-(N-isopropylidene-N'-benzoylhydrazine)nickel(II) is a rather interesting compound in that two forms have been isolated, one red and diamagnetic, the other green and paramagnetic.[23] The solution spectra and cryoscopic determination of the molecular weight in benzene indicate an equilibrium between the two forms. It would appear probable that polymerisation of the monomeric red, square planar form occurs, resulting in an octahedral configuration for the green form, in an analogous manner to trimeric bis-(acetylacetonato)nickel(II).[24] Further work is continuing in an endeavour to elucidate the nature of this complex.[25]

Ohta[26] has reported the preparation of a number of copper(II) and nickel(II) complexes of N-benzoylhydrazine condensed with a series of aliphatic aldehydes of varying chain length from acetaldehyde to n-decanal. All the ligands are reported to give rise to square planar bis-complexes.

There is evidence to suggest that ligands represented by (VIII) can also coordinate in the keto form in an analogous manner to the uncondensed parent compounds. A complex analysing for bis-(N-isopropylidene-N'-benzoylhydrazine)copper(II) dichloride dihydrate has been prepared[21] and the corresponding bis- cobalt(II) dichloride complex is also formed.[16] Since complexes of this type, together with the free ligand, contain only one N-H group, the presence or absence of this group should be detectable by infrared spectroscopy, and provide evidence for the state of the ligand apart from that suggested by the stoichiometries of the complexes. An investigation along these lines has now been carried out (see Chapters 6 and 7) and confirms the suggested mechanism for enolisation.

(2.2) REDUCING PROPERTIES OF N-ACYLHYDRAZINES.

The reducing properties of hydrazine are well known. Depending on the conditions, copper(II) is easily reduced to copper(I) or to the metal.[1b]

With N-acylhydrazines, reduction of copper(II) does not normally occur unless the solutionsare made strongly alkaline. In the presence of chloride ion, however, some unusual effects have been observed.[22] Although the keto complex $(BH)_2CuCl_2$ crystallizes from cold aqueous solutions of N-benzoylhydrazine and copper(II) chloride, this ligand and also N-acylhydrazine in hot solutions produce complexes analysing for the stoichiometry $(ligand)_2Cu_2Cl_3$. Evolution of nitrogen occurs and from the BH reaction mixture N,N'-dibenzoylhydrazine can be isolated. Magnetic measurements on the complexes indicate that they contain the trichlorocopper(I) anion. By varying the preparation conditions, or by reducing copper(II) with sulphur dioxide in the presence of BH in the cold, the complex $(BH)_2CuCl_2 \cdot 3CuCl$ crystallizes.

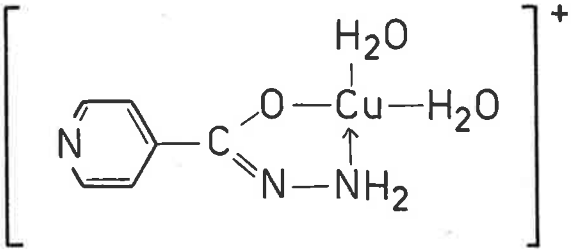
The suggested formulation of these complexes would necessitate the ligand being coordinated in the keto form. Further evidence for this has now been obtained from a study of the solid state visible absorption spectra, the results of which are presented in section 5.3.

The observation that N,N'-dibenzoylhydrazine was produced under the conditions outlined above has led to an investigation of the benzoylating properties of BH.[27] Oxidation by persulphate has been found to be catalysed by trace amounts of copper(II); when carried out in the presence of amines such as p-toluidine, good yields of the benzoyl derivatives were obtained.

(2.3) COMPLEX FORMATION WITH ISONICOTINOYLHYDRAZINE AND RELATED LIGANDS.

The tuberculostatic properties of isonicotinoylhydrazine (INH) (I) have been briefly mentioned in Chapter 1. Since this discovery, a multitude of acylhydrazines and their derivatives have been tested for antitubercular activity, but few have been found which approach the effectiveness of INH.[28,29]

The possibility that chelation might play an important role in the mode of action of INH against M. tuberculosis was realised early, and many investigations have been conducted with this in mind. Sorkin et al.[30] have isolated a 1:1 chelate with copper(II) with the suggested structure (IX). Spectrophotometric evidence

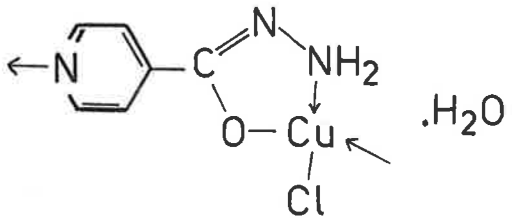


(IX)

for a 2:1 neutral chelate was also obtained,[31] and Albert[32] indicated the existence of both from stability constant measurements. Suggestions that complex formation prevents the utilization of essential metal ions by the bacterium[33,34] now seem unlikely in view of the observations of Albert[35] that other hydrazides form complex which are equally or more stable than INH complexes, but are biologically inactive. It was also found that the 1:1 copper(II) chelate was equally as active as INH alone.[36] Foye and Duval[37] have synthesised chelates formulated as $(INHCu)^{+}HSO_4^{-}.2H_2O$, $(INH)_2Cu.3H_2O$, $(INH)_2Co.4H_2O$, $(INHZn)^{+}HSO_4^{-}.2H_2O$ and $(INHFe)^{+}HSO_4^{-}.2H_2O$ and found both 1:1 and 2:1 chelates to be equally effective as INH when tested in vivo. These observations suggested that the antitubercular activity of

INH does involve complex formation since the concentration of free ligand and hence the activity should be greatly reduced when administered in the complexed form.

INH would appear to be coordinated in the enol form in all the complexes so far discussed. The spontaneous liberation of protons on formation of $(\mathrm{INHCu})^+\mathrm{HSO_4}^-.2\mathrm{H_2O}$ has been observed,[37], but such a formulation may be questionable in view of the possibility of protonation of the heterocyclic nitrogen atom. Nagano et al.[6,7] have studied the infrared spectrum of $\mathrm{INHCuClH_2O}$, where the carbonyl stretching frequency of INH (1668 cm^{-1}) shifts to 1210 cm^{-1}, indicating almost single bond character and occurring close to that of the sodium salt of the ligand (1096 cm^{-1}). From small shifts to higher energy of the bands ascribed to pyridine ring vibrations, these authors have concluded that the pyridine nitrogen is also coordinated in this complex and the analogous complex derived from nicotinoylhydrazine. A polymeric structure is proposed on this basis, as indicated for the INH complex in (X).



(X)

These authors have also prepared a 1:1 enol complex of p-nitrobenzoylhydrazine containing one chloride ion and one water molecule which are both presumably coordinated to copper(II). This complex was obtained simply from the reactants in ethanol solution, so that under these conditions spontaneous liberation of hydrogen ion apparently occurs. This is probably a result of the greater electron-withdrawing properties of the nitro group, since this effect is not observed with BH itself.

Picolinoylhydrazine (PICH) presents an interesting problem as to the manner in which the ligand can coordinate. The presence of the hydrazide grouping ortho to the pyridine nitrogen means that there are three possible ways in which a keto complex and two possible ways in which an enol complex can be formed. Nagano et al. have isolated two complexes, $(PICH)CuCl_2$ and $(PICH)CuCl.H_2O$, and propose that chelation occurs through the pyridine nitrogen and terminal $-NH_2$ groups for the former keto complex, giving a six-membered ring. For the latter enol complex, a five-membered ring involving the pyridine nitrogen and enol oxygen atoms is suggested.

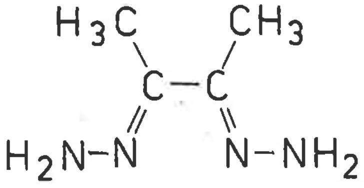
Considering the complexity of the infrared spectra of these ligands and complexes, it is doubtful whether too much reliance can be placed on the deductions of these authors as complete, unambiguous band assignments are required. As will be indicated presently (section 5.4) it is difficult to make clear-cut assignment of the carbonyl stretching frequency in keto N-benzoylhydrazine complexes. The effects of variation in lattice forces, hydrogen bonding, and resolution may well be complicating factors.

Further complexes of INH reported include a series of tetrathiocyanatomercury salts,[38] $(M(INH)_2)(Hg(SCN)_4)$, and a series of 1:1 and 2:1 benzoate salts.[39] A number of 1:1 copper(II) complexes ($INHCuX.2H_2O$) and copper(I) complexes (INHCuX) ($X = Cl^-$, Br^-, NO_3^- etc.) have also been reported.[40] The copper(I) complexes are possibly dimeric, the ligand either coordinated in the keto form, or else in the enol form with protonated pyridine nitrogen.

Coordination of _o_-, _m_- and _p_-aminobenzoylhydrazines presents similar problems to those evident for the pyridinecarboxylic acid hydrazides. The preparation of 1:1 and 2:1 complexes of these ligands with a number of metal ions has been reported,[41] all containing anions equivalent to the charge on the metal ion, but little evidence for the structure of these complexes was presented. The more intense colour of the copper(II) _o_-amino-complexes was taken to indicate coordination of the _o_-amino nitrogen atom, together with the carbonyl oxygen atom in the enol form. Protonation of the free terminal hydrazine nitrogen was suggested to account for the positive charge of the chelate. For the _m_- and _p_-isomers, coordination by the enol hydrazide grouping, with protonated free amino group, was suggested.

Some evidence that the closely related N-salicoylhydrazine forms a 1:1 complex with manganese(II) has been presented.[42]

Brief mention must be made of complexes of other hydrazine-containing ligands. Busch and co-workers have investigated the complexes of biacetyldihydrazone (XI)[43-45] and related compounds which are strong-field ligands



(XI)

producing spin-pairing in complexes of iron(II). The existence of intraligand repulsions has been indicated in some of the complexes.[46] Complexes of glyoxal bis-(guanylhydrazone),[47] biacetylhydrazone oxime[48] and many other ligands have also been reported.

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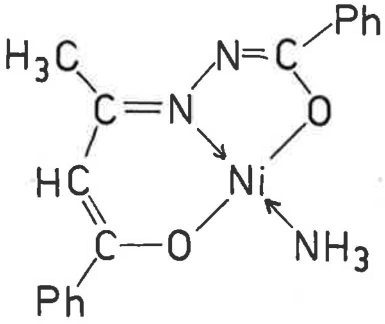
CHAPTER 3.

MULTIDENTATE LIGANDS CONTAINING HYDRAZINE.

(3.1) TRIDENTATE AND QUADRIDENTATE LIGANDS.

The versatility of the acylhydrazine grouping in complex formation is demonstrated by the variety of complexes which have been isolated from the condensation products with diketones and hydroxyaldehydes. By far the greater proportion of published work on complexes of this type must be attributed to Sacconi. No attempt will be made to present a detailed account here, as the multitude of complexes reported is prohibitive. Only complexes which are characteristic of each particular type will be mentioned.

The monoacylhydrazones of β-diketones are capable of acting as tridentate chelating agents with the formation of fused five- and six-membered rings. Thus benzoylacetonebenzoylhydrazone gives rise to the neutral complex (XII) with nickel(II), isolated with ammonia coordinated in the fourth position.[1] Salicylaldehydebenzoylhydrazone

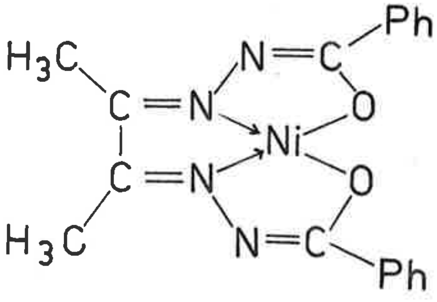


(XII)

forms a similar complex.[2] Complexes of this type were found to be diamagnetic, indicating square planar configurations.

The salicylaldehyde derivatives of long chain aliphatic hydrazides were found to form bis- complexes of nickel(II) for which a tetrahedral structure was postulated.[3] With the benzoylhydrazine derivative, acting as a tridentate ligand, a planar complex containing uncondensed benzoylhydrazine coordinated in the fourth position was obtained. In this complex benzoylhydrazine would appear to act as a monodentate ligand coordinated only through the terminal hydrazine nitrogen. Further reaction of this complex with salicylaldehyde yielded a symmetrical bis- complex. Salicylaldehyde-o-aminobenzoylhydrazine, a potentially quadridentate ligand, was found to give rise to a 1:1 chelate for which a tetrahedral structure was suggested. This complex also reacted further with a molecule of the uncondensed hydrazine to give a diamagnetic compound, presumed to contain the salicylaldehyde derivative coordinated as a tridentate ligand.[3,4] The ultraviolet spectra of these complexes has been studied.[5]

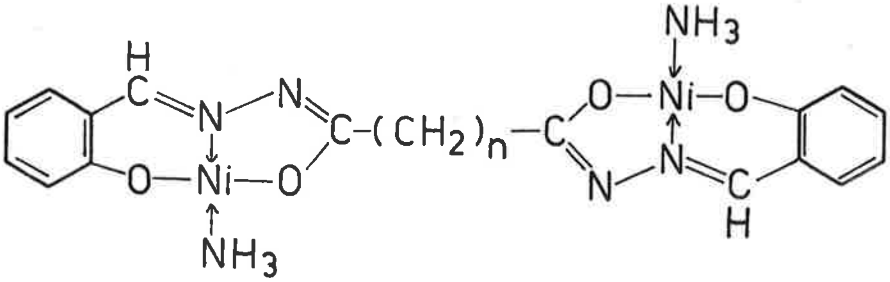
The α-diketone biacetyl can be condensed with two molecules of benzoylhydrazine. The neutral complex of this ligand (XIII) was found to be diamagnetic, indicating a square planar structure.[1] This complex was later studied in detail when it was found that two molecules of



(XIII)

heterocyclic bases could be added forming octahedrally coordinated nickel(II). Further discussion of this work is presented in section 4.4.

By condensation of o-hydroxycarbonyl compounds with a number of diacyldihydrazines, Sacconi has prepared ligands able to function as bis-tridentate chelating agents.[6] Thus salicylaldehyde gives rise to the series of complexes represented by (XIV). Their diamagnetism would again indicate square planar configurations. When treated with



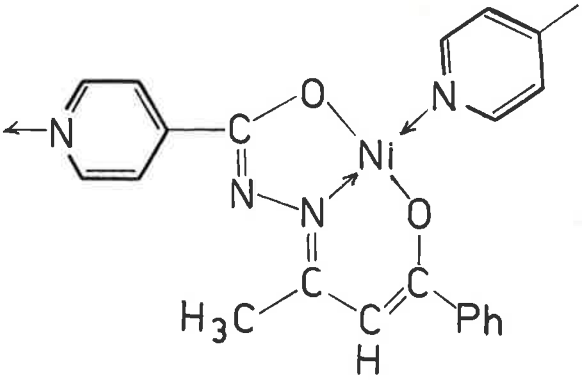
(XIV)

sodium hydroxide, ammonia was lost and the sodium salts of the corresponding hydroxo complexes were formed.

Closely related to the above binuclear complexes are the complexes formed by disalicylaloxalhydrazimidine.[7]

These are represented by (XIV) with n = 0, the enol hydrazide oxygen replaced by = N-, and the nitrogens attached to the central carbon atoms protonated. The complexes were isolated as the anionic compounds with acetate, thiocyanate, nitrite and cyanide coordinated in the fourth positions. Replacement of acetate by ammonia, pyridine and other organic bases produced neutral complexes. Removal of the phenolic oxygen atom (i.e. the dibenzal derivative) gave rise to an insoluble complex presumed to be polymeric.

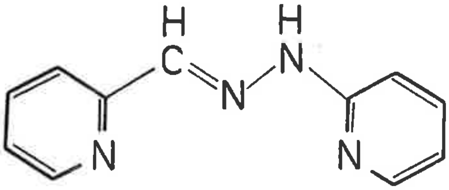
Other complexes which are probably polymeric have been prepared from the benzoylacetone derivatives of nicotinoylhydrazine and isonicotinoylhydrazine.[1] Although these ligands are quadridentate, it would appear unlikely that the pyridine nitrogen could coordinated to the same metal ion as the functional tridentate part of the molecule. Consequently the structure (XV) is proposed for the INH derivative. Similar structures are indicated for the



(XV)

complexes of the salicylidene derivatives of these ligands.[2] A complex containing one ammonia molecule per eight monomer units was isolated, indicating the possibility of chain termination by the coordination of ammonia in the fourth position. Picolinoylhydrazones (pyridine-2-carboxyhydrazones) were found not to form definite nickel(II) complexes,[2] probably as a result of steric hindrance to coordination of the pyridine nitrogen atom. All the presumably polymeric complexes isolated were found to be insoluble, thus preventing further elucidation of their structures.

Complex formation with ligands such as pyridine-2-aldehyde-2-pyridylhydrazone (XVI) has attracted much attention in recent years. Lions and Martin[8] have reported the isolation of a cationic bis- complex with iron(II), indicating that the ligand functions as a tridentate chelating agent. Further preparations of cationic and neutral complexes of (XVI) and ligands substituted at the aldehyde carbon atom have also been reported.[9] The formation and acid dissociation constants of complexes of

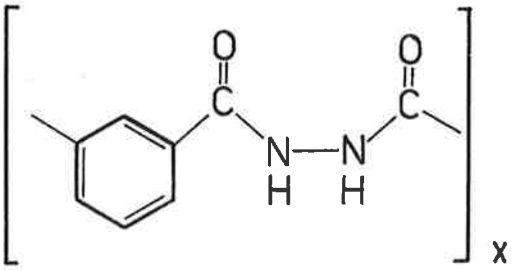


(XVI)

(XVI) have been measured in aqueous solution.[10]

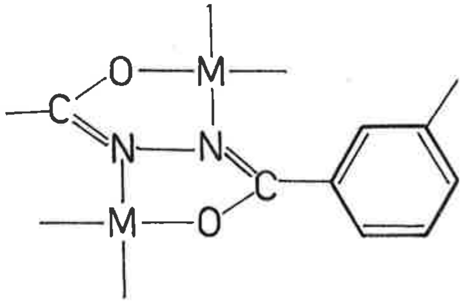
Condensation of 2-pyridylhydrazine with α-diketones produced tridentate ligands from which cationic or neutral complexes were isolated.[11] Evidence for the protonated nitrogen in the cationic complexes was obtained from infrared spectroscopy. The quadridentate bis-(2-pyridylhydrazone) of butane-2,3-dione (biacetyl) was similarly found to produce four-coordinated cationic or neutral complexes with copper(II), nickel(II) and palladium(II)[12]

One further investigation to be mentioned is that of Frazer and Wallenberger[13] who examined the reaction of metal ions (Ni(II), Ca(II), Ag(I), Hg(II), Zu(II), Cd(II), Cu(II)) with some polyhydrazides prepared from e.g. isophthalic dihydrazide and isophthaloyl dichloride (XVII).



(XVII)

These authors found that one metal ion per hydrazide link was incorporated into the polymer and suggested that coordination occurred through the two oxygen atoms (in the enol form) in the configuration as shown. However, no indication as to the groups filling the third and fourth coordination positions was given. Coordination in this manner must be considered improbable, particularly as it would lead to the formation of seven membered chelate rings. In keeping with the coordinating properties of the monoacylhydrazine ligands, it is more likely that coordination occurs with the diacylhydrazine groups arranged in the anti form, giving rise to a two-dimensional polymeric structure, linked between chains by the metal ions coordinated as shown in (XVIII).



(XVIII)

The above discussion is not intended to be an exhaustive survey, but merely to illustrate the variety of hydrazine-containing ligands which have been investigated. More attention has been focused on the work of Sacconi since many of the ligands used by this author are related to those studied in the present investigation.

(3.2) COMPLEXES OF POLYMETHYLENE-N,N-DIACYLDIHYDRAZINES.

Apart from the work of Jensen and Bak, reviewed in section 1.2, complex formation with the dihydrazide series of ligands has been little studied. The bis-tridentate disalicylidene derivatives of a number of the series and the bis-bidentate dibenzal derivative of oxalhydrazimidine were investigated by Sacconi (section 3.1). Otherwise, oxalyldihydrazine would appear to be the only ligand which has attracted much attention.

Hofmann and Ehrhardt[14] have reported the isolation of dipotassium bis-(oxalyldihydrazine)copper(II), in which the ligand presumably coordinates through the enol form of only one of the hydrazide groupings. A complicated nickel(II) compound was described but not characterized; this may be polymeric in nature.

Nilsson[15] has reported that the condensation products of oxalylhydrazine with various oximinoketones produce colours with metallic iron in alkaline solution. Oxalylhydrazine with a number of aldehydes and ketones produces an intense violet colour with copper(II);[16] this reaction has since been developed to provide a colourimetric method for the determination of copper(II).[17] Malonyldihydrazine and other dihydrazines have been examined in this respect.[16,18] The reaction between oxalyldihydrazine and copper(II) has also been used in the colourimetric estimation of aldehydes and ketones.[19]

Vallon and Badinand have reviewed the previous work on this method for the estimation of copper and have carried out a spectrophotometric investigation into the type of complex responsible for the intense colour. Their results indicated the presence of both monohydrazones (giving blue or green colours) and dihydrazones (giving violet or red colours), depending on the conditions used. Continuous variation studies indicated the existence in solution of 2:1, 3:1 and 4:1 complexes. The systems are thus very complicated.

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CHAPTER 4.

THE STEREOCHEMISTRY AND VISIBLE REGION SPECTRA OF COPPER(II) COMPLEXES.

(4.1) STEREOCHEMISTRY AND LIGAND FIELD THEORY PREDICTIONS.

Copper(II), in its complexes, is characterised by a wide variation in stereochemistry. In the solid state, distorted octahedral, square pyramidal, planar, flattened tetrahedral and distorted trigonal bipyramidal configurations are established. Since the latter two stereochemistries are rarely encountered, they will be omitted from the review presented in this chapter.

As discussed by Orgel,[1] the distorted octahedral structure containing four short bonds in the plane and two axially elongated bonds is commonly observed. Indeed this is frequently achieved in otherwise planar molecules by packing in the crystal in such a way that neighbouring donor atoms are situated above and below each copper(II) ion, as is readily apparent from the bond distances of some representative examples listed in table 4.1. This phenomenon has important consequences in the visible spectra of copper(II) complexes. With the advent of Ligand Field Theory, the reasons for this distortion and its effect on spectra have become apparent and are considered as resulting from the operation of the Jahn - Teller theorem.

TABLE 4.1. COPPER-LIGAND DISTANCES IN SOME COPPER(II) COMPLEXES (IN ANGSTROM UNITS).

$CuCl_2$ [2]	4Cl, 2.30; 2Cl, 2.95.
$CuCl_2.2H_2O$ [3]	$2H_2O$, 2.01; 2Cl, 2.30; 2Cl, 2.99.
$CuCl_2.2py$ [4]	2N, 2.02; 2Cl, 2.28; 2Cl, 3.05.
$Cu(NH_3)_4SO_4.H_2O$ [5]	4N, 2.05; H_2O, 2.59; H_2O, 3.37.
Cu(dimethylglyoxime)$_2$ [6]	4N, 1.94; O, 2.43.
Cu(en)$_2$(NO$_3$)$_2$ [7]	4N, 2.03; 2O, 2.59.
Cu(glycine)$_2$.H$_2$O [8]	2N, 2.00; 2O, 1.95; O(H$_2$O), 2.41; O(gly), 2.74.
Cu(dithiocarbamate)$_2$ [9]	4S, 2.32; S, 2.71.
Cu(N,N'-disalicylidenepropane-1,2-diamine). H$_2$O. 10	N, 1.78; N, 1.95; O, 1.94; O, 1.88; O(H$_2$O), 2.53.
Cu(acac)$_2$ [11]	4O, 1.92.
Cu$_2$(acetate)$_4$.2H$_2$O [12]	4O, 1.97; H$_2$O, 2.20; Cu, 2.64.
Cu(N,N'-disalicylideneethylenediamine) 13	N, 2.08; N, 1.94; O, 2.03; O, 1.91; O, 2.41.
Cu(formate)$_2$.4H$_2$O [14]	4O, 2.00; 2H$_2$O, 2.36.

In terms of electrostatic crystal field theory, the degenerate d orbital energies of a transition metal ion will be split on the application of an octahedrally oriented field provided by the surrounding ligands, which are considered as point charges or dipoles (static plus induced). The ${}^2D$ term of copper(II) will thus be split into a lower triplet,

$t_{2g}(d_{xy}, d_{xz}, d_{yz})$ and an upper doublet, $e_g(d_{x^2-y^2}, d_{z^2})$.[1,15] There are then two possible configurations for the d^9 ground state, $t_{2g}{}^6(d_{x^2-y^2})^2(d_{z^2})^1$ or $t_{2g}{}^6(d_{x^2-y^2})^1(d_{z^2})^2$. Jahn and Teller[16] have shown that the energy of a non-linear molecule with a degenerate electronic state may become lowered by distortion to lower symmetry, separating the degenerate energy levels. Hence the energy levels of copper(II) will be split in various configurations as shown in figure 4.1.

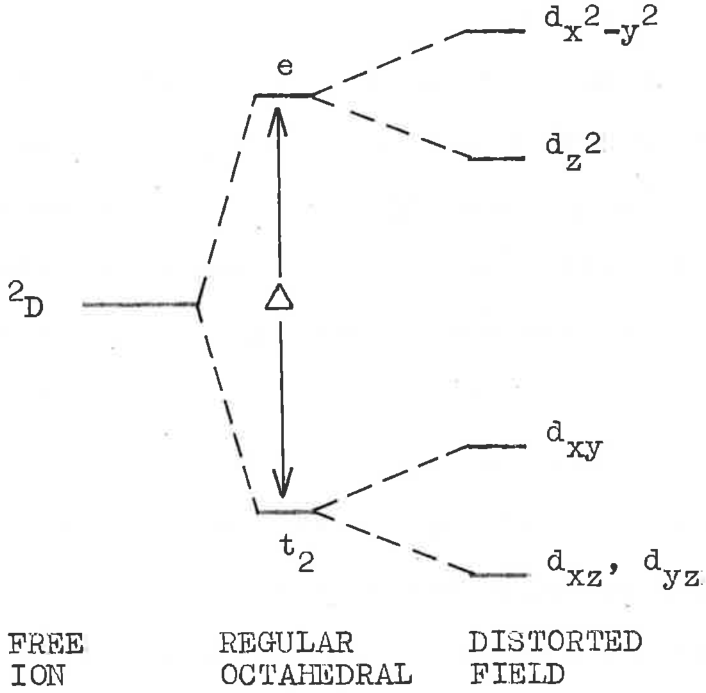

Figure 4.1. Orbital energy level scheme for octahedral and axially elongated octahedral copper(II) stereochemistries (after Orgel and Dunitz[1]).

The Jahn - Teller theorem gives no information as to the type of distortion to be expected, only that there will be a distortion. Hence a structure in which there are four long and two short bonds could be considered equally feasible as one in which there are four short and two long bonds. Orgel and Dunitz[1] have proposed that the observed structures may be explained by considering a simple electrostatic model in which the single unpaired electron of the d^9 configuration exists in the $d_{x^2-y^2}$ orbital (with extensions along the x and y axes). This would allow closer approach of the ligands in the plane due to reduced shielding of the copper(II) nucleus compared with the effect of two electrons in the d_{z^2} orbital, and would result in the tetragonally distorted structures observed. The driving force favouring distortions of this type is not readily apparent, although Öpik and Pryce[17] have calculated that a tetragonal structure is more likely from a consideration of the potential energy due to the restoring forces.

The methods of the Molecular Orbital Theory[1] lead to the same results concerning static Jahn - Teller distortions in copper(II) as are obtained on the electrostatic model. Although the problem is regarded from two separate viewpoints, those of covalent versus electrostatic bonding, the general conclusions of both theories are the same, i.e. there will be a splitting of the five degenerate d orbitals into two separate energy levels in a regular octahedral environment, followed by further splitting because of the Jahn - Teller effect. Thus the theories must be regarded as complementary[18], the true state of the molecule being between the limits of the two approaches. The energy difference between the e_g and t_{2g} sets, Δ of figure 4.1, can then be considered as consisting mainly of four contributions:[19a]

$$\Delta \simeq \text{electrostatic first-order perturbation} + \sigma(L \rightarrow M) - \pi(L \rightarrow M) + \pi(M \rightarrow L)$$

thus the effect of σ-bonding will be to markedly increase Δ compared to systems in which electrostatic bonding may be considered more important, while π-bonding will act to decrease or increase Δ, depending on whether the interaction is between filled ligand orbitals and empty metal orbitals or filled metal orbitals and empty ligand orbitals.

In discussing the spectra of copper(II) complexes, it is convenient to consider that electron transitions from the ground state to higher energy levels may be represented as single "positive hole" (positron) transitions.[15] This has the effect of reversing the splittings shown in figure 4.1, thus in an octahedral environment a single $e_g \rightarrow t_{2g}$ positron transition is to be expected. It must be remarked that such transitions are forbidden by the Laporte selection rule and can become "allowed" through vibrations of the nuclei which remove the centre of symmetry of the molecule. Hence the intensities of these transitions are very much less than the strong, Laporte - allowed transitions which constitute charge transfer bands.

With reference to figure 4.1, it is apparent that copper(II) in a square planar environment should produce a spectrum containing at least three transitions. Generally only a single, or sometimes two, broad bands are evident in the visible or near infrared regions. In many cases such bands can be resolved by Gaussian analysis into two or three components. There has been a great deal of controversy as to which is the correct procedure (see Section 4.3) and consequently the assignment of absorption bands to definite transitions is a difficult process.

The band positions of some typical absorption spectra of copper(II) complexes are listed in table 4.2. By comparing the wavenumbers of the principal band of a copper(II) complex (σ Cu) with the first spin-allowed band of the corresponding high spin, octahedral nickel(II) complex (σ Ni), Jørgensen[19b] has discerned three main classes of copper(II) complexes.

(1) Highly tetragonal complexes (i.e. tending towards square planar) with σCu/σNi = 1.6 to 1.8 having only one absorption band.

(2) Complexes of six identical ligands with σCu/σNi = 1.4 have a shoulder at lower wavenumber than σ Cu.

(3) Complexes of low tetragonality (i.e. approaching regular octahedral), as in the tris-heterocyclic diimine complexes, with σCu/σNi = 1.1 have two or three absorption bands. The bis complexes, with cis-octahedral or other

distorted symmetry,[20a] and the tris(aminoethyl)amine (tren) complex also belong to this class. In the latter complex, formation of a square planar structure is prevented by steric hindrance.

TABLE 4.2. ABSORPTION MAXIMA FOR SOME COPPER(II) COMPLEXES AND THE RATIO σ Cu/σ Ni (AFTER JØRGENSEN[19b]).

COMPLEX	MAXIMUM (cm^{-1})	σ Cu/σ Ni
$Cu(glycine)_2 \cdot 2H_2O$	15,800	1.60
$Cu(en)_2 \cdot 2H_2O^{2+}$	18,200	1.73
$Cu(NH_3)_4 \cdot 2H_2O^{2+}$	16,900	1.7
$Cu(NH_3)_6^{2+}$	15,600; (11,700)	1.45
$Cu(H_2O)_6^{2+}$	12,600; (9,400)	1.48
$Cu(en)_3^{2+}$	16,400; (11,800)	1.44
$Cu(dipyridyl)_2 \cdot 2H_2O^{2+}$	13,900; 10,500	1.1
$Cu(dipyridyl)_3^{2+}$	14,700; ~9,000	1.20
$Cu(O\text{-}phen)_2 \cdot 2H_2O^{2+}$	13,300; 10,200	1.1
$Cu(O\text{-}phen)_3^{2+}$	14,700; 8,000	1.20
$Cu(tren) \cdot 2H_2O^{2+}$	(14,700); 11,600; (9,600)	1.07

This classification of copper(II) spectra will be considered in greater detail in subsequent sections, expecially with regard to variations produced by alterations of stereochemistry in specific series of complexes.

(4.2) THE COPPER(II) - AMMONIA SYSTEM.

The tendency of copper(II) to exhibit a "charcteristic" coordination number of four has been demonstrated by the work of Bjerrum in determining the formation constants for the successive replacement of water in the coordination sphere of the aquated ion by ammonia. The formation constants have been reported[20b] as: $K_1 = 12,000$; $K_2 = 3,000$; $K_3 = 800$; $K_4 = 120$; $K_5 = 0.3$. These results were verified by spectrophotometric as well as by potentiometric data,[21] and illustrate the important feature of copper(II) chemistry that a relatively stable complex containing four-coordinated copper(II) can undergo expansion of coordination number by the addition of at least a fifth weakly bound ligand in solution as well as in the solid state.

By resolving the mixed spectra of equilibrium solutions, Bjerrum has estimated the spectra of the intermediate complexes containing 1, 2, 3 and 4 molecules of ammonia. The maximum is steadily shifted to higher energies in this series (table 4.3), but the coordination of a fifth ammonia molecule produces an anomalous shift to lower energies, accompanied by the appearance of a shoulder on the infrared side of the main band. This unusual shift has been termed the "pentammine effect".

Following the moderate success of Hartmann and Ilse in applying the theories of Bethe and van Vleck to the aqueous spectrum of the titanium(III) ion, Bjerrum, Ballhausen and Jørgensen[21] have used Crystal Field Theory to explain the changes in the spectra of the copper(II) - ammonia series and to obtain information on the structure of the copper(II) ion in aqueous solution. They calculated the energy of the transitions by considering the perturbing effect due to the ligand dipoles for various stereochemical arrangements, making use of equations which may be summarised as:

$$\nu_n = \mu . f(R,Z)$$

where ν_n is the frequency of the maximum, μ is the effective dipole moment of the ligand, R is the metal - ligand distance and Z is the effective charge on the cupric ion. ν_n was calculated for a range of values of μ and R, considering the environment of copper(II) to be square planar, tetrahedral, square pyramidal and regular octahedral. Comparison with the spectra of the aquated copper(II) ion and copper(II) in liquid ammonia indicated that the planar or pyramidal configurations were more likely. The regular tetrahedral and octahedral configurations were also precluded by the fact that the above spectra can be resolved into at least two bands, whereas only one transition is to be expected on these models (section 4.1).

Further calculation showed that in order to obtain the best agreement with the observed positions of the two bands, the structure of the aquated or ammoniated copper(II) ion should be a tetragonal bipyramid with two ligands at a greater distance. This result is thus in agreement with that derived by Orgel[15] from consideration of the Jahn - Teller theorem and is also in agreement with structures observed in the solid state.

TABLE 4.3 OBSERVED POSITIONS OF MAXIMA (cm^{-1}) IN THE COPPER(II) - AMMONIA SYSTEM.[21]

	Observed ν_1	Observed ν_2	Calculated ν_1
$Cu(H_2O)_4(H_2O)_2^{2+}$	12,650	9,450*	-
$Cu(NH_3)(H_2O)_3(H_2O)_2^{2+}$	13,400		14,100
cis-$Cu(NH_3)_2(H_2O)_2(H_2O)_2^{2+}$	14,700		14,900
(trans-$Cu(NH_3)_2(H_2O)_2(H_2O)_2^{2+}$)	~16,700		16,100
$Cu(NH_3)_3(H_2O)(H_2O)_2^{2+}$	15,500		15,150
$Cu(NH_3)_4(H_2O)_2^{2+}$	17,000		16,950
$Cu(NH_3)_4(NH_3)(H_2O)^{2+}$	15,600	11,700*	-
$Cu(NH_3)_4(NH_3)_2^{2+}$	15,600	11,700*	-

* Shoulder, resolved by Gaussian analysis.

If such a tetragonal structure does predominate in coordinating solvents, a "pentammine" effect should operate for the complex $Cu(NH_3)_4(H_2O)_2^{2+}$, the spectrum of which, however, is remarkably symmetrical but could possibly contain a second band of low intensity. Thus it can be seen that the presence of a "pentammine" effect can be taken as good evidence for a tetragonally distorted structure, but non-observance of such an effect does not necessarily mean that the structure is otherwise.

Bjerrum et al. also propose that the similarity of the spectra of $Cu(NH_3)_4(NH_3)(H_2O)^{2+}$ (in water) and $Cu(NH_3)_4(NH_3)_2^{2+}$ (in liquid ammonia) can be accounted for by assuming that the effective (i.e. permanent plus induced) dipole moments of the last water molecule and the sixth ammonia molecule are nearly equal.

The authors have also remarked on the possibility of cis - trans isomerism in the complex $Cu(NH_3)_2(H_2O)_2(H_2O)_2^{2+}$ and have calculated the positions of the corresponding maxima (Table 4.3). It is claimed that the interpolated diammine spectrum indicates that both forms are present in solution, with the equilibrium displaced strongly in favour of the cis isomer. This is supported by analogy with the spectra of the monoethylenediamine complex (necessarily cis, maximum at 14,900 cm^{-1}) and the dipyridinato complex (showing two bands at approximately 15,000 and 16,000 cm^{-1}, and indicating a large proportion of the trans isomer).

Grant and Kollrack[22] have more recently re-examined the copper(II) water/ammonia system and report good agreement of the observed band positions with those reported by Bjerrum et al. They have suggested, however, that the band position of $Cu(NH_3)_2(H_2O)_4^{2+}$ is indicative of a trans configuration. Bjerrum[23] has discussed this proposal, suggesting a misinterpretation by these authors, and has reaffirmed the original proposal that the cis isomer is predominant in solution.

The agreement between the observed and calculated band positions (table 4.3), as presented by Bjerrum et al. is indeed remarkable even though the parameters have been chosen (within the bounds of reason) to explain the experimental results, and in view of the many assumptions involved. This illustrates an important feature of the ligand field theory which, although it may not necessarily be rigorous in its derivation,[24] can provide a mathematical basis on which experimental results can be interpreted. The work of Bjerrum et al. has been criticized,[25] particularly in view of the value of Z chosen.

(4.3) SOLVENT EFFECTS ON THE SPECTRA OF BIS-(ACETYLACETONATO)COPPER(II) AND RELATED COMPOUNDS.

The visible absorption spectra of bis-(acetylacetonato)-copper(II) ($Cu(acac)_2$) and related complexes of substituted acetylacetone ligands have been extensively investigated over the last few years in an attempt to reach some definite conclusion concerning assignment of the ligand field transitions of copper(II). These systems have proved popular because, with a fair degree of certainty, the complexes should exist as planar, four-coordinated structures in weakly or non-coordinating solvents. When dissolved in strongly coordinating solvents such as the heterocyclic bases, pronounced changes in the spectra are observed, making them ideal systems for studying the change from square planar to octahedral stereochemistry.

The visible spectra in benzene or chloroform generally consist of two broad bands centred at approximately 18,000 and 15,000 cm^{-1}. From considerations of ligand field theory (section 4.1), three bands in the visible region are expected from a d^9 configuration in a square planar environment, hence there has been much controversy over the assignments of the two observed bands. To further complicate matters, a band in the region of 27,000 cm^{-1} is observed as a poorly resolved shoulder and there has been some indecision as to whether this higher energy band is or is not a ligand field transition. However, the following details have thrown some light on this matter:

(1) The molar extinction coefficient of this band (ε = 400-500) is anomalously high compared to the other ligand field transitions of copper(II) in these complexes. Graddon[26] had originally proposed that this band is indeed a ligand field transition and that its high extinction was due to some form of interaction with the adjacent intense charge transfer band, but has recently revised this opinion.[27]

(2) The polarised single crystal spectrum of Cu(acac)$_2$ has been examined by Ferguson[28] and found to consist of three bands in the visible region as well as containing the higher energy band. It was proposed that all four bands are due to transitions within the d-shell, the assignments indicating failure of the simple crystal field model. Piper and Belford[29] have subsequently demonstrated that

Ferguson's assignments are improbable, since a three-dimensional structure determination has shown that the inclination of the molecular plane in the unit cell is appreciably different from that reported for the two-dimensional structure determination used by Ferguson.

(3) The crystal spectrum of bis-(3-phenylacetylacetonato)copper(II) has been shown[30] to consist of four bands in the visible region, in addition to the high energy shoulder, when measured at liquid nitrogen temperatures. At room temperature only two bands were observed in the visible region. Belford et al. have assigned the four bands to transitions between the five possible energy states arising from the d orbitals, but remark that the two lowest frequency bands could be due to the same electronically allowed transition "differing by a strongly coupled carbonyl vibration quantum in the upper state". In either case, only a ligand transition could be responsible for the high energy band.

Thus, although this problem has not been completely solved, the currently favoured opinion is that the high energy band is due to a transition involving ligand orbitals.[31*] The problem of resolution of the bands in the visible region also remains. It has been demonstrated that Gaussian analysis into either two or three components can adequately describe the spectrum.[26]

[*] See also Cotton, F.A. and Wise, J.J., J. Amer. Chem. Soc., 88, 3451 (1966).

In examining solvent effects on the spectra of bis-(acetylacetonato)copper(II) and bis-(3-ethylacetylacetonato)copper(II), Belford, Calvin and Belford[25] have chosen to resolve the visible spectra into three Gaussian components. These authors have also used the electrostatic point charge model to calculate an energy level diagram for positron transitions of copper(II) in various environments, and have interpreted the spectral shifts in solvents of increasing base strength according to this diagram, the essential features of which are illustrated in figure 4.2.

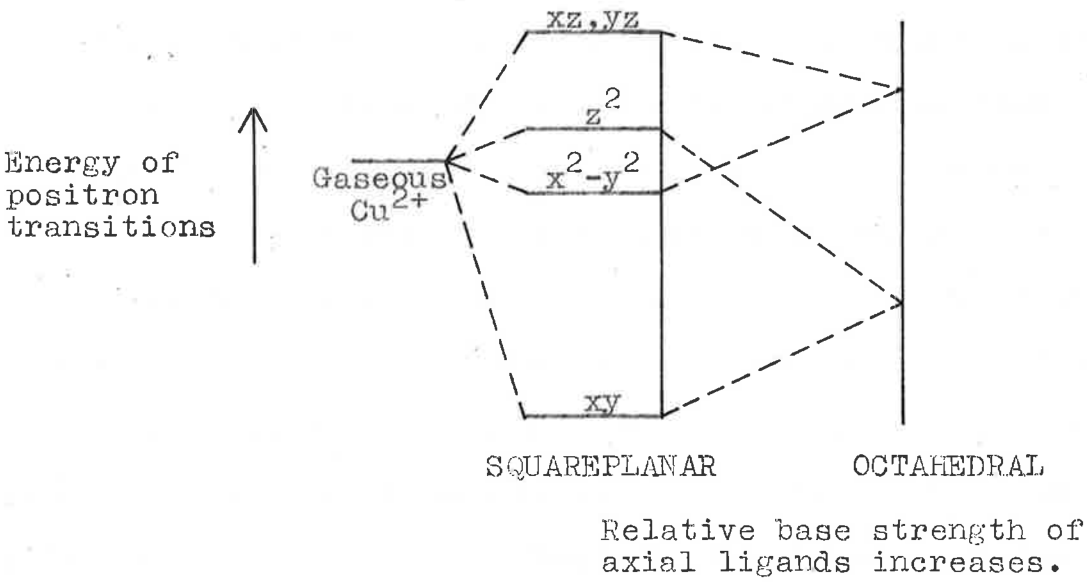

FIGURE 4.2. Schematic representation of positron energy levels of Cu(II) in varying environments. After Belford, Calvin and Belford.[25]

The notation of the orbitals in figure 4.2 arises from the choice of coordinate axes. Since the bond angle O-Cu-O of the chelate ring is 93.5°[29] the symmetry of the molecule requires the choice of x axis as the bisector of this angle, with the y axis taken at right angles in the same plane. The z axis remains normal to these axes.

With this choice of axes, d_{xy} will become the ground state for positron transitions since this orbital is now directed towards the ligand atoms. The "positive hole" will then be situated in this orbital in the ground state to account for the observed direction of the Jahn - Teller distortion, and $d_{x^2-y^2}$ will be directed between the axes. In a regular octahedral configuration d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}, d_{xy} would form the two degenerate energy levels.

Having arrived at an energy scheme for splitting of the d orbitals, Belford et al. incorporated this in a simplified molecular orbital treatment and the two approaches were shown to be equivalent. It was suggested that changes in the positions of the three resolved bands on increasing the base strength of axially coordinated ligands, and also the increased energy of all three bands in comparing bis-(3-ethylacetylacetonato)copper(II) and bis-(acetylacetonato)copper(II) could be accounted for on the above scheme. This latter effect was explained on the basis that the increased base strength of the planar acetylacetone oxygen atoms (as a result of the electron donating properties of the ethyl group) would mostly affect the d_{xy} orbital, causing it to increase in energy (decrease in energy on the positron scheme).

From a more detailed examination of the band energies as a function of the coordinating power of the solvent (see appendix) it is evident that the procedure of resolving the spectra into three bands used by Belford et al. is not compatible with the energy scheme they propose. Graddon and Schulz[27] have suggested that resolution into only two components is justified experimentally, and this would appear to be best procedure for obtaining an empirical energy level diagram which is also in agreement with ligand field theory predictions. The diagram so obtained is shown in figure 4.3, not drawn to scale (see appendix for details), and depicts the energy of the upper levels relative to the ground state as zero energy.

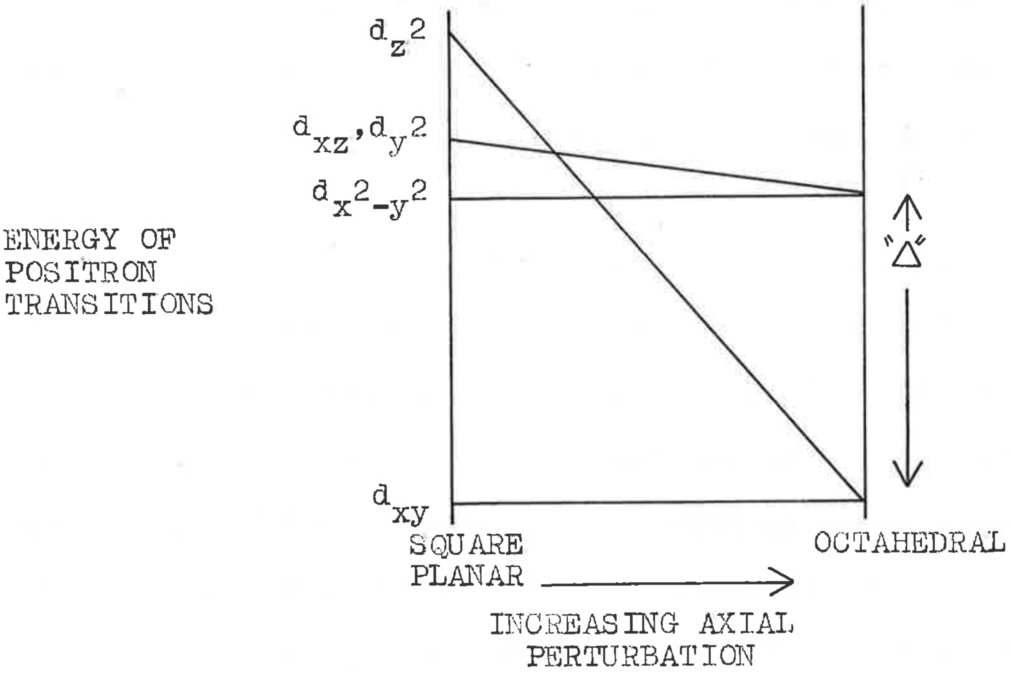

Figure 4.3. REVISED ENERGY LEVEL DIAGRAM FOR POSITRON TRANSITIONS OF $Cu(acac)_2$ IN SQUARE PLANAR AND OCTAHEDRAL ENVIRONMENTS (RELATIVE TO THE GROUND STATE AS ZERO ENERGY).

According to figure 4.3, the observance of two bands in the spectrum of Cu(acac)$_2$ in chloroform solution (18,800 cm^{-1} and 15,200 cm^{-1}) is seen to result from d_{z^2} being raised in energy above d_{xz}, d_{yz} and $d_{x^2-y^2}$. The 15,200 cm^{-1} band is presumed to contain transitions to the latter orbitals, irresolvable because of the broad nature of the bands and the close proximity of the maxima. The spectrum in more strongly coordinating solvents (e.g. n-pentanol) consists of a single broad band which would contain the transitions to all three levels. In piperidine, the appearance of a shoulder on the infrared side of the main band would result from d_{z^2} being further lowered in energy. The value of "Δ", the splitting in a theoretical regular octahedral environment, is estimated to be 14,000 - 15,000 cm^{-1}.

When treated in a similar manner, the spectra of bis-(3-ethylacetylacetonato)copper(II)[25] (Cu(3-Et-acac)$_2$) and bis-(4-ethoxyacetylacetonato)copper(II)[26] (Cu(acest)$_2$) can be shown to conform to the pattern of figure 4.3. The inaccuracy of the extrapolation procedure makes comparison of "Δ" for the three complexes unwise, although the value for Cu(3-Et-acac)$_2$ would appear to be greater than for Cu(acac)$_2$ in agreement with the electron donating properties of the 3-ethyl group. For the electron withdrawing 4-ethoxy group, "Δ" would be expected to be smaller than for Cu(acac)$_2$, but the extrapolated value lies approximately in the same range.

The indication that d_{z^2} lies highest in energy in the square planar configuration (i.e. lowest in energy for electron transitions) in the case of the copper(II) acetylacetonato complexes receives some support from studies of low spin d^8 complexes (square planar palladium(II) and platinum(II)[19c]) and high spin d^6 (square planar iron(II) in the mineral Gillespite, $BaFeSi_4O_{10}$)[32] where the spectra have also been interpreted as suggesting that d_{z^2} lies lowest in energy.

It would appear that the energy level scheme of figure 4.3 should be generally applicable to copper(II) complexes in which pi-bonding is negligible and in which the molecular plane shows no appreciable deviation from perfect planarity. Thus the observance of the "pentammine" effect in $Cu(NH_3)_5(H_2O)^{2+}$ is analogous to the effect of strongly coordinating solvents in the acetylacetonato complexes. The hexaquo ion also shows this effect; in these complexes the apical ligand field is strong enough to perturb d_{z^2} so that its energy lies below that of the other levels. In $Cu(NH_3)_4(H_2O)_2^{2+}$ however, the apical field is weaker than the field in the molecular plane so that d_{z^2} will be similar in energy to the other levels, the single broad band observed being the resultant of three narrowly separated bands. The small shift of the main band to lower energy (1,400 cm^{-1}, see table 4.3) on addition of a fifth ammonia molecule would indicate that d_{z^2} may lie above the other levels, the resultant maximum of the three bands being at higher energy in the tetrammine than the resultant maxima of the two bands in this region in the pentammine.

The presence of a single broad band in the aqueous solution spectra of other complexes containing ligands in the plane which are placed after water in the spectrochemical series (i.e. produce a greater splitting than water), can similarly be accounted for. These are compounds which belong to Jørgensen's classification of highly tetragonal complexes (section 4.1).

For complexes in which the bonding of four ligands deviates appreciably from planarity, the situation is more complicated. The relative splitting of (d_{xz}, d_{yz}) and $d_{x^2-y^2}$ should be most affected. By removal of ligands out of the plane the overall splitting should be reduced, thus three bands at lower energy are observed for $Cu(tren).2H_2O^{2+}$ (table 4.2).

Pi-bonding would also be expected mainly to affect (d_{xz}, d_{yz}) and $d_{x^2-y^2}$ and may reverse their energies. This effect has been indicated from the E.S.R. spectra of copper(II) phthalocyanine[34] and tetraphenylporphine,[35] although interpretation of the data is hampered by the lack of reliable assignments of excitation energies. This is mainly because of the presence of strong charge transfer bands, extending into the visible region and masking the d-d transitions.[35]

One further complication in discussing solvent effects on the spectra of square planar complexes is the observation of Graddon[36] that $Cu(acac)_2$ and some related compounds would appear to add only one molecule of heterocyclic base in solutions of the bases. Consequently the adducts have been termed "five-coordinate".[36] Since this is a simple addition of apical molecules and not a replacement reaction, the explanation of Bjerrum et al.[21] for the similarity in spectra of $Cu(NH_3)_5(H_2O)^{2+}$ and $Cu(NH_3)_6{}^{2+}$ (section 4.2) is not applicable if, as would seem possible, two molecules of base are added to $Cu(acac)_2$. However, the presence of strongly electron-withdrawing groups (e.g. trifluoromethyl-) in the acetylacetone residue may in some cases enable identification of mono- and bis- adducts with different spectra. It would thus appear that the ligand field of $Cu(acac)_2$ in coordinating solvents is essentially that of an axially elongated square pyramid. The above observations will be further discussed in sections 4.4 and 4.5.

(4.4). FORMATION CONSTANT OF THE ADDUCTS OF HETEROCYCLIC BASES WITH BIS-(ACETYLACETONATO)COPPER(II) AND RELATED COMPLEXES.

In view of the synthesis and spectrophotometric investigation of a number of heterocyclic base adducts of copper(II) N-acylhydrazine complexes (Chapter 7), a review of the published work on adducts of bis-(acetylacetonato)-copper(II) and related complexes will be presented here and in the following section (4.5).

The work of Sacconi, Lombardo and Paoletti[37] on the thermodynamics of the interaction between heterocyclic bases and biacetyl-bis(benzoylhydrazone)nickel(II) (BBHNi) will firstly be discussed, as this is a thoroughly investigated system which serves as a model for understanding the factors governing the addition of molecules in the fifth and sixth positions of square complexes.

In view of an extensive conjugated system in this quadridentate ligand, the neutral complex would be expected to be square planar, which is also indicated by its diamagnetism. Solutions in pyridine and other donor solvents are paramagnetic, and paramagnetic bis-adducts can be isolated. These observations, together with spectral changes, are taken as good evidence for a change in stereochemistry from square planar to octahedral by apical coordination of donor solvent molecules.

The authors observed pronounced spectral changes on the addition of donor solvents to benzene solutions of the complex, which enabled equilibrium constants to be determined spectrophotometrically. The total formation constant was found to obey the equation:

$$K = \frac{(\mathrm{BBHNi.2base})}{(\mathrm{BBHNi})(\mathrm{base})^2}$$

The thermodynamic data thus derived by the usual relationships are not complicated by entropy changes arising from differences in the solvation states of reactants and products, which are important in aqueous solutions.

In relating the values of log K to the base strength of the donor solvent (with reference to the proton), Sacconi et al. distinguished two groups of bases:

(1) Pyridine and 3-, 4-, 3,4- substituted pyridines

(2) 2-substituted methylpyridines (2-, 2,4-, 2,6-dimethylpyridine).

The log K values for the first group of bases were found to parallel the base strength, suggesting that the main factor which determines the coordinating ability of these bases towards BBHNi is the availability of electrons on the nitrogen atom. For the second group, log K was some 3.5 logarithmic units lower than the first group, although pK_a values are of the same order. This effect is ascribed to steric hindrance to the coordination of the nitrogen atom, caused by the presence of a bulky methyl group in the 2- position. Quinoline (2,3-benzopyridine) showed a log K value greater than the other group (2) bases, presumably due to accomodation of the ortho hydrogen atom of the benzene ring inside the chelate ring of BBHNi. With the 2-methylpyridines, free rotation of the methyl group would prevent any of the hydrogen atoms from easily penetrating the chelate ring, thus accounting for the steric effects apparent in this group of bases.

Anomalous values were also obtained for piperidine and pyrrolidine. Log K for these saturated bases was found to be lower than expected from their pK_a in comparison with the group(I) bases. These results are taken to indicate the possibility of pi-bonding in the pyridine bases, which would account for the relatively increased bond strength. The calculated entropy changes are in agreement with this proposal. Larger negative values for the formation of the pyridine adducts can be ascribed to a reduction in the freedom of rotation of the pyridine bases about the nickel-nitrogen bond, as would occur if π-bonding was operative in these systems.

The effect of heterocyclic bases on the solvent extraction of BBHNi has also been studied.[38] Synergic effects observed in these systems have been accounted for in terms of adduct formation.

The reaction of bis-(acetylacetonato)copper(II) with heterocyclic bases should parallel the BBHNi system in that a change of stereochemistry from square planar to octahedral (tetragonal) is to be expected. In the case of copper(II), magnetic moments are of little use as evidence for this change,[39] although it has been calculated that magnetic moments of square pyramidal complexes could be in the range 2.1 - 2.2 B.M.[40] However, this result was obtained without consideration of Jahn - Teller distortions and it has been generally observed that the magnetic moments of most monomeric copper(II) complexes lie in the range 1.7 - 2.0 B.M.[39] In the absence of any X-ray structure determinations for the adducts of $Cu(acac)_2$ and related complexes, most information must be inferred from spectral and E.S.R. studies.

Graddon[41] has reported the results of a spectrophotometric study of the reaction of $Cu(acac)_2$ with pyridine in chloroform solution. With increasing concentrations of pyridine, a series of absorption curves was obtained showing a single isosbestic point, taken to indicate that only two complex species exist in solution. The equilibrium constant was found to conform to the equation:

$$K = \frac{(Cu(acac)_2 \cdot pyridine)}{(Cu(acac)_2)(pyridine)}$$

indicating the coordination of one only molecule of pyridine. The extrapolated spectra were shown to conform with the spectrum of the complex in pure pyridine, thus only one molecule of base is apparently coordinated even under these conditions. The greater solubility of bis(4-ethoxyacetylacetonato)copper(II) in cyclohexane enabled the determination of the formation constants of the adducts with piperidine, pyridine, 4-methylpyridine and 2-methylpyridine, which follow the general trend observed by Sacconi et al. for BBHNi.[37]

The five-coordinated structure proposed for these adducts has been questioned by Traill,[42] who suggested opening of one of the chelate rings and coordination of pyridine in the plane of the copper(II) ion. Graddon and Watton[43] have provided evidence against this structure from consideration of the visible and infrared spectra. The replacement of oxygen by nitrogen should produce a shift to higher energy in the visible spectrum, whereas the opposite is observed, akin to the effect of coordinating a fifth ammonia molecule to $Cu(NH_3)_4^{2+}$. Infrared spectra in chloroform solution containing the heterocyclic base and in Nujol mulls of the solid adducts[36] show only bands characteristic of the chelated β-diketonate ring, and no significant reduction in the intensity of these bands is apparent on comparison with the spectrum of the parent complex. Coupled with the low stability of the adducts, these facts are convincing evidence for apical coordination of the bases.

Graddon and Watton[36] have further determined formation constants for the adducts of $Cu(acac)_2$, bis-(4-ethoxyacetylacetonato) (acest) and bis-(4-phenylacetylacetonato) (bzac) copper(II) with pyridine and 2-, 4-, 2,6-methylpyridines in a variety of solvents. Table 4.4 shows some representative results obtained by these authors.

Three generalisations emerge from this study.

(1) For each complex, K increases along the series of bases listed in table 4.4. This result is expected in

TABLE 4.4. FORMATION CONSTANTS FOR THE ADDUCTS OF β-DIKETONE COMPLEXES WITH HETEROCYCLIC BASES IN CHLOROFORM SOLUTION ACCORDING TO GRADDON AND WATTON[36]) (l.moles^{-1}).

	2,6-dimethyl-pyridine	2-methyl-pyridine	pyridine	4-methyl-pyridine
$Cu(acest)_2$	0.44	1.6	3.3	8.0
$Cu(bzac)_2$	0.25	0.74	2.8	3.9
$Cu(acac)_2$	0.23	0.66	2.0	2.7

view of the reduction of steric hindrance to coordination in changing from 2,6-dimethylpyridine to pyridine. The effect of increased base strength in 4-methylpyridine relative to pyridine is also apparent.

(2) Irrespective of the base (or solvent) used, K increases in the order:

$Cu(acac)_2 < Cu(bzac)_2 < Cu(acest)_2$

which can be correlated with the inductive effect of the substituents. Thus the electron donating methyl groups in $Cu(acac)_2$ would tend to reduce the effective positive charge of copper(II), resulting in smaller formation constants of the adducts. Similarly, the electron-withdrawing effect of C_2H_5O- in $Cu(acest)_2$ should result in a relatively larger effective charge, and the formation constants are greater.

(3) The effect of solvent variation is to increase K in the order chloroform < acetone < benzene. This could be

caused by decreasing attraction of the solvent molecules to copper(II) in the complexes, but since dipole moments and dielectric constants of the solvents increase in the reverse order, the authors favour an explanation of this effect in terms of decreasing solvation energy of the bases. Evidence for this is found in the considerable evolution of heat when the bases are dissolved in chloroform, less heat being produced in the other solvents. On coordination of the bases in chloroform solution, some of this energy would have to be restored, leading to lower formation constants for the adducts.

In relation to points (1) and (3) above, May and Jones[44] have since determined the formation constants and heats of reaction for the addition of eight heterocyclic bases to $Cu(acac)_2$ in benzene solution. Considering the heat of reaction (determined calorimetrically) to approximate to the bond strength of the apically coordinated bases, these authors have observed that the bond strength roughly increases with the base strength. Electron donating substituents attached to the base were found to have a larger effect than electron attracting substituents, for which the heat of reaction tended to a limiting value.

No such correlation was observed with the formation constants. The authors suggest that effects due to solvation or steric interaction overpower the relatively small electronic effects when the bond formed is very weak.

The formation of adducts in the solvent extraction of copper(II) has been shown to account for the synergistic effect observed when mixtures of chelating agents and neutral donor molecules are used.[45,46] Formation constants have been measured and a number of solid adducts isolated.[47,50]

The apparent limitation to the coordination of only one molecule of heterocyclic base in solution has been the subject of some controversy. Further aspects of this problem will be reviewed in the following section.

(4.5) SOLID ADDUCTS OF HETEROCYCLIC BASES WITH β-DIKETONE COPPER(II) COMPLEXES.

By recrystallization of $Cu(acac)_2$ from 4-methylpyridine, Walker[48] has isolated the complex $Cu(acac)_2$.4-methylpyridine, which has also been reported by Graddon and Watton[36] together with $Cu(acest)_2$.(4-methylpyridine)$_2$, $Cu(bzac)_2$.4-methylpyridine, $Cu(acest)_2$.(pyridine)$_2$ and $Cu(bzac)_2$.pyridine. All these solid adducts are rather unstable, losing base on exposure to air and reverting to the parent compound, but can be preserved in closed containers.

After unsuccessfully trying to obtain mono-adducts from the bis-adducts listed above by partial decomposition or by reaction in a variety of solvents, Graddon and Watton have concluded that the second molecule of base is not coordinated to copper(II), but simply occupies a space in the crystal lattice. The similarity of the solid state spectra of the bis-adducts to the calculated mono-adduct spectrum in solution and in pure heterocyclic base solution is taken as additional evidence for this structure.

Further work has, however, indicated that the bis-adducts may in fact contain six-coordinated copper(II). Gillard and Wilkinson[49] have prepared both mono- and bis-pyridine adducts of bis-(trifluoroacetylacetonato)copper(II) which show different visible absorption spectra and similar infrared spectra for vibrations of the pyridine molecules, indicating that both are in a similar environment.

Walker and Li[50] have more recently reacted heterocyclic bases with the copper(II) chelates of thenoyltrifluoroacetone (TTA), trifluoroacetylacetone (TFacac) and hexafluoroacetylacetone (HFacac), and have isolated the adducts $Cu(TTA)_2.(4\text{-me-py})_2$, $Cu(TFacac)_2.(4\text{-me-py})_2$, $Cu(HFacac)_2.(4\text{-me-py})_2$, $Cu(HFacac)_2.4\text{-me-py}$ and $Cu(HFacac)_2.(py)_2$. Examination of the visible spectra of the parent complexes in benzene with increasing concentrations of 4-methylpyridine demonstrated the existence of both mono- and bis-adducts in solution. In each case a general increase in extinction in the range 17,000 - 12,500 cm^{-1} occurred, up to approximately equimolar proportions of complex and base, followed by a decrease in extinction as the ratio base:complex was made greater than 1:1. This behaviour may be contrasted with that of $Cu(acac)_2$, which showed only a gradual increase in extinction up to ratios of 1000:1 or more.

The relative stabilities of the bis-adducts may be gauged from the ratio base:complex required to produce the observed depression of extinction. In the case of $Cu(TTA)_2$ this ratio was 2000:1, for $Cu(TFacac)_2$, 50:1, while for $Cu(HFacac)_2$ increasing the ratio above 5:1 produced little change in the spectrum. The exceptional behaviour of the hexafluoro derivative may be ascribed to the large electron-withdrawing effect of two CF_3- groups, also demonstrated by the lower formation constant of the parent complex. Thus the bis-adduct was sufficiently stable to be recrystallized from ether and benzene.

It is therefore apparent that the two main factors governing the formation constants of copper(II) β-diketone adducts of heterocyclic bases without steric interference are: (1) The base strength of the apically coordinated ligand, and (2) the inductive effect of substituents attached to the chelate rings, although solvation effects are obviously important in view of the weak bond formed. These factors should also be responsible for the type of solid adduct formed, thus $Cu(acac)_2$ at one end of the scale forms only an unstable mono-4-methylpyridine adduct while $Cu(HFacac)_2$ forms very stable mono-adducts and quite stable bis-adducts. Thus it is possible that all β-diketone complexes in heterocyclic base solution may contain effectively six-coordinated copper(II) although this may not be readily apparent from the visible spectra in some instances. Since the existence of only the mono-adduct in solution is inferred from the observance of but one isosbestic point, the possibility of two species (mono and bis) with nearly identical spectra cannot be disregarded. It appears therefore that the larger spectral change is caused by the addition of only one molecule of base in systems where the formation constant for this process is very small. When formation constants (and presumably bond strengths) are larger, the difference in spectra is more readily discernable.

(4.6) THE EFFECT OF SYMMETRY VARIATIONS ON THE VISIBLE BAND INTENSITIES OF COPPER(II) CHELATES.

Belford and Yeranos[51] have investigated two series of copper(II) chelates, one based on acetylacetone and the other on salicylaldehyde, in an attempt to relate changes of molecular symmetry. Since electronic transitions between the energy states arising from d^n configurations are normally forbidden on symmetry grounds but occur by vibrational removal of the molecule's centre of symmetry, destroying the centre of symmetry by structural modifications may be expected to enhance band intensities. Thus the intensities, as well as the energies of bands, may give information about the molecule.

In confining remarks to the acetylacetone (acac), acetylacetoneimine (acim, N-methylacetylacetoneimine (meacim) and bis-(acetylacetone)ethylenediimine (ac_2en) series of complexes, it must be remarked that similar spectral changes are observed in the corresponding salicylaldehyde series. The major difference appears to be an overall intensity increase in the latter series due to the presence of the ligand transitions at lower energies.

Table 4.5 shows the position of bands in the region 23,000 - 13,000 cm^{-1} from the spectra reported by Belford and Yeranos. The effect of pyridination was also studied by these authors.

<u>TABLE 4.5.</u> VISIBLE SPECTRA OF THE ACETYLACETONE SERIES OF COPPER(II) CHELATES IN THE REGION 23,000 - 13,000 cm^{-1} (FROM BELFORD AND YERANOS[51]).

COMPLEX	SOLVENT	MAXIMUM, cm^{-1} (ε)
$Cu(acac)_2$	$CHCl_3$	18,600 (30), 15,500 (36)
	py	15,200 (78)
$Cu(acim)_2$	$CHCl_3$	17,700 (45)
	py	17,500 (58)
$Cu(meacim)_2$	$CHCl_3$	17,200 (67)
	py	16,900 (72)
$Cu(ac_2en)$	$CHCl_3$	18,500 (190), ~15,800 (sh) (60)
	py	18,200 (240), ~15,700 (110)

It was found that replacement of =O by =NH (in Cu(acim)$_2$) produced little change in intensity of the chloroform solution spectra, although it would appear that at least the band observed at 15,500 cm^{-1} in Cu(acac)$_2$ has moved to higher energy, in agreement with the expected stronger field of the acim ligand. From the considerations of section (4.3), a higher energy band in the region of 21,000 cm^{-1} would also be expected and may in fact be masked by the charge transfer band.

The effect of replacing =N-H by =N-CH$_3$ is more pronounced. A considerable increase in intensity of the 17,200 cm^{-1} band was observed, ascribed to a small deviation from perfect planarity in Cu(meacim)$_2$. Some evidence for this has been obtained from dielectric measurements on N-alkylsalicylaldimine copper(II) complexes.[52] Distortion is also indicated by the small shift to lower energy, opposite to that expected from the increased base strength of the nitrogen atoms due to inductive effects of the methyl groups.

The drastically increased intensity of the visible region bands of Cu(ac$_2$en) is seen to be due to the strong static acentricity of the ligand field (cis arrangement, cf. trans arrangement in the other complexes).

All the complexes in pyridine solution show increased intensities, expected from symmetry considerations if the molecules are assumed to be monopyridinated. It is interesting to note that $Cu(acim)_2$ shows little shift in the position of the band at 17,700 cm^{-1} on pyridination, compared with the large shifts of some bands as discussed previously for $Cu(acac)_2$. This is somewhat surprising in view of the expected planar configuration of the unpyridinated complex, and may indicate that there is little tendency to form a five-coordinated structure in view of a reduced effective positive charge of copper(II), akin to the effect of electron-donating substituents in $Cu(acac)_2$-type complexes. Alternatively, a second band in the region 10,000 - 12,000 cm^{-1} might be expected; it is unfortunate that Belford and Yeranos have not reported their spectra below 13,000 cm^{-1}.

Similar remarks apply to $Cu(meacim)_2$ in pyridine solution, although the effect of pyridination may be to restore the nearly coplanar ligands to a more perfectly planar structure, thus producing little variation in the spectrum. An analogous situation occurs in $Cu(ac_2en)$, which simply shows an overall intensity increase in pyridine solution. Belford and Yeranos suggest that here too, a gabled structure may become more planar on pyridination, the two effects countering each other. The presence of a shoulder at approximately 15,800 cm^{-1} on the red side of the main band in both chloroform and pyridine solution could thus indicate that the distorted structure exists in both solutions if negligible pyridination occurs, or else the two opposing effects cancel each other as discussed above.

(4.7) CRYSTAL SPECTRA OF COPPER(II) COMPLEXES.

Much evidence for the presence of three absorption bands in the visible region spectra of copper(II) complexes has been forthcoming from determination of the spectra of single crystals using polarised light. Thus, Holmes and McClure[53] have found that the single crystal spectrum of $CuSO_4 \cdot 5H_2O$ can be resolved into bands at 14,500, 13,000, and 10,500 cm^{-1}, although the accuracy of these band positions may be dubious since the authors state there is only a moderately good fit to the experimental curves.

From group-theoretical considerations, the direction of polarisation of an absorption band may provide evidence for the assignment of the transition responsible. The work of Ferguson on bis(salicylaldehyde)ethylenediiminecopper(II)[54] is interesting in view of its bearing on the problems discussed in the preceding sections. The crystal spectrum of this complex shows a band at 17,300 cm^{-1}, also present at 17,900 cm^{-1} in chloroform solution, and a shoulder at 20,800 cm^{-1}, not observed in chloroform solution. The crystal structure has been determined[13]; the molecules occur in pairs in which each copper(II) ion is contained in a five-coordinated pyramidal environment.

Ferguson reported that the 20,800 cm^{-1} band was strongly polarized in the x direction, any z component (if present at all) being much less. No clear decision could be made if the band had any y component. The 17,300 cm^{-1} band was found to be polarised in the y direction.

Belford and Piper[55] have reported the purely electronic selection rules in C_s (cis-pyramidal) and C_{2v} (cis-planar) symmetries. With d_{xy} taken as the ground state, transitions to the upper levels are expected to occur in the polarizations shown in table 4.6.

TABLE 4.6. ELECTRONICALLY ALLOWED POLARISATIONS OF POSITRON TRANSITIONS IN C_s AND C_{2v} SYMMETRIES.[55]

TRANSITION	C_s	C_{2v}
$xy \rightarrow z^2$	y	y
x^2-y^2	y	y
x^2	y	-
y^2	x, z	z

On the assumption that the symmetry of the molecule approximates to C_{2v} in solution in non-polar solvents, these authors have attributed the 17,300 cm^{-1} band to a hole transition from the xy antibonding orbital to an antibonding orbital formed from x^2-y^2 and z^2. They remark that the x-polarization of the 20,800 cm^{-1} band in the solid state is inconsistent with it being due to a d-level transition and tentatively propose that it is a ligand transition between two states of the same symmetry.

Considering the energy level diagram of figure 4.3, it is tempting to propose that the appearance of the band at 20,800 cm^{-1} in the solid state is due to the $xy \rightarrow z^2$ transition, which shifts to higher energy in the more effectively planar structure in chloroform solution. Against this is the observed polarization of the band, which according to Belford and Piper should be y-polarized. However, their selection rules are for a purely electronic mechanism and as remarked in their paper it is possible that other factors could cause deviations, notably the effect of molecular vibrations. Faint shoulders have been observed[51] at 25,000 - 26,000 cm^{-1} in the chloroform solution spectra of $Cu(sal_2en)$ and related complexes which may possibly be due to the $xy \rightarrow z^2$ transition.

Belford and Piper[55] have suggested that the relatively small effects of coordinating solvents such as pyridine on the spectrum of $Cu(sal_2en)$ and complexes of other acentric tetradentate ligands is indicative that the ligand field may be adequately described by C_{2v} symmetry. It is also possible that the symmetry is effectively C_s, with the transition to d_{z^2} shifted to lower energy and included in the main band.

Bis-(acetylacetone)ethylenediiminecopper(II) was also examined by Ferguson,[54] but the crystal spectrum was found to be unchanged from that in solution, indicating a similar environment of copper(II) in both states.

(4.8) MAGNETIC AND SPECTRAL PROPERTIES OF BINUCLEAR AND POLYMERIC COPPER(II) COMPLEXES.

Since there exists the possibility that the polymethylene-N,N-diacyldihydrazine series of ligands could give rise to binuclear or polymeric complexes (see Chapter 1), a review of the magnetic and spectral properties of such complexes is presented here in order to indicate features which may aid in distinguishing them from normal monomeric complexes.

The complexes formed by copper(II) with carboxylic acids have been extensively investigated over the last few years in view of the unusual magnetic properties displayed by many of these compounds. With the establishment of a binuclear structure for copper acetate monohydrate by X-ray methods[12], the short Cu-Cu distance of 2.64A has been taken to indicate the presence of a metal-metal bond.[56] The reduced magnetic moment of 1.42 B.M.[57] at room temperature is then seen to result from interaction of the spins of the unpaired electron on each copper(II) ion. However, the exact nature of this interaction remains uncertain;[58,59] δ-bonding through sideways overlap of the $d_{x^2-y^2}$ orbitals[57,60] or σ-bonding by overlap of the d_{z^2} orbitals[61] have been proposed but have failed to provide a convincing interpretation of the observed spectrum.[59]

The magnetic properties of binuclear copper(II) carboxylates will not be discussed in detail, except to remark that the susceptibility does not follow a Curie-Weiss Law, the susceptibility versus temperature curve showing maxima (at 260°K for copper acetate monohydrate[57]). This behaviour can be described in terms of spin-singlet ground state and a thermally accessible spin-triplet state.[57] Several authors[56,62,63] have reviewed this subject in detail.

Lewis[56] has reported a study of the magnetic behaviour of a series of substituted benzoate complexes. The formation of either binuclear or polymeric forms is apparently dependent on the pK_a of the acid; complexes of weaker acids tend to form binuclear structures while polymeric structures are favoured for complexes of stronger acids. The presence of ortho-substituents may result in deviations from this rule; such effects can be explained in terms of steric hindrance to the formation of a polymeric structure, thus the o-chlorobenzoate appears to be dimeric while the weaker meta- and para- acids form polymeric complexes. In carboxylates in which steric effects are negligible, the effect of variation of pK_a in determining the type of structure formed may be interpreted in terms of changes in the polarizability of the carbonyl oxygens. Thus the stronger acids should have less polarizable oxygens, the effective charge on copper(II) would be greater, leading to stronger repulsion between the two coppers of a binuclear structure and hence favouring a polymeric structure. This effect can also account for the difference in magnetic behaviour of copper formate to copper acetate since formic is a stronger acid than acetic. Several forms of copper formate have been isolated,[64] none showing the copper acetate behaviour, with magnetic moments in the range 1.61 - 1.90 B.M. The absence of dimeric structures has been demonstrated by crystal structure determinations for the tetrahydrate[14] and one of the anhydrous forms.[65] In both cases formate ions act as bridging groups between copper ions, resulting in polymeric structures. Water or formate oxygens complete a distorted octahedral arrangement.

The subnormal moment of 1.64 B.M. for copper(II) formate tetrahydrate led Martin and Waterman[64] to suggest that interaction between neighbouring copper(II) ions occurs via a superexchange process, involving the π-electron systems of the bridging formate groups, since the Cu-Cu distance of 5.8A was considered too large to allow direct interaction. It has since been found that several classes of compounds exhibit subnormal moments which can be attributed to this mechanism. These compounds have been reviewed by Kato et al.,[62] so it will suffice here to mention that structure containing halogen bridges (e.g. $KCuF_3$), oxygen bridges (e.g. Cu(pyridine N-oxide)Cl_2, Cu(8-hydroxyquinoline)Cl or Br) and hydroxide bridges (e.g. Cu($(C_2H_5)_2NCH_2CH_2N(C_2H_5)_2$)(OH)(ClO_4)) show subnormal moments. Compounds containing alkoxide groups, e.g. $Cu(OCH_3)_2$,[66] (2-aminopyridine)$_2$$Cu(OCH_3)(NO_3)_2$,[67] presumed to exist as polymers or dimers bridged through the alkoxide oxygen, also exhibit this phenomenon.

A particularly interesting series of complexes showing reduced moments through the superexchange mechanism is comprised of the so-called "tridentate" type complexes. Kishita et al.[68] predicted dimeric structures for these complexes, later confirmed by X-ray determination of the structure of acetylacetone-mono(O-hydroxyanil)copper(II),[69] in which a coordination number of four is achieved for each copper(II) ion by bridging oxygen atoms. The complexes of salicylaldehydebenzoylhydrazone and some of its derivatives similarly show subnormal moments, however the coordination of pyridine in the fourth position produces complexes displaying normal magnetic behaviour.[70] A dimeric structure has also been established for the "three-coordinated" complexes N-salicylidene-N'-caprinylhydrazinocopper(II) and N-salicylidene-N'-palmitylhydrazinocopper(II) by cryoscopic determination of molecular weights.[71]

The visible absorption spectrum of copper(II) acetate monohydrate shows two bands, one at 27,000 cm^{-1} (bandII) and the other at 14,400 cm^{-1} (band I) which have been observed in the crystal and in solution in weakly or non-coordinating solvents.[62] Tsuchida and Yamada[72] have proposed that the 27,000 cm^{-1} band may be taken as an indication of the Cu-Cu linkage in view of the polarization in the z direction of this band and its non-observance in most other copper(II) compounds which do not have the copper(II) acetate type structure. Higher members of the alkanoate series also show this band[73] and have been shown to possess similar magnetic properties to copper(II)acetate.[74]

As mentioned earlier, theoretical interpretations of the copper(II) acetate spectrum have not been particularly successful.[59] In view of the insensitivity of band II to coordinating solvents and the presence of a similar band in bis-(acetylacetonato)copper(II) and related complexes (section 4.3), Martin et al.[59] have proposed that these bands may be of similar origin, being due to electron transfer from ligand π-orbitals to the metal or vice versa.

Coordination of pyridine bases in the two apical positions of the binuclear acetate structure has little effect on the magnetic properties of the dimer. Kokot and Martin[75] have isolated a number of such compounds and have noted that band I moves to lower energy in pyridine solution, as is to be expected from the effects of apically coordinated molecules in other copper(II) complexes. They have suggested that this band may contain transitions from $d_{x^2-y^2}$ to d_{xz}, d_{yz} and/or d_{z^2} in the positive hole formalism. More recently, an additional band has been observed in the crystal spectrum of the monohydrate.[76]

This band, occurring at approximately 11,000 cm^{-1} as a shoulder on the infrared side of band I, may possibly contain the transition to d_{z^2}, as indicated by its polarization in the z direction.

Coordination of aniline type bases in the apical positions of the acetate dimer was found to produce anomalous effects.[75] Although showing similar temperature dependence to the pyridine base complexes, the aniline complexes showed magnetic moments close to the spin-only value at room temperature. This difference in behaviour was attributed to a reduction in the singlet - triplet separation, which may be influenced by variations in charge density on the coordinating atoms. In the case of pyridine, π-bonding may be important, providing a mechanism whereby the effective positive charge of copper(II) may be reduced. Evidence for this effect is found in the pyridine base adducts of copper(II) formate[77] which show considerably reduced magnetic moments, indicative of the dimeric structure which is not exhibited by the hydrated or anhydrous complexes.

It is surprising, however, that anhydrous, hydrated and pyridinated copper(II) acetates do not show more variation in their magnetic behaviour if such effects operate in the pyridine adduct.

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CHAPTER 5

COPPER(II) COMPLEXES OF N-ACYLHYDRAZINE AND POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE LIGANDS COORDINATED IN THE KETO FORM.

(5.1) SPECTRAL CHARACTERISTICS OF KETO BIS-(N-ACYLHYDRAZINE) COPPER(II) COMPLEXES IN THE VISIBLE REGION.

In Chapter 2, the manner in which the N-acylhydrazine grouping may be coordinated to a metal ion was discussed in regard to the stoichiometry of complexes reported previously. The composition of the cationic complexes of copper(II), nickel(II) and cobalt(II) is indeed in agreement with the postulate that the ligand is coordinated in the keto form by attachment of the terminal amino nitrogen and the carbonyl oxygen. Little evidence has been previously put forward in support of this idea, apart from the work of Nagano et al.[1] on the infrared spectra of $BHCuCl_2$ and $BHCdCl_2$ in relation to the complexes of isonicotinoylhydrazine. In the present chapter the results of an investigation of the visible absorption spectra of cationic bis-(N-acylhydrazine)copper(II) complexes will be discussed and are shown to be in agreement with the proposed mode of coordination.

In addition to the previously characterised complexes (see Chapter 2), $(BH)_2Cu(ClO_4)_2$ was prepared from aqueous solutions of N-benzoylhydrazine and copper(II) perchlorate hexahydrate. $(PH)_2CuSO_4.0.5H_2O$ was obtained from

N-isopropylidene-N'-propionylhydrazine, which loses acetone readily on hydrolysis; this indirect method was used as attempts to prepare the complex from N-propionylhydrazine led to impure products. The formulation as a hemihydrate was indicated on analytical figures - repeated recrystallisation from aqueous methanol resulted in an identical analysis.

The visible spectra of these complexes (table 5.1) consists of a single, broad band. In aqueous solution, the bis-(N-benzoylhydrazine) complexes have maxima in the vicinity of 14,000 cm^{-1}, placing the ligand between water and ammonia in the spectrochemical series when compared with the complexes $Cu(H_2O)_6^{2+}$ and $Cu(NH_3)_4(H_2O)_2^{2+}$ (table 4.3). Comparison with the interpolated spectra of cis- and trans- $Cu(NH_3)_2(H_2O)_4^{2+}$ (table 4.3) would indicate that the ligands may have a cis configuration in $(BH)_2Cu^{2+}$ although this seems unlikely in view of possible steric interactions of the benzene rings in this configuration.

Assuming that the ligand field of the coordinated hydrazine nitrogen is similar to that of ammonia, the carbonyl oxygen of the N-acylhydrazine group should be placed before water in the spectrochemical series, hence any assignment of configuration on the basis of the position of the absorption maximum in comparison with the maxima of the $Cu(NH_3)_2(H_2O)_4^{2+}$ isomers is probably not justified.

The aqueous solution spectra of $(AH)_2CuSO_4$ and $(PH)_2CuSO_4 \cdot 0.5H_2O$ are practically identical to that of the N-benzoylhydrazine complexes, indicating that these ligands occupy a similar position in the spectrochemical series. Thus the ligand field strength of the N-acylhydrazine grouping is not greatly affected whether the external group is phenyl-, methyl- or ethyl-.

TABLE 5.1. ABSORPTION SPECTRA OF KETO BIS-(N-ACYLHYDRAZINE) COPPER(II) COMPLEXES IN THE REGION 30,000 - 6,000 cm^{-1}.

COMPLEX	MEDIUM	MAXIMUM (cm^{-1}) (ε)
$(BH)_2CuSO_4 \cdot 2H_2O$	Mull	15,000
$(BH)_2CuSO_4$	Mull	15,400
	Water	13,800 (31.4) (3 cm cells)
$(BH)_2Cu(NO_3)_2$	Mull	16,300
	Water	14,200 (33.0)
$(BH)_2Cu(ClO_4)_2$	Mull	16,100
	Water	14,100 (31.5)
$(BH)_2CuCl_2 \cdot 4H_2O$	Mull	14,800
$(BH)_2CuCl_2$	Mull	15,200
	Water	14,300 (34.6)
$(AH)_2CuSO_4$	Mull	15,500
	Water	14,300 (30.0)
$(PH)_2CuSO_4 \cdot 0.5H_2O$	Mull	14,900
	Water	14,300 (30.8)

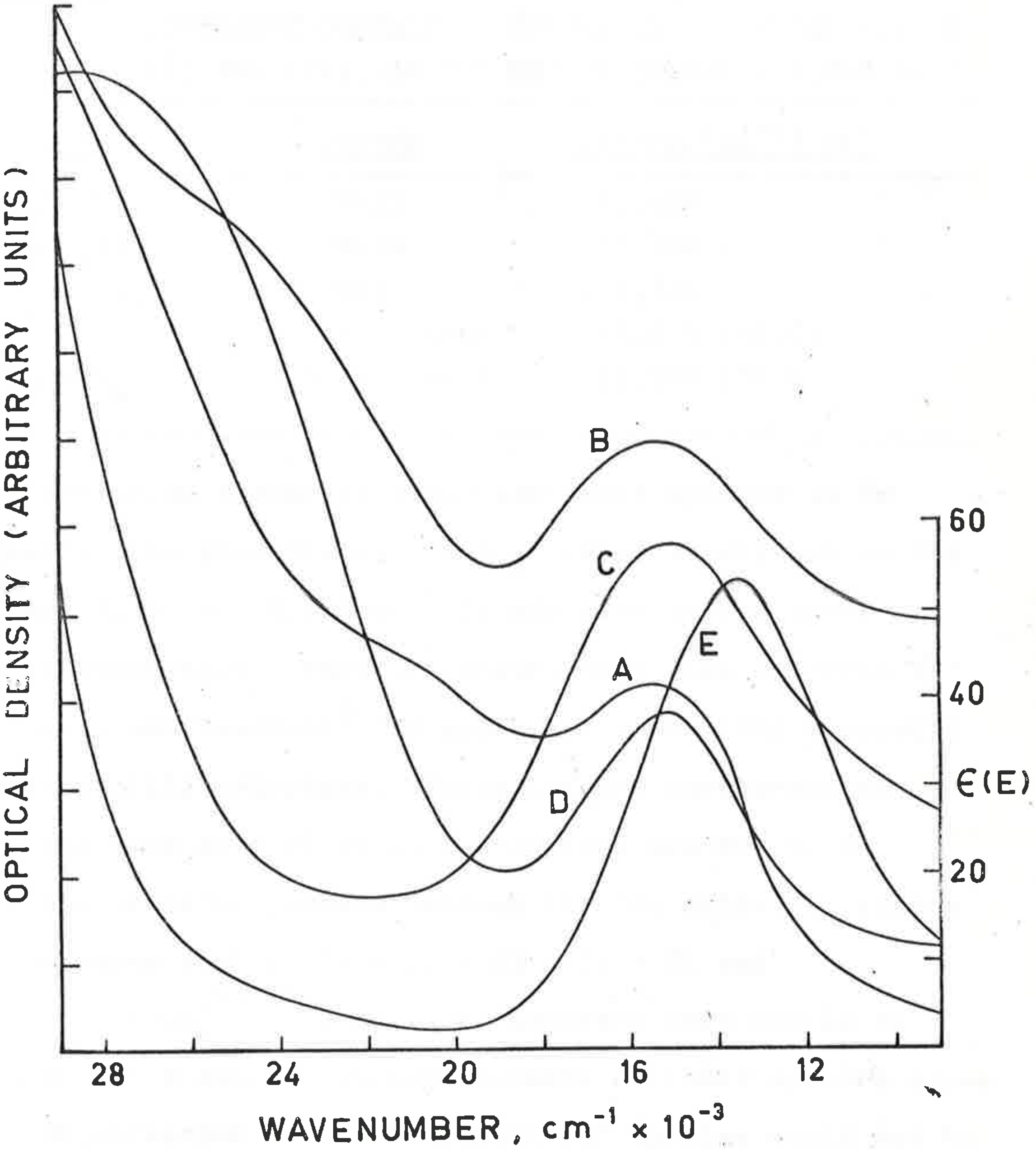
In the solid anhydrous complexes the maxima all occur at higher energies compared with the corresponding aqueous solutions (table 5.1). This is presumably due to the ligand field in the planar, four-coordinate complexes although small variations of the maxima of $(BH)_2Cu^{2+}$ complexes containing the sulphate, nitrate, perchlorate and chloride anions suggest that they may have some perturbing effect on the energy levels of copper(II) in this environment, but this effect could also arise from variations in crystal structure. The difference between the solid state and solution spectra, however, is readily interpreted as the result of coordination of water molecules in the apical positions of the metal ion, analogous to Bjerrum's "pentammine" effect,[2] although separation of the bands was not observed.

A similar but smaller shift to lower wavenumbers occuring in the solid state is apparent on comparing the positions of the maxima of anhydrous $(BH)_2CuSO_4$ and $(BH)_2CuCl_2$ with the respective dihydrate and tetrahydrate (table 5.1). This shift could indicate that water molecules are coordinated in the apical positions of the metal in the solid hydrates. The larger shift demonstrated by the aqueous solutions suggests that water molecules are more firmly bound in solution, while in the solid state the bond is weaker, which could be a result of hydrogen bonding of the water molecules to neighbouring ligand atoms in the crystal lattice. The alternative explanation, that in solution water molecules could replace the carbonyl oxygens, seems unlikely in view of the fact that the solid hydrates readily lose their water molecules on drying in vacuo over phosphorus pentoxide. In any case, replacement by water molecules would no doubt result in the solution maximum occuring at higher energies than is observed, as discussed above. However, in the case of $(PH)_2CuSO_4.0.5H_2O$ the remaining water could not be removed under similar conditions and the maximum occurs between that of anhydrous $(AH)_2CuSO_4$ and the aqueous solution of either complex. The stoichiometry and spectrum of this complex is thus in agreement with a structure in which one water molecule is retained in the crystal lattice as a bridging group between the apical positions of two copper(II) ions.

(5.2) THE VISIBLE ABSORPTION SPECTRA OF KETO N-ACYLHYDRAZINE COMPLEXES CONTAINING COPPER IN OXIDATION STATES (I) AND (II).

The isolation and characterisation of the complexes $(BH)_2Cu^{2+}.CuCl_3^{2-}$, $(AH)_2Cu^{2+}.CuCl_3^{2-}$ and $(BH)_2CuCl_2.3CuCl$ has been discussed (Chapter 2). In view of the dark green colours of these complexes, presumed to contain the bis-(n-acylhydrazine)copper(II) cation which is normally blue, it was interesting to examine their solid state visible spectra which are shown in figure 5.1 with $(BH)_2CuCl_2$ for comparison. The ligand field transitions of copper(II) are apparent in these spectra and the position of the absorption maxima at approximately 15,300 cm^{-1} (table 5.2) is indicative of a similar environment to the

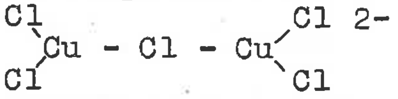
FIGURE 5.1. Visible region spectra of: (A) $(BH)_2Cu_2Cl_3$ (mull; (B) $(BH)_2Cu_4Cl_5$ (mull); (C) $(BH)_2CuCl_2$ (mull); (D) $(AH)_2Cu_2Cl_3$ (mull); (E) $(AH)_2Cu_2Cl_3$ (10% aqueous ethanol).



anhydrous bis-keto complexes.

TABLE 5.2 ABSORPTION SPECTRA OF KETO N-ACYLHYDRAZINE COMPLEXES CONTAINING COPPER IN OXIDATION STATES (I) AND (II), IN THE REGION 20,000 - 6,000 cm^{-1}.

COMPLEX	MEDIUM	MAXIMUM (cm^{-1}) (ε)
$(BH)_2Cu_2Cl_3$	Mull	15,400
$(BH)_2Cu_4Cl_5$	Mull	15,300
$(AH)_2Cu_2Cl_3$	Mull	15,300
	10% aqu. EtOH	13,500 (52.8)
$(BH)_2CuCl_2$	10% aqu. EtOH	13,500 (56.4)

The green colour of these complexes appears to be caused by the presence of a rather broad absorption in the region 28,000 to 18,000 cm^{-1} in addition to the lower energy absorption. Similar spectra have been observed by McConnell and Davidson[3] for solutions containing copper(I) and copper(II) chlorides. These authors have proposed that the dark colours of such solutions are due to an electron transfer process between the two oxidation states in complexes such as Cl - Cu - Cl - Cu - Cl and  , but unfortunately were unable to remark on the extinction coefficients of their spectra since the concentration of the "interaction" species could not be determined.

With reference to figure 5.1, it can be seen that the extinction of the mixed oxidation state N-acylhydrazine complexes in the region of 24,000 cm^{-1} is some two to three times the value at the maximum of the ligand field bands. This would indicate ε at 24,000 cm^{-1} is probably within the range 200 to 400 1. $mole^{-1}$ cm^{-1}, thus the bands in this region cannot be ascribed to a pure charge-transfer process. The spectrum of $(AH)_2Cu.CuCl_3$ in aqueous ethanol is also recorded in figure 5.1. The complex could be recrystallised from this solvent although it is rapidly decomposed by water alone. The blue solution showed no evidence of anomalous absorption at higher wavenumbers and its spectrum is practically identical to that of $(BH)_2CuCl_2$ in the same solvent (table 5.2). This would suggest that on dissociation, with separation of anion and cation, there is no electron transfer occuring between the two oxidation states, which process must therefore result from the close proximity of the ions in the solid state. Should a chloride bridge between the two copper ions be an essential feature of such a structure, as indicated by McConnell and Davidson, this would necessarily have to occur via the apical coordination positions of copper(II) since the N-acylhydrazine ligands must be contained in the four planar positions. The ligand field band of a complex in such an environment might be expected to show a shift to lower wavenumbers compared to the planar $(BH)_2Cu^{2+}$ cation, although this would be small in view of the position of the chloride ion in the spectrochemical series. Such a shift is observed in comparison with the absorption maxima of $(BH)_2Cu(ClO_4)_2$

and $(BH)_2Cu(ClO_4)_2$ (table 5.1). The lower energy of the maximum of $(BH)_2CuCl_2$ would also point to the possibility of apically coordinated chlorides in this complex in the solid state.

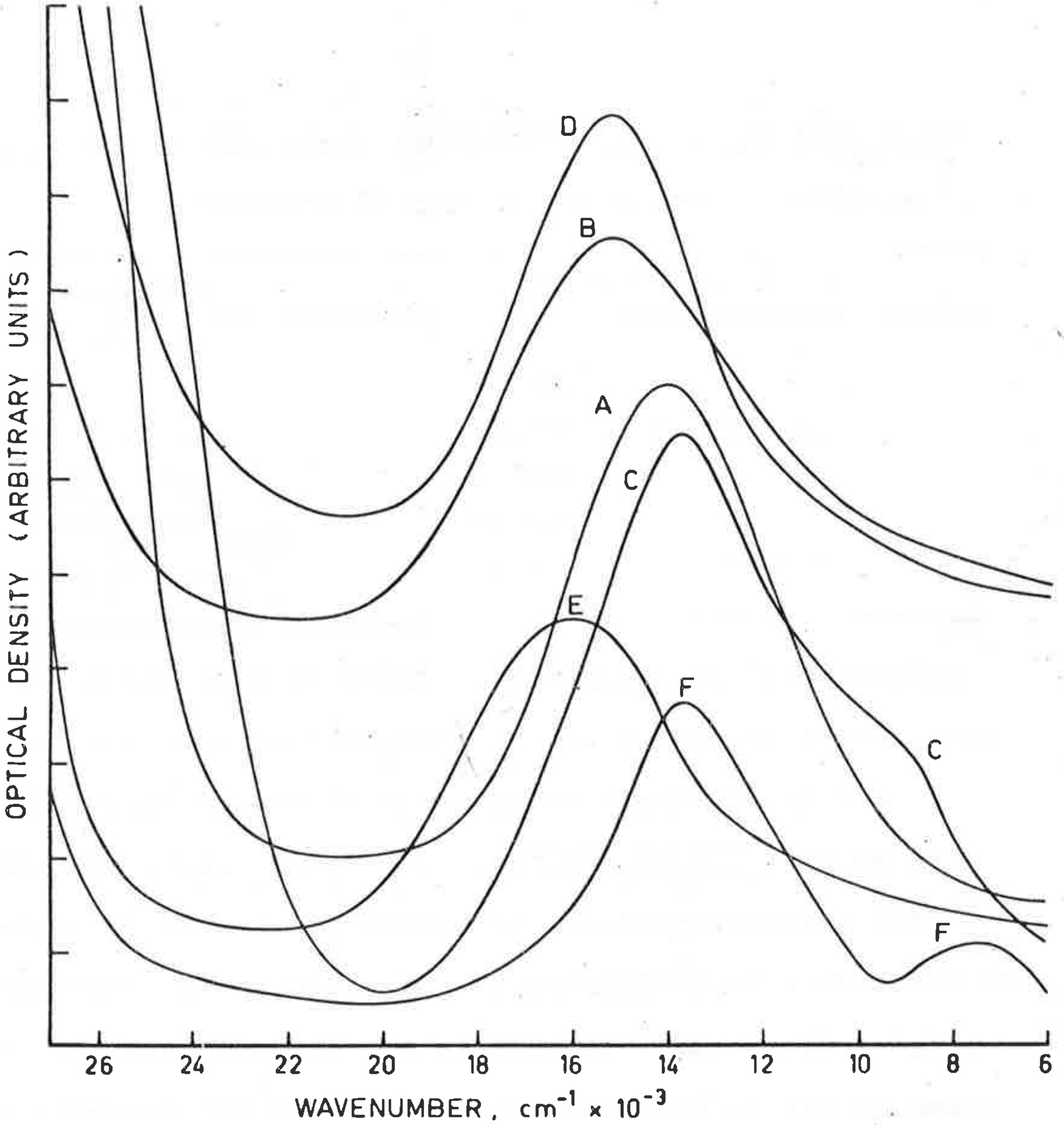
(5.3) KETO TRIS- AND TETRAKIS-(N-BENZOYLHYDRAZINE)COPPER(II) COMPLEXES.

When N-benzoylhydrazine and copper(II) chloride in molar ratios of 3:1 or greater were mixed in cold aqueous solution and allowed to crystallise slowly, hydrated $(BH)_3CuCl_2$ was deposited in blue-green prisms. When powdered and dried the anhydrous green complex was obtained. The reaction of N-benzoylhydrazine with copper(II) perchlorate under similar conditions yielded a green oil, the supernatant depositing pale green crystals of anhydrous $(BH)_3Cu(ClO_4)_2$.

It was found that the complex $(BH)_4CuCl_2$ was produced from mixtures containing the reactants in a 5:1 ratio when caused to crystallise rapidly. Copper(II) perchlorate under these conditions yielded a large quantity of the green oil mentioned above which solidified on removal of the solvent under reduced pressure. Analysis of this compound indicated it to be impure $(BH)_4Cu(ClO_4)_2$; recrystallisation produced $(BH)_3Cu(ClO_4)_2$.

The solid state visible spectra of these complexes, together with $(BH)_2CuCl_2$, $(BH)_2Cu(ClO_4)_2$ and the previously reported $BHCuCl_2$[1,4], are shown in figure 5.2. Positions

FIGURE 5.2. Solid state visible region spectra (in Nujol mulls) of: (A) $BHCuCl_2$; (B) $(BH)_2CuCl_2$; (C) $(BH)_3CuCl_2$; (D) $(BH)_4CuCl_2$; (E) $(BH)_2Cu(ClO_4)_2$; (F) $(BH)_3Cu(ClO_4)_2$.



of the bands are listed in table 5.3. This series of complexes provides a good illustration of the usefulness of visible spectra in providing information about their structures.

TABLE 5.3 SOLID STATE ABSORPTION SPECTRA OF $(BH)_nCuX_2$ COMPLEXES IN THE REGION 30,000 - 6,000 cm^{-1}.

COMPLEX	MAXIMUM (cm^{-1})
$BHCuCl_2$	14,000
$(BH)_2CuCl_2$	15,200
$(BH)_3CuCl_2$	13,700 ; ~9,500 (sh)
$(BH)_4CuCl_2$	15,200
$(BH)_2Cu(ClO_4)_2$	16,100
$(BH)_3Cu(ClO_4)_2$	13,700 ; 7,500

In the case of $BHCuCl_2$, the shift to lower energy with reference to $(BH)_2CuCl_2$ would appear to result from replacement of one BH molecule in the plane by two chloride ions. $(BH)_3CuCl_2$ and $(BH)_3Cu(ClO_4)_2$ show a larger shift with reference to the corresponding bis-complexes, accompanied by the separation of a shoulder on the infrared side of the main band. This is thus taken as evidence for coordination number five or six in these complexes, as indicated by their stoichiometry. The almost complete separation of the two bands would indicate a fairly strong axial field such as would be produced by coordination of nitrogen rather than the carbonyl group. This is further indicated by the infrared spectra (section 5.4) of these complexes.

In $(BH)_4CuCl_2$, two possible structures are considered to be most likely. Firstly, two of the ligands could act as bidentate chelating agents as indicated in the normal 2:1 complexes, with two more ligands coordinated apically through the hydrazine nitrogen in view of the greater base strength of this group. Such a structure can be considered to be unlikely since the visible spectrum shows a shift to higher energy compared with $(BH)_3CuCl_2$ and no separation of bands is observed.

Secondly, it is conceivable that the four ligands act as monodentate groups coordinating only through hydrazine nitrogens. This structure is in agreement with the shift of the absorption maximum to higher energy, although the maximum occurs close to that of $(BH)_2CuCl_2$. However, the shift in replacing two water molecules by ammonia in trans - $Cu(NH_3)_2(H_2O)_2(H_2O)_2^{2+}$ to form $Cu(NH_3)_4(H_2O)_2^{2+}$ (table 4.3) is only in the order of 300 cm^{-1}, according to Bjerrum et al.[2] In comparing $(BH)_4CuCl_2$ to the bis-complex, we must also consider that if the carbonyl group is positioned before water in the spectrochemical series as indicated in section (5.1), a larger shift than observed in the water-ammonia system is to be expected on replacement of two carbonyl oxygens by nitrogens.

The small shift found does not necessarily invalidate the conclusions on the structure of this complex since coordination of chloride ions or two of the four free carbonyl groups in the apical positions should reduce the expected shift.

From the relatively easy preparation of complexes of the series $(BH)_nCuCl_2$ from n = 1 to 4 by simply varying the preparation ratio, it is apparent that an equilibrium involving all four will exist in solution. A study of the formation constants would no doubt provide enlightning information on the distribution of each species and help to substantiate the inferences based on the visible spectra of these complexes.

(5.4) THE INFRARED SPECTRA OF KETO N-BENZOYLHYDRAZINE COPPER(II) COMPLEXES.

The infrared spectrum of N-benzoylhydrazine has been investigated by two groups of workers[5,6] who have proposed tentative assignments of bands in the range 4,000 - 650 cm^{-1}. In both cases support for the assignments was obtained from examination of the N-deuterated compounds, prepared by recrystallisation from D_2O.

Our examination of the infrared spectra of the series of keto N-benzoylhydrazine copper(II) complexes was carried out in an attempt to ascertain the shifts of the carbonyl group on coordination and hence lend support to deductions based on visible region spectra as presented above. Hence discussion of the IR spectra will be contained to the region 1,700 - 1,500 cm^{-1}, in which the C = O stretching frequencies of secondary amides are known to occur.[7A] Unfortunately the spectrum of N-benzoylhydrazine in this region is not simple, hence an unambiguous assignment of the bands is made difficult. The assignments of Mashima and Nagano et al. are presented in table 5.4 for comparison.

<u>TABLE 5.4</u> TENTATIVE ASSIGNMENTS OF THE INFRARED SPECTRA OF N-BENZOYLHYDRAZINE AND ITS N-D_3 DERIVATIVE.

	MASHIMA[5]			NAGANO ET AL.[6]	
BH	BH-D_3	ASSIGNMENT	BH	BH-D_3	ASSIGNMENT
	1652		1662	1655 1635	Amide I
1664	1627	Amide I			
1618		NH_2 bend.	1613		NH_2 bend.
1608 (sh)	1603(sh)	(C-C) str.			
1582	1573	(C-C) str.	1578	1581	(C-C) str.
			1566		Amide II
			1547(sh)	1547	(C-C) str.
1527		Amide II			
	1507				
1492	1490	(C-C) str.	1487	1495	(C-C) str.

It is apparent that each group of workers has failed to observe a number of bands reported by the other group. This inconsistency would appear to result from the occurrence of rather broad bands in this region (figure 5.3), however we have been able to identify all the bands reported for BH by Mashima and Nagano et al, which are listed in table 5.5.

The spectra of the complexes are presented in figures 5.3, 5.4 and 5.5; band positions are collected in table 5.5 to aid comparison. In view of the reasonable certainty of the assignment of the 1662 cm^{-1} band as the carbonyl stretching frequency (amide I), one can identify strong bands in this region in the spectra of $(BH)_3CuCl_2$, $(BH)_3Cu(ClO_4)_2$ and $(BH)_4CuCl_2$ as resulting from uncoordinated (or weakly coordinated) carbonyl groups in these complexes. This is supporting evidence for their structures as indicated in section 5.3, but although coordination number 5 or 6 with nitrogen coordinated apically is apparent, one cannot distinguish between the several possible isomers in the case of the tris complexes, nor whether the carbonyl group is coordinated apically in the case of the tetrakis complex.

It would be useful to be able to assign bands due to carbonyl groups coordinated in the plane in all the complexes, however this has proved to be a difficult procedure. It is tempting to give this assignment to the band observed between 1628 - 1646 cm^{-1} in most of the complexes, but the absence of such a band in $(BH\text{-}D_3)_2CuCl_2$ leaves this open to doubt. In this complex the weak band at 1618 cm^{-1} is probably due to the presence of undeuterated BH in the molecule, since examination of the N-H and N-D stretching

FIGURE 5.3. Infrared spectra of $(BH)_2Cu(ClO_4)_2$, $(BH)_3Cu(ClO_4)_2$ and BH in the region 1700 - 1500 cm^{-1} (Nujol mulls).

FIGURE 5.4. Infrared spectra of $BHCuCl_2$, $(BH)_2CuCl_2$ and $(BH\text{-}D_3)_2CuCl_2$ in the region 1700 - 1500 cm^{-1} (Nujol mulls).

FIGURE 5.5. Infrared spectra of $(BH)_3CuCl_2$, and $(BH)_4CuCl_2$ in the region 1700 - 1500 cm^{-1} (Nujol mulls).

FIGURE 5.3.

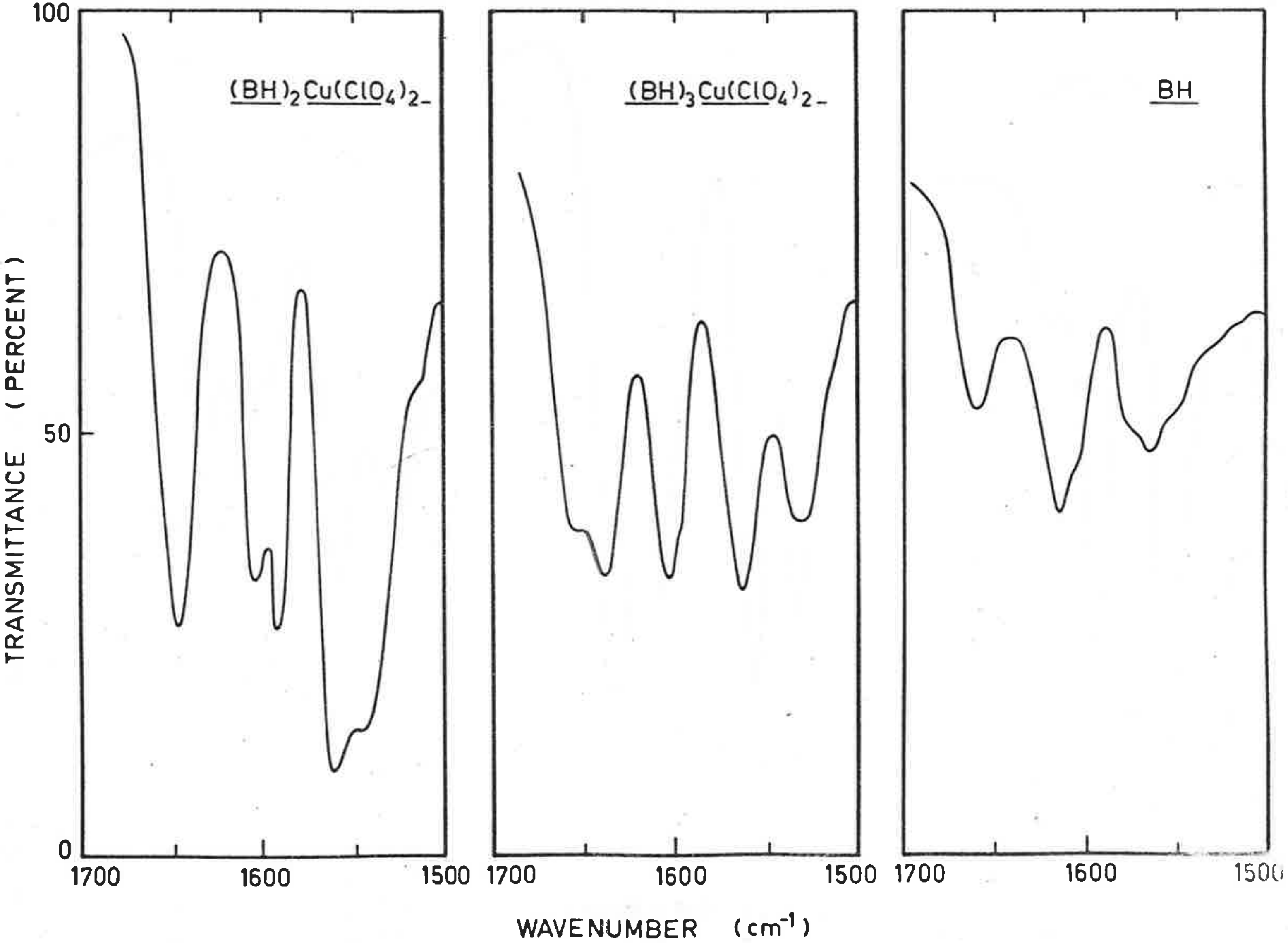

100
50
0
TRANSMITTANCE (PERCENT)
$(BH)_2Cu(ClO_4)_2$
$(BH)_3Cu(ClO_4)_2$
BH
1700
1600
1500
1700
1600
1500
1700
1600
1500
WAVENUMBER (cm^{-1})

FIGURE 5.4.

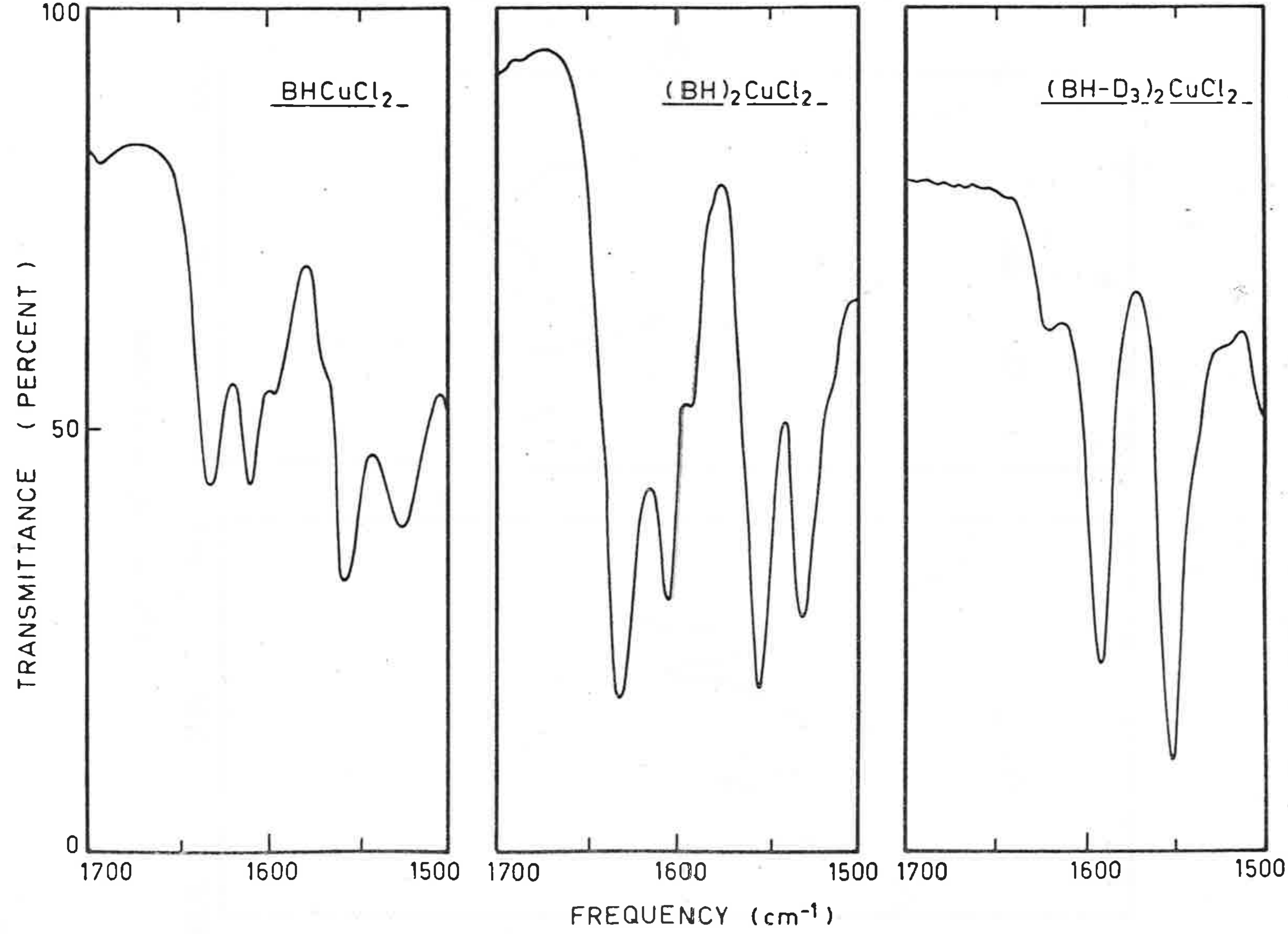

BHCuCl$_2$
(BH)$_2$CuCl$_2$
(BH-D$_3$)$_2$CuCl$_2$
100
50
0
TRANSMITTANCE (PERCENT)
1700
1600
1500
1700
1600
1500
1700
1600
1500
FREQUENCY (cm^{-1})

FIGURE 5.5

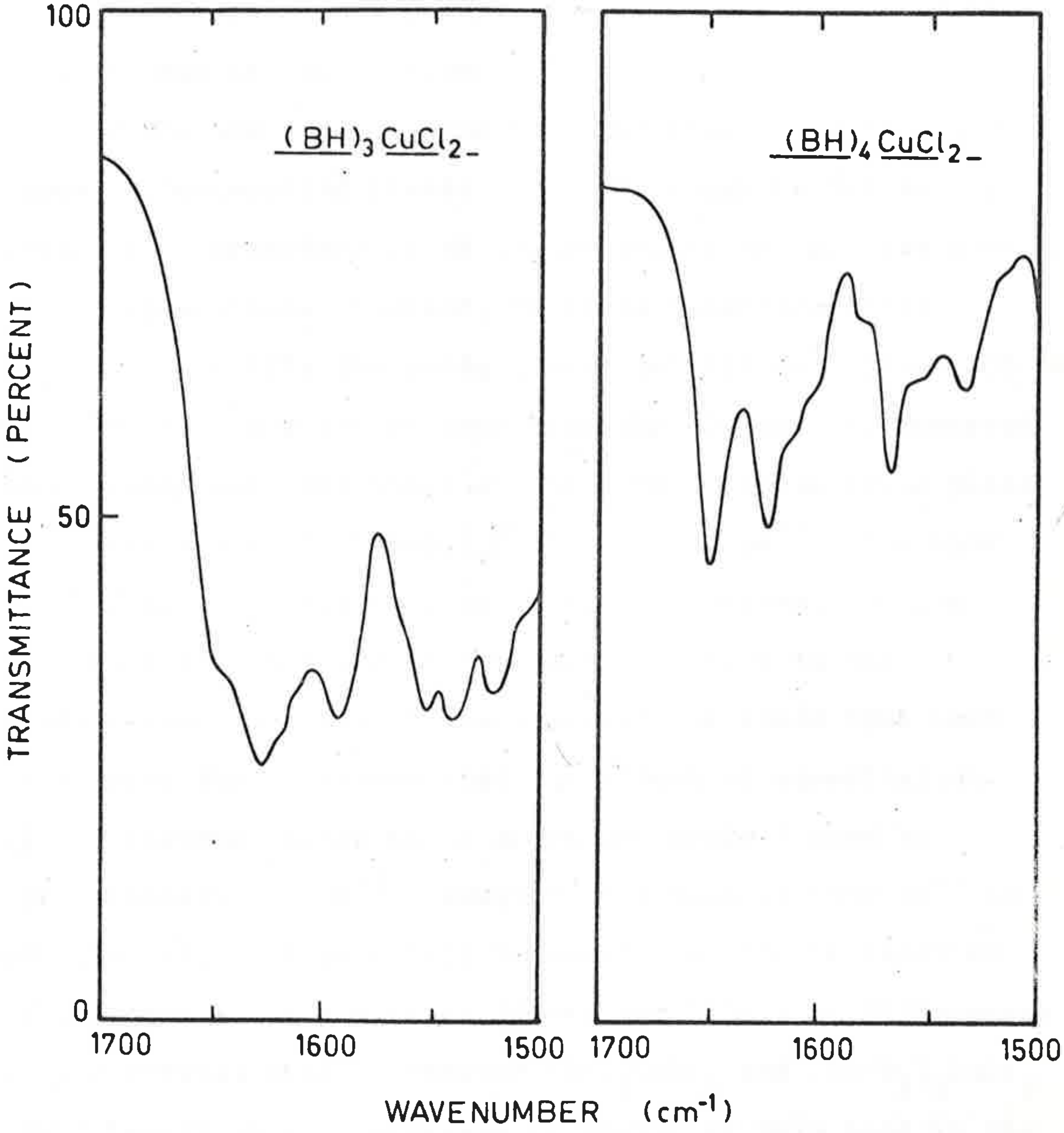


FIGURE 5.5

regions indicated that deuteration had proceeded to approximately 60 - 80%. The agreed assignment that this band in the ligand is due to the $-NH_2$ bending vibration is reasonable, as both groups of workers have observed it to disappear on deuteration.

In BH, the amide I band is apparently split into two bands on deuteration (table 5.4). This may be due to the presence of undeuterated BH in the sample or may have some other explanation. However, if it is considered that deuteration shifts the amide I band to 1627 cm^{-1} (i.e. -35 cm^{-1}) and also that a shift of approximately -30 cm^{-1} is incurred on coordination, the total of these two effects would place the amide I band in $(BH\text{-}D_3)_2CuCl_2$ at 1597 cm^{-1}. The band at 1592 cm^{-1} in this complex is indeed observed to have increased considerably in intensity relative to the undeuterated complex. These observations would thus tend to support the inference that the effect of coordination of the carbonyl group is to shift the amide I band by approximately -30 cm^{-1}. However, the band at 1592 cm^{-1} in $(BH)_2Cu(ClO_4)_2$ (figure 5.3) is equally strong in relation to adjacent bands and it is indeed possible that differences in the crystal packing between $(BH)_2CuCl_2$ and $(BH\text{-}D_3)_2CuCl_2$ could result in the increased intensity of this band in the latter complex.

Adding to the uncertainty of the above assignment, another explanation is possible. Coordination of the $-NH_2$ group might be expected to raise the energy of the bending vibration and thus the bands in the region of 1630 cm^{-1} could be ascribed to this effect in all complexes. The non-observance of this band in $(BH\text{-}D_3)_2CuCl_2$ would then be expected, and one would be required to look for the amide I band at lower wavenumbers. Nagano et al.[1] have in fact assigned a band at 1555 cm^{-1} to the coordinated carbonyl group in $BHCuCl_2$, although they give little evidence to support this. A band in this region is observed in all complexes including $(BH\text{-}D_3)CuCl_2$ (table 5.5) and also in the ligand where it is ascribed to the amide II band by Nagano et al., but not by Mashima (table 5.4). This band is observed to disappear on deuteration of BH.

The origin of the amide II band in secondary amides has been the subject of some controversy.[7B] The more favoured opinion is that it is a mixed vibration - an out of phase combination of OCN and NH vibrations in which the angular displacement of the hydrogen atom plays the greater part. Hence this band would be expected to alter appreciably on N-deuteration and to some extent on coordination, any may have possibly shifted to 1530 cm^{-1} in $(BH)_2CuCl_2$, where a weak shoulder is observed in $(BH\text{-}D_3)_2CuCl_2$. Corresponding bands can be observed in the spectra of all the other complexes.

Thus, on the basis of the results discussed above, it

TABLE 5.5. INFRARED DATA OF KETO N-BENZOYLHYDRAZINE COPPER(II) COMPLEXES IN THE RANGE 1700 - 1500 cm^{-1} (NUJOL MULLS).

BH	$BHCuCl_2$	$(BH)_2CuCl_2$	$(BH\text{-}D_3)_2CuCl_2$	$(BH)_2Cu(ClO_4)_2$	$(BH)_3CuCl_2$	$(BH)_3Cu(ClO_4)_2$	$(BH)_4CuCl_2$
1662(s)					1645(sh)	1655(sh)(s)	1650(s)
	1632(s)	1632(s)		1646(s)	1628(s)	1638(s)	
1614(s)	1612(s)		1618(m)		1618(sh)		1624(s)
1607(sh)		1605(s)		1605(s)	1610(?)	1605(s)	1610(sh)
	1598(sh)	1595(sh)	1592(s)	1592(s)	1593(s)	1597(s)	1600(sh)
1580(sh)	1570(sh)	1570(?)			1580(?)	1573(sh)	1580(sh)
1565(s)	1560(s)	1557(s)		1560(s)	1565(?)	1563(s)	1565(s)
1550(sh)			1551(s)	1544(sh)	1552(s)	1553(?)	1550(sh)
	1526(s)	1530(s)	1535(?)		1540(s)	1532(s)	1533(m)
1520(?)	1515(?)	1515(?)	1520(w)	1515(sh)(w)	1522(s)	1510(sh)	1515(?)
1485(m)	1495(s)	1492(s)	1500(m)	1494(m)	1503(m)	1490(m)	1495(m)

s = strong, m = medium, w = weak, sh = shoulder,
? = presence of band uncertain (generally a very weak shoulder).

is impossible to arrive at an unambiguous assignment for the coordinated carbonyl group stretching frequency. It is possible that further examination using higher resolution techniques could clarify the situation although interpretation would still be hindered by the complexity of the spectra.

(5.5) COPPER(II) COMPLEXES OF OXALYL- AND MALONYLDIHYDRAZINES.

(5.5.1) CATIONIC ENOL COMPLEXES.

While the reaction between copper(II) salts and monoacylhydrazine ligands in aqueous solution results in the crystallisation of keto complexes, reaction with oxalyldihydrazine (OXDH) and malonyldihydrazine (MADH) produces entirely different results. As discussed in Chapter 1, this is not unexpected in view of the structures of these ligands since they must necessarily act as bis-bidentate rather than tridentate or quadridentate ligands. However certain aspects of the reactions were surprising.

The addition of copper(II) sulphate solution to OXDH or MADH in solution produced a finely divided blue precipitate. The supernatant in these reactions became strongly acid, indicating the release of protons from the ligands and suggesting that these complexes might contain the ligand in its enol form (section 2.2). However, the precipitate in each case was shown to contain sulphate, demonstrating that some rather unusual complexes were formed.

On drying the OXDH complex at room temperature in vacuo over phosphorus pentoxide, the colour changed to green and the complex continued to lose weight slowly even after several weeks. The marked change in colour indicates that this was probably due to slow loss of water from the co-ordination sphere of copper(II). Such a process made it difficult to be certain that the complex was absolutely dry when analysed. Similar effects were observed with the MADH complex. An attempt to dry the OXDH complex at elevated temperatures in vacuo resulted in some decomposition occuring (see later). These peculiarities apparently account for the reluctance of Jensen and Bak[8] to quote analytical results for the complexes of OXDH and MADH in their earlier investigation, other than to remark that the ratio of ligand to copper was approximately 1:2.

The OXDH complex dried at room temperature, however, analysed in reasonable agreement with the composition $(OXDH)_2Cu_3SO_4.5H_2O$. A preparation carried out in sodium acetate solution (conditions which should favour the formation of an enol complex) showed approximately the same hydrazine analysis although the copper figure was some 9% higher.

In view of the uncertainty in drying this complex, the system was investigated more thoroughly by determining the ratio of hydrazine to copper on freshly prepared samples obtained under varying conditions of preparation. This was done in order to ascertain whether the compositions of the dried samples were reliable or whether different complexes might be formed by altering the conditions of preparation. The results of this investigation are summarised in table 5.6, from which several points are noteworthy.

(1). The ratio OXDH:Cu in the freshly prepared samples was between 0.67 and 0.77 over the range of conditions investigated.

(2). The order of mixing the reagents apparently made little difference to the product.

(3). Preparation carried out in hot solution produced a precipitate containing a slightly lower ration than that obtained from a cold solution under otherwise identical conditions. Hot conditions could result in some of the copper being reduced - the precipitate formed on addition of the first few ml of copper sulphate solution appeared green in colour, but came down blue thereafter.

(4). Decreasing the preparation ratio resulted in the precipitate ratio being lowered.

(5). Precipitates prepared from solutions buffered at pH 5-7 had a higher ratio than precipitates from solutions buffered at lower pH.

The large difference in ratios determined on a sample prepared from sodium acetate solution, part dried at room

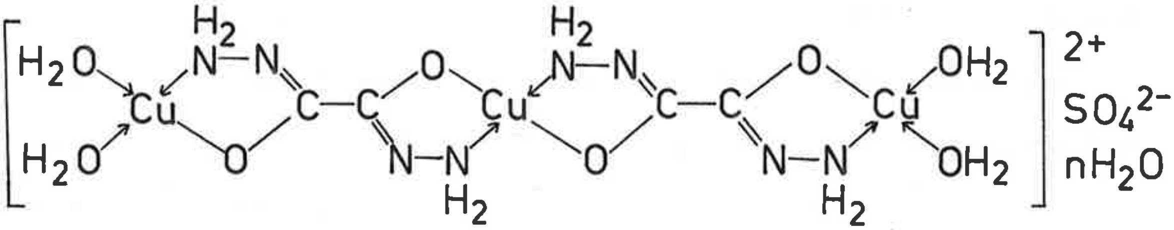
TABLE 5.6 RATIO OXDH : Cu DETERMINED ON THE PRECIPITATE FORMED UNDER VARYING CONDITIONS FOR THE REACTION OF OXDH WITH COPPER(II) SULPHATE.

PREPARATION RATIO OXDH : Cu	PRECIPITATE RATIO OXDH : Cu	CONDITIONS
1.00	0.661	Neutral solution, Cu added to OXDH, complex dried at room temperature.
2.00	0.620	NaAc soln., Cu to OXDH, dried at room temperature.
	0.405	Part of previous sample dried at 110° in vacuo.
0.928	0.710	Neutral, cold Cu to OXDH.
0.501	0.686	" " "
0.667	0.698	" " "
"	0.694	" " OXDH to Cu.
"	0.698	" " Cu to OXDH in very dilute solutions.
"	0.689	Neutral, 90° Cu to OXDH.
2.000	0.773	pH 7.55 to 5.31 (NaAc) Cu to OXDH.
"	0.749	pH 5.00 to 4.89 (NaAc/HAc) Cu to OXDH.
"	0.694	pH 4.00 to 4.00 (NaAc/HAc) Cu to OXDH.
"	0.708	pH 2.99 to 2.51 (NaAc/H_2SO_4) Cu to OXDH.
"	0.718	pH 2.00 to 1.73 (H_2SO_4) Cu to OXDH.
1.000	0.684	pH 2.96 to 2.31 (NaAc/H_2SO_4) OXDH to Cu.
0.500	0.669	pH 2.97 to 2.36 " OXDH to Cu.

pH range corresponds to start and completion of precipitation. Reagents used to adjust pH of OXDH solution before addition of Cu are given in parentheses.

temperature and part at 110°, indicates that some decomposition of the heated sample occured. It is thus possible that slow decomposition, as well as loss of water, was responsible for the difficulty in drying the complex to constant weight at room temperature.

The major component of the precipitate, however, seems to be the 2:3 species, hence polymerisation may occur until this insoluble oligomer separates from solution. The structure of this complex would most likely be as shown in (XIX).

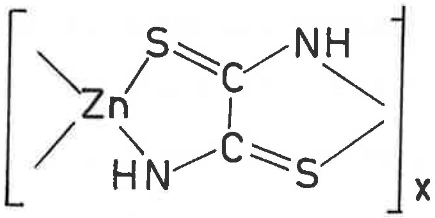


(XIX)

Apart from reasonable agreement with the theoretical ratio, titrates of the hydrogen ions liberated on formation of the complex also indicates at 2:3 ratio and is in agreement with the number of hydrogen ions expected to be released in forming the enol structure (See page 111). The presence of at least four firmly bound waters is also significant, presumably terminating the chain as shown.

The reason why oxalyldihydrazide spontaneously releases two protons on complex formation in neutral solution may be appreciated in terms of the presence of two adjacent polarised carbonyl groups, which activate the hydrogen atoms attached to the nitrogens next to them. Another manifestation of this effect is apparent in the preparation of the ligand from diethyl oxalate and hydrazine hydrate. Unless carried out in dilute solution, this reaction is extremely violent, whereas preparation of all the other acylhydrazines encountered required several hours refluxing by this method.

It is possible that the trimeric structure could be formed by coordination of the imino nitrogen and enol oxygen atoms of adjacent hydrazide groups, rather than the end-to-end coordination of separate hydrazide units as shown in (XIX). This alternative method of coordination would thus involve the formation of five-membered rings containing both carbon atoms, similar to the structure established for bis-(dimethylglyoximato)copper(II) and suggested for tris-(biacetyl-bis-methylimine)iron(II) iodide[10] and tris-(biacetyldihydrazone)iron(II) tetrachloroferrate(II)[11]. The proposed structure (XX) of the polymeric zinc derivative of dithiooxamide[12] provides a more analogous example. With this ligand, coordination of



(XX)

sulphur and nitrogen atoms to form a four-membered ring is improbable, but no decision can be reached as to which of the two possible coordination modes of OXDH is more likely to occur.

It is probable that preparations of $(OXDH)_2Cu_3SO_4.nH_2O$ carried out from higher ligand : copper ratios may show higher ratios due to the attachment of ligand to the terminal copper ions of this unit in some molecules contained in the precipitate. Preparation from solutions buffered at pH5-7 may tend to favour this process or may result in co-precipitation of the anionic complex $(OXDH)_2Cu^{2-}$, the potassium salt of which has been reported (see Section 3.2) This complex has an intense green colour, and its presence may account for the green colour of the preparations at higher pH.

Several attempts were made to prepare $K_2(OXDH)_2Cu$ in order to determine if the 2:3 complex could be synthesised simply by addition of copper(II) sulphate to a solution of this complex. However the anionic complex appeared to be unstable in solution, slow evolution of gas occuring; its extreme solubility in water made it difficult to isolate. A process of solution in water followed by precipitation with ethanol was carried out several times, the final product showing a ratio 1.63:1 for OXDH:Cu, thus indicating some decomposition. However, a sample of this solution was used to study the effect of addition of copper(II) sulphate.

A green precipitate was produced showing a 0.525:1 ratio, which could indicate the formation of a 1:2 complex. However, since the $K_2(OXDH)_2Cu$ solution was initially pH11.4 (which dropped to 4.3 on addition of excess copper(II) sulphate) it is probable that the 2:3 complex was precipitated, contaminated with copper(II) hydroxide.

It was found that the addition of dilute sulphuric acid to $K_2(OXDH)_2Cu$ solution also caused precipitation. The ratio in the green precipitate formed in this case was found to be 0.86:1, indicating that precipitation of the 2:3 complex is favoured under these conditions.

The search for a suitable solvent for $(OXDH)_2Cu_3SO_4.5H_2O$ proved fruitless. The complex was insoluble in all solvents tried. However, the freshly prepared complex did dissolve in a warm, strong solution of glycine in water and a blue-green precipitate was deposited on cooling. This compound behaved similarly to the 2:3 complex on drying but was of different composition. The possibility that glycine was coordinated to the terminal copper ions in this complex was precluded by the fact that the total nitrogen content could be recovered as hydrazine, demonstrating that no glycine was present in the molecule. Presumably such a process is however responsible for solution of the complex.

Following the conclusions from the above investigation, no attempt was made to dry the complex produced from the reaction of OXDH with copper(II) chloride, particularly as the presence of the chloride ion tends to cause copper(II) monoacylhydrazine complexes to decompose on standing over long periods (see Section 2.2). On the dropwise addition of copper(II) chloride to a cold OXDH solution, the pH fell rapidly from 5.9 to about 2.0 during the addition of one molar equivalent and little precipitation occured. The addition of a further 0.5 equivalent resulted in complete precipitation. This precipitate showed a ratio OXDH:Cu:Cl^- of 2.01:3:1.98, indicating that the insoluble cation $(OXDH)_2Cu_3^{2+}$ is common to both the sulphate and chloride systems. The lack of precipitation up to a 1:1 reaction ratio could indicate that other more soluble oligomers are formed in the chloride system.

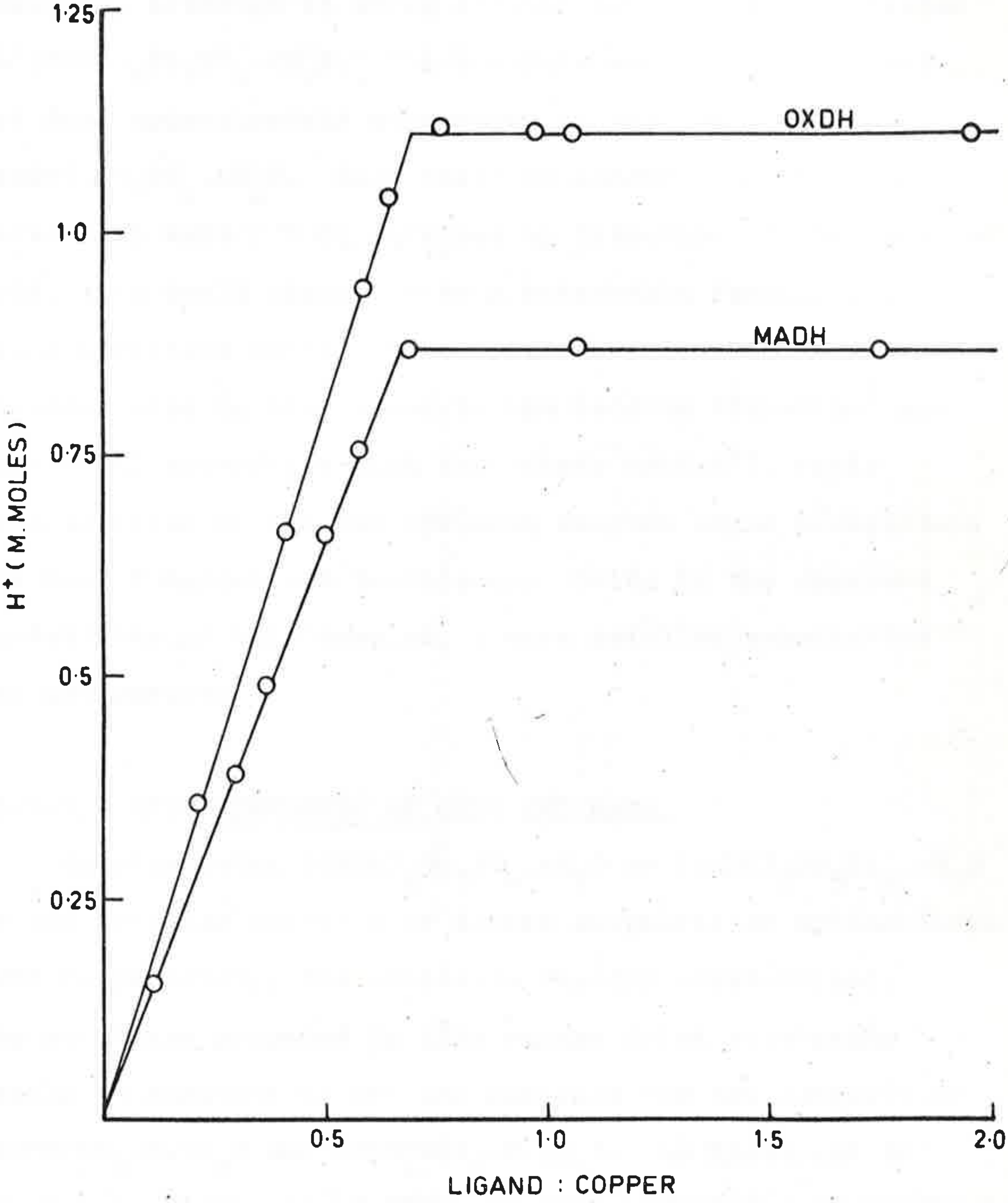
Further information to verify the composition of the OXDH/$CuSO_4$ complex was obtained by utilizing the property that protons are released in the reaction. In view of the large difference in equivalent conductance between the proton and the copper(II) ion[13], a conductance titration was performed. The end point proved to be by no means sharp, and two results obtained using different initial concentrations of reactants gave the OXDH:Cu ratio as 0.73:1 and 0.63:1, corresponding to the ratio of reactants at which the maximum number of protons was released. Although this result is not very satisfactory, it does roughly correspond to the ratio in the precipitate determined analytically.

A more conclusive result was obtained by determining the concentration of hydrogen ions released at various preparation ratios by pH titration with standard alkali. The OXDH/$CuSO_4$ and MADH/$CuSO_4$ systems were studied using this technique, the results of which are shown in figure 5.6. The presence of the precipitate was found to interfere in the OXDH system, possibly due to uptake of hydroxyl ions by copper(II) released in the rearrangement of $(OXDH)_2Cu_3^{2+}$ to $(OXDH)_2Cu^{2-}$ at higher pH, or to the replacement of water coordinated to the terminal copper ions by hydroxyl ions. Removal of the precipitate by centrifugation with attentive washings resulted in a much sharper end point, however this was unnecessary in the MADH system as no such interference was observed.

These studies provided two useful pieces of evidence. Firstly, in the OXDH system the ratio for maximum release of protons at 0.69 OXDH : 1 Cu corresponds very well with the results obtained from actual ratio determinations on the precipitate. Secondly, the titrated acid in both systems up to the inflexion point corresponded very well to the expected amount for the release of two protons per molecule of ligand. Enol structures of the complexes are thus strongly indicated.

An attempted preparation of the MADH copper(II) sulphate complex from neutral solution resulted in the deposition of a dark blue oil. When the preparation was

FIGURE 5.6. Acid released in the reaction of oxalyldihydrazine and malonyldihydrazine with copper(II) sulphate as a function of the ligand to copper ratio ($CuSO_4.5H_2O$ kept constant, 8.52×10^{-4} moles for OXDH; 6.65×10^{-4} moles for MADH).


1·25
1·0
0·75
0·5
0·25
H⁺ (M. MOLES)
OXDH
MADH
0·5
1·0
1·5
2·0
LIGAND : COPPER

carried out in sodium acetate solution a blue-green precipitate was formed. This latter complex was dried and analysed, although it shows similar drying characteristics to $(OXDH)_2Cu_3SO_4.nH_2O$. The analysis was rather uncertain, but does approximately correspond to the composition $(MADH)_2Cu_3SO_4.nH_2O$. When taken in conjunction with the ratio 0.66 MADH : 1 Cu obtained by titration of the released acid, this would appear to be a reasonable formulation. Since hydrazine could not be determined in this complex (malonic acid is brominated in the bromate titration[8] and copper(II) interferes with the iodate method[4]), ratio determination on freshly prepared samples would necessitate the use of manometric techniques. Owing to the apparent instability of this complex, a more detailed examination was not pursued.

(5.5.2) KETO COMPLEXES OF OXDH AND MADH.

On dissolving $(OXDH)_2Cu_3SO_4.nH_2O$ or $(OXDH)_2Cu_3Cl_2.nH_2O$ by the dropwise addition of dilute sulphuric or hydrochloric acid respectively, the solutions rapidly crystallised. The complexes prepared in this manner dried relatively easily to constant weight and analysed for the composition $OXDHCuSO_4.0.5H_2O$ and $OXDHCuCl_2.0.5H_2O$. As discussed in Chapter 1, complexes of OXDH and MADH with a 1:1 formulation might be expected to be polymeric in nature although the chain could be relatively short provided it contained one copper(II) and one ligand as end groups.

On the addition of water to these complexes, the solution became acid with apparent decomposition of the complexes to form the more stable enol type $(OXDH)_2Cu_3^{2+}$ compounds, hence the detailed study of the keto complexes in aqueous solution was precluded. The formulation as hemihydrates, however, raises some interesting possibilities as to the structure of these complexes.

(1) The complexes could be of large molecular weight containing a water molecule bonded apically between two copper ions in separate chains for every monomer unit.

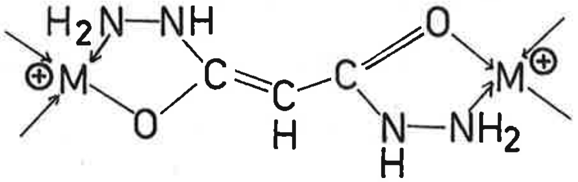
(2) They may consist of monomer units with sulphate or chloride coordinated in the plane of the end group copper and a bridging water molecule apically between two units.

(3) They may consist of four monomer units, two water molecules would then be coordinated to the end group copper.

Unfortunately, it is difficult to decide which of these possibilities must be considered most likely. The visible region spectra (Section 5.7) are of little help.

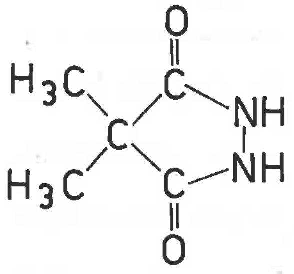
By an analogous method (see experimental section for details), a complex was obtained which analysed in reasonable agreement with the formulation $(MADH)_4Cu_5(SO_4)_3$. Although its purity may be open to some doubt, such a stoichiometry is compatible with the ligand containing one keto and one enol acylhydrazine grouping.

This possibility raises the question of the manner in which MADH enolises. In view of the ease in which both hydrazide groupings may be reprotonated in the enol OXDH complexes, it would appear unlikely that there should be a large difference in the dissociation constant of each ionisable hydrazide proton in MADH, hence one of the methylene hydrogens may be involved. Such hydrogen atoms are "active" in β-diketones, to which MADH is rather similar, as a result of strong polarisation effects in the adjacent carbonyl groups, and are involved in enolate formation in e.g. acetylacetone. One possible form in which the singly protonated ligand may coordinate is shown in (XXI).

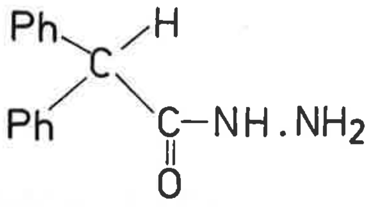


(XXI)

In order to obtain information on this problem, it was proposed to examine complexes formed by MADH disubstituted at the methylene carbon atom. Accordingly, synthesis of dimethylmalonyldihydrazine and diphenylmalonyldihydrazine was attempted by reaction of the corresponding ester with hydrazine hydrate. In both cases the desired product was not obtained. Reaction of the diethyl ester of dimethylmalonic acid with hydrazine hydrate resulted in cyclisation to produce 4,4-dimethyl-3,5-diketopyrazolidine (XXII), and the diethyl ester of diphenylmalonic acid produced N-diphenylacetylhydrazine (XXIII).



(XXII)



XXIII)

(5.6) COMPLEXES OF KETO POLYMETHYLENEDIACYLDIHYDRAZINE LIGANDS FROM n = 2 TO n = 10.

From aqueous reaction mixtures of the polymethylenediacyldihydrazine ligands SUDH (n = 2) to DDDH (n = 10) with copper(II) sulphate or copper(II) perchlorate, the complexes listed in table 5.7 were isolated.

All complexes, with the exception of the higher member perchlorates, crystallised from solution with a number of water molecules, the compositions indicated being obtained on drying to constant weight in vacuo over phosphorus pentoxide. For example, the loss of weight on drying of the complex in which n = 4 corresponded to four water molecules, hence the complex crystallised as the 4.5 hydrate.

The sulphate series of complexes, previously investigated by Jensen and Bak[8], were reported by these authors as

TABLE 5.7 COMPLEXES OF POLYMETHYLENEDIACYLDIHYDRAZINES FROM n = 2 TO 10.

n	COMPLEX	COLOUR	COMPLEX	COLOUR
2	$SUDHCuSO_4.0.5H_2O$	Blue	-	
3	$GLDHCuSO_4.H_2O$	"	-	
4	$ADDHCuSO_4.0.5H_2O$	"	$ADDHCu(ClO_4)_2(?)^a$	Blue
5	$PMDHCuSO_4.0.5H_2O$	"	$PMDHCu(ClO_4)_2(?)^b$	"
6	$SRDHCuSO_4.0.5H_2O$	"	$SRDHCu(ClO_4)_2(?)^b$	"
7	$AZDHCuSO_4$	"	$(AZDH)_3Cu_2(ClO_4)_4$	"
8	$SBDHCuSO_4$	"	$(SBDH)_3Cu_2(ClO_4)_4$	Pale green
10	-		$DDDHCu(ClO_4)_2$	Blue
10	-		$(DDDH)_3Cu_2(ClO_4)_4$	Pale green

a. Not analysed, dangerously explosive.
b. Not analysed, probably explosive.

anhydrous compounds. It may thus be queried whether the complexes in table 5.7 listed as hydrates or hemihydrates were perfectly dry on analysis. However, constant weight was obtained in all cases and preparations of $GLDHCuSO_4.H_2O$ and $PMDHCuSO_4.0.5H_2O$ carried out in triplicate (from different ratios of reactants) gave both hydrazine and copper analyses agreeing within 0.5%.

Jensen and Bak remarked that agreement of their analyses with the theoretical values was not as good as for the monoacylhydrazine complexes they prepared. In every case the copper content is low and the "molecular weight" (based on hydrazine analysis) is generally high, indicating a low hydrazine figure. These results, however, are much closer to the theoretical anhydrous values than was observed in the present work. The reason for this discrepancy is not readily apparent since the complexes were dried in an identical manner. A sample of $ADDHCuSO_4.0.5H_2O$ was found to lose only 0.1% of its weight on further drying in vacuo over P_2O_5 at 100° for twelve hours. A recrystallised sample, dried to constant weight in the oven at 105°, showed almost identical hydrazine and copper analyses to the sample dried at room temperature.

It is thus felt that the formulation of these complexes as hydrates or hemihydrates is justified. Confirmation of the presence of water in $ADDHCuSO_4.0.5H_2O$ by examination of the infrared spectrum proved inconclusive due to the presence of N-H stretching vibrations in the 3500 to 3000 cm^{-1} region.[14,15] The major difference between the spectrum of ADDH and its complex was the appearance of two reasonably sharp bands at 3600 cm^{-1} and 3500 cm^{-1} in the latter, not observed in the ligand. These bands may correspond to the antisymmetric and symmetric stretching vibrations of the water molecule,[16] but the explanation of their appearance could lie in a reduction of hydrogen bonding in the complex, resulting in some N-H stretching vibrations occuring at higher energies, or as a result of differences in lattice forces.

The preparation of pure $AZDHCuSO_4$ and $SBDHCuSO_4$ was more difficult. Several preparations gave inconsistent analyses. The procedure finally adopted was to remove the first crop of crystals, then initiate crystallisation of the mother liquor by the dropwise addition of methanol. One possible reason for this inconsistency was apparent on examination of the perchlorate complexes formed by DDDH, from which ligand both a 1:1 and 3:2 complex were isolated. The blue 1:1 complex in this case was quite unstable - washing with water caused decomposition with formation of the pale green 3:2 complex. The 3:2 perchlorate complexes only were isolated from AZDH and SBDH.

The dangerous nature of the adipoyldihydrazine copper(II) perchlorate complex has been remarked on in Chapter 1. Although the PMDH and SRDH perchlorate complexes were prepared, they were not investigated further.

(5.7) VISIBLE SPECTRA OF KETO POLYMETHYLENEDIACYLDIHYDRAZINE COPPER(II) COMPLEXES.

In the region 30,000 - 6000 cm^{-1} the solid state spectra of keto polymethylenediacyldihydrazine complexes show broad bands with maxima at the wavenumbers listed in table 5.8.

Considering firstly the sulphate complexes from n = 2 to 8, appart from $SRDHCuSO_4.0.5H_2O$ little variation in the spectra was apparent. With maxima between 14,700 and

TABLE 5.8 ABSORPTION SPECTRA OF SOLID KETO POLYMETHYLENEDIACYLDIHYDRAZINECOPPER(II) COMPLEXES IN THE REGION 30,000 - 6,000 cm^{-1}.

n	COMPLEX	MAXIMUM (cm^{-1})
0	OXDHCuSO$_4$.0.5H$_2$O	14,000
0	OXDHCuCl$_2$.0.5H$_2$O	13,700
2	SUDHCuSO$_4$.0.5H$_2$O	15,100
3	GLDHCuSO$_4$.H$_2$O	14,700
4	ADDHCuSO$_4$.0.5H$_2$O	15,000
5	PMDHCuSO$_4$.0.5H$_2$O	14,800
6	SRDHCuSO$_4$.0.5H$_2$O	14,200, ~11,000 (sh)
7	AZDHCuSO$_4$	15,200
8	SBDHCuSO$_4$	15,000
10	DDDHCu(ClO$_4$)$_2$	15,400
10	(DDDH)$_3$Cu$_2$(ClO$_4$)$_4$	13,300, 7,300

15,200 cm^{-1}, the spectra are very similar to the monoacylhydrazine sulphate complexes (table 5.1). However, it is difficult to decide if the remaining water in these complexes is in the coordination sphere of copper(II) or simply held in the crystal lattice, although the shift towards the infrared on comparing solid state spectra with solution spectra (as determined from solutions containing excess ligand in the perchlorate system, table 5.9) is much less (200 - 300 cm^{-1}) than is observed with the anhydrous monoacylhydrazine complexes (1000 - 2000 cm^{-1}). This suggests that water is in fact coordinated apically in the dihydrazine hydrates, indicating a similar environment in the solid state and in solution.

TABLE 5.9 WAVENUMBER OF THE MAXIMA OF POLYMETHYLENE-DIACYLDIHYDRAZINE COPPER(II) PERCHLORATE COMPLEXES IN AQUEOUS SOLUTION (AS DETERMINED FROM SOLUTIONS CONTAINING COPPER(II) PERCHLORATE AND EXCESS (3:1) LIGAND.)

LIGAND	MAXIMUM (cm^{-1})
GLDH (n = 3)	14,500
ADDH (n = 4)	14,700
PMDH (n = 5)	14,600
SRDH (n = 6)	14,500

In relation to figure 1.1 and the discussion in Chapter 1, three possible schemes for coordination of the dihydrazide ligands from n = 2 upwards must be considered.

(1) The lower members could be tridentate with water occupying the fourth coordination position (monohydrate) or bridging between two copper ions (hemihydrate) of a dimer.

(2) They could also be tridentate polymeric with nitrogen coordinated to the neighbouring molecule and water coordinated apically to each copper (monohydrate) or between two coppers of neighbouring chains (hemihydrate).

Such structures would necessarily be cis. The possibility of a bridging carbonyl group can probably be excluded in view of the weak coordinating properties of this group.

In both (1) and (2), a cis-quadridentate structure would become probable at higher values of n.

(3) The ligands could be bis-bidentate throughout the whole series, in effect forming dimers. Water could be coordinated apically to each copper (monohydrate) or between the two coppers of the dimer (hemihydrate). Such structures would probably be cis, at least for smaller values of n.

In relation to the above structural possiblities, some expected changes in the visible spectra must be considered.

(1) If the conclusions of Bjerrum et al.[2] are reliable, a trans arrangement of the coordinating groups should result in maxima at higher energies than a cis arrangement.

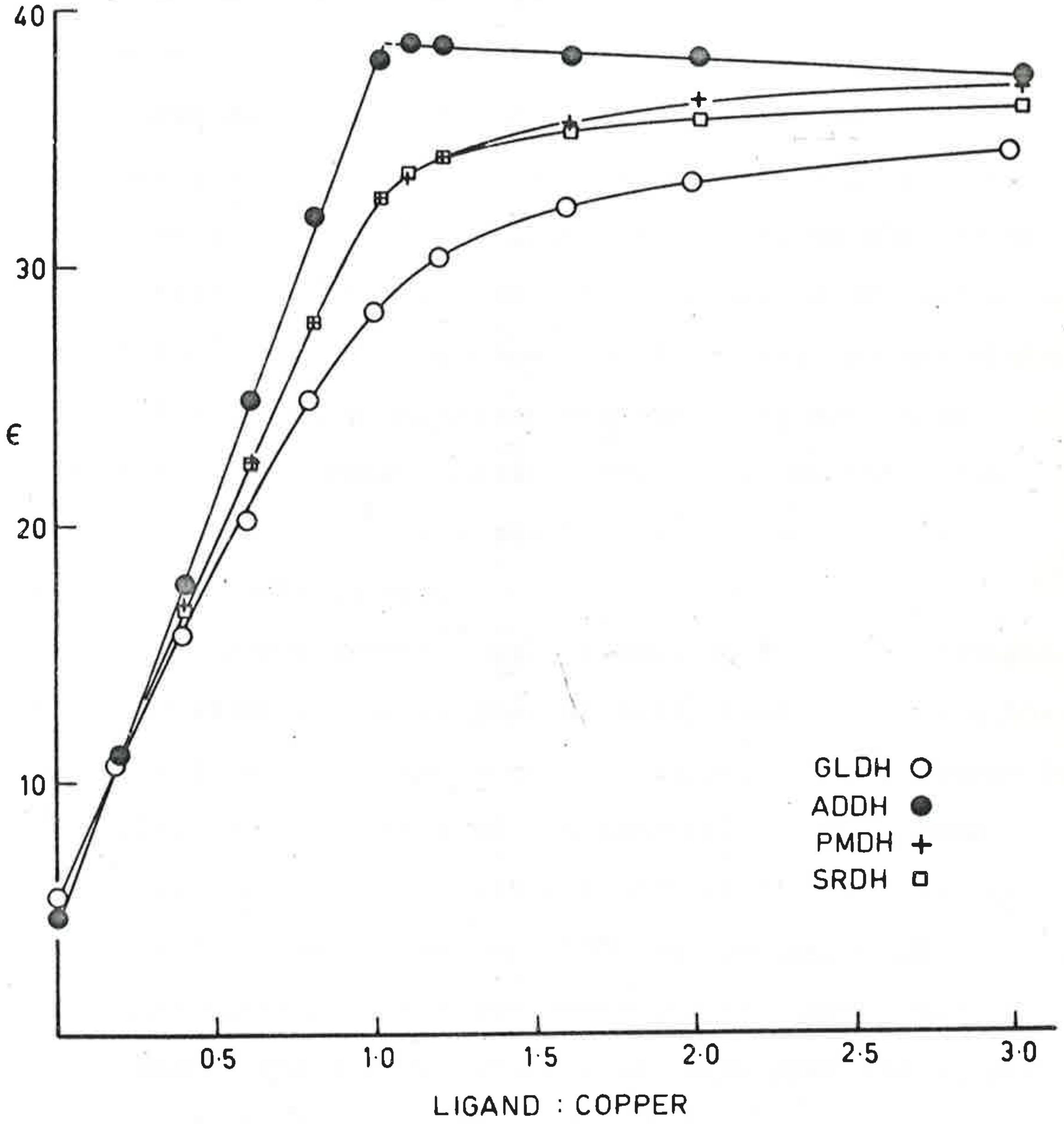
(2) The effect of replacing N by O (water) would be to shift the maximum to lower energies. Replacement of O (carbonyl) by O (water) could possibly shift the maximum slightly to higher energies.

Considering the anhydrous 1:1 complexes (n = 7, 8, 10) the maxima are observed at lower energies (uncertainly for the sulphate complexes, but definitely for the perchlorate complex) than in the case of the corresponding monoacylhydrazine complexes (c.f. table 5.1), which would indicate a cis rather than trans configuration. However, owing to the tendency of these complexes to revert to the 3:2 complexes, the structures are obviously strained and this may indeed affect the spectrum in a complicated manner. The considerations above thus tend to favour a cis quadridentate structure for these complexes. The limited solubility of both the ligands and complexes (together with the tendency to revert to the 3:2 complexes) prevented determination of the solution spectra, intensity data from which might provide evidence for the cis configuration (see Section 4.2).

The lower energy of the maximum and separation of a shoulder towards the infrared in $SRDHCuSO_4.0.5H_2O$ must be considered as good evidence for apically coordinated water. The situation is more clouded in the lower complexes (n = 2 - 5) since no separation of bands was observed. As discussed above, the similarity of the solid state and solution spectra probably indicates that water molecules are also apically coordinated in these complexes.

Some information on the relative stabilities of the complexes was obtained from a spectrophotometric investigation of the perchlorate complexes at varying ligand:copper ratio in solution (figure 5.7). The wavelength chosen for study was that observed in 3:1 mixtures (table 5.9). From figure 5.7, it is apparent that 1:1 complexes are formed in solution, and of the systems investigated the ADDH complex

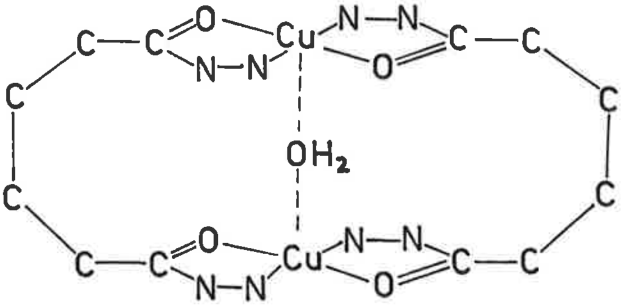
FIGURE 5.7. Variation of the molar extinction coefficient as a function of the ligand to copper ratio: copper(II) perchlorate with N,N-diacyldihydrazines. GLDH; $Cu = 1.682 \times 10^{-2}M$; ADDH, PMDH, $Cu = 1.660 \times 10^{-2}M$; SRDH, $Cu = 8.30 \times 10^{-3}M$. Measured at the wavenumbers given in table 5.9.


40
30
20
10
ε
0·5
1·0
1·5
2·0
2·5
3·0
LIGAND : COPPER
GLDH ○
ADDH ●
PMDH +
SRDH □

would appear to be most stable, although from the shape of the curve at higher ligand:copper ratios there may be a tendency for ligand to be coordinated apically. GLDH, PMDH and SRDH, on either side of ADDH demonstrate a less definite break at the 1:1 ratio indicating some 80 - 90% formation of the complexes at this point.

These results are to be expected on the scheme which involves a tridentate polymeric structure changing to a quadridentate structure as n increases. Hence ADDH would be expected to form the more stable tridenate structure, a result indicated from examination of models. As the chain length increases, a quadridentate structure should be favoured, but somewhat unstable for SRDH. However, the above results do not necessarily invalidate the bis-bidenate dimeric scheme.

Hawkins and Perrin[17] have suggested that a tridentate type structure should be energetically less favourable than linear polymeric chains or cyclic polynuclear structures in the 2,7-diaminosuberic acid - copper(II) system. This ligand is structurally similar to adipoylihydrazine. In the diacyldihydrazine series, SUDH and probably GLDH would necessarily form a cis structure if coordinated in this manner (see figure 1.1-vi), but with ADDH and higher members of the series, either cis or trans structures such as (XXIV) would be possible. Internal coordination of a water molecule might then account for the formulation of many of the complexes as hemihydrates.



(XXIV)

The visible spectra of $OXDHCuSO_4 \cdot 0.5H_2O$ and $OXDHCuCl_2 \cdot 0.5H_2O$ (table 5.7) have maxima at lower wave-numbers than any of the other keto complexes in the solid state. No distinct separation of a low energy shoulder was observed although the bands appeared to be slightly assymmetrical. It is thus not possible to ascertain if the water is apically coordinated in these compounds. The lower energy of the maxima could be due to this, but may have another explanation, viz. coordination of sulphate or chloride in the planar positions of a monomeric unit.

From the above considerations, it is evident that visible absorption spectra are unable to provide unambiguous evidence for the structures of polymethylenediacyldihydrazine-copper(II) complexes, as too many uncertainties are involved in these complicated systems. It is unfortunate that a complex suitable for molecular weight determination was not obtained.

The spectrum of $(DDDH)_3Cu_2(ClO_4)_4$ (figure 5.8), with a definite band on the infrared side of the main band, does

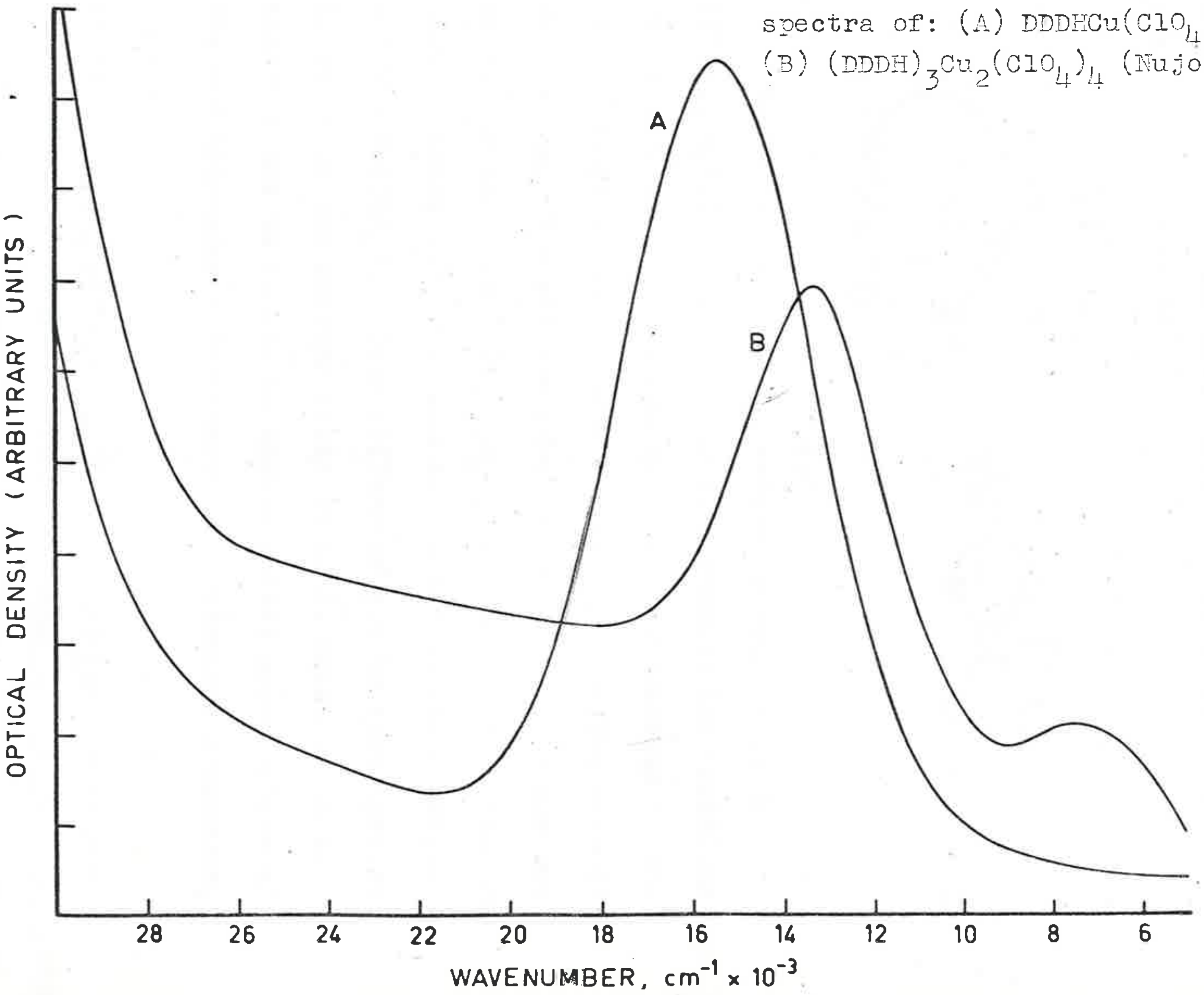
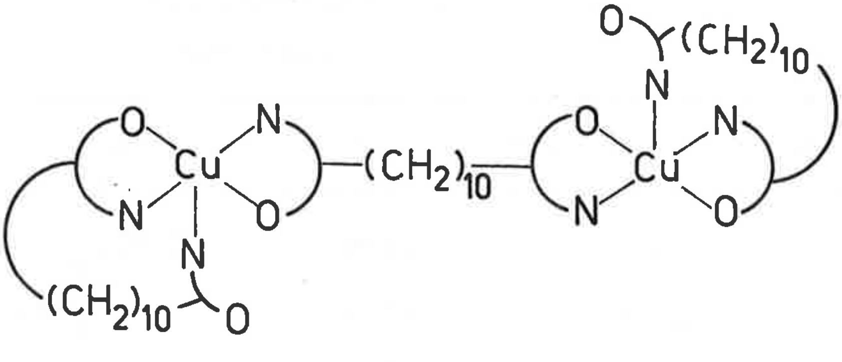


FIGURE 5.8. Visible region spectra of: (A) DDDHCu$(ClO_4)_2$; (B) $(DDDH)_3Cu_2(ClO_4)_4$ (Nujol mulls).

provide good evidence that in this complex a nitrogen atom is coordinated apically to the copper(II) ion, possibly as in (XXV).



(XXV)

Probably a similar structure is applicable to $(SBDH)_3Cu_2(ClO_4)_4$ since both this complex and $(DDDH)_3Cu(ClO_4)_4$ are a very pale blue-green colour. The spectrum of the former complex was not measured due to possible detonation on mulling. The difference in colour between these two complexes and $(AZDH)_3Cu_2(ClO_4)_2$ is considerable, the AZDH complex being blue, similar to the 1:1 sulphate complexes and $DDDHCu(ClO_4)_2$. This difference can be accounted for in terms of the shorter chain in AZDH, which would be insufficient in length to enable apical coordination of the end hydrazine nitrogens in an unstrained structure.

(5.8) MAGNETIC PROPERTIES OF KETO N-ACYLHYDRAZINE AND POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE COPPER(II) COMPLEXES.

The room temperature magnetic moments of the copper(II) complexes of both series of ligands are listed in table 5.10. In all cases except for $(OXDH)_2Cu_3SO_4.5H_2O$, moments of about 1.9 B.M. are typical of copper(II) complexes which are magnetically dilute.[18]

TABLE 5.10. MAGNETIC MOMENTS OF KETO N-ACYLHYDRAZINE AND POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE COPPER(II) COMPLEXES.

COMPLEX	T(^{o}K)	$10^{6}\chi_{M}$corr.	μeff. (B.M.)
$(BH)_2CuSO_4 \cdot 2H_2O$	293.6	1535	1.91
$(BH)_2CuSO_4$	293.6	1557	1.92
$BHCuCl_2$[4]	296.0	1355	1.80
$(BH)_2CuCl_2$[4]	296.6	1348	1.80
$(BH)_3CuCl_2$	290.0	1501	1.87
$(BH)_4CuCl_2$	290.2	1494	1.87
$(AH)_2CuSO_4$	293.6	1515	1.89
$(PH)_2CuSO_4 \cdot 0.5H_2O$	293.8	1532	1.91
$(OXDH)_2Cu_3SO_4 \cdot 5H_2O$	292.5	3181	1.58
$OXDHCuCl_2 \cdot 0.5H_2O$	289.8	1490	1.87
$SUDHCuSO_4 \cdot 0.5H_2O$	289.5	1521	1.89
$GLDHCuSO_4 \cdot H_2O$	289.5	1540	1.90
$ADDHCuSO_4 \cdot 0.5H_2O$	289.5	1530	1.89
$PMDHCuSO_4 \cdot 0.5H_2O$	289.5	1506	1.88
$SRDHCuSO_4 \cdot 0.5H_2O$	290.8	1565	1.92
$AZDHCuSO_4$	290.8	1383	1.80
$SBDHCuSO_4$	289.5	1468	1.85

The somewhat lower value of 1.58 B.M. for $(OXDH)_2Cu_3SO_4 \cdot 5H_2O$ may be considered suspect in view of the difficulty in obtaining the pure complex (section 5.5.1), although if the structure is as postulated (XIX), some reduction below the normal value may be expected to occur by the superexchange process (section 4.8). The value of 1.87 B.M. for $OXDHCuCl_2.0.5H_2O$ may therefore suggest that this complex is not polymeric in nature.

It is interesting to note that the moment of $GLDHCuSO_4.H_2O$ is normal. A binuclear structure for this complex as in (XXIV) might be expected to show a reduced value due to direct interaction of the copper(II) ions, since the Cu-Cu distance would undoubtedly be small and may approach that observed in copper(II) acetate. This would suggest that if the complex is binuclear, the arrangement of ligands is such that the copper(II) ions are well separated, as indicated by the structure illustrated in figure 1.1-vi.

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CHAPTER 6.

COPPER(II) COMPLEXES OF KETO N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE AND POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE LIGANDS.

(6.1) KETO N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE COMPLEXES.

The N-isopropylidene derivatives of acylhydrazines are easily prepared by recrystallization from acetone. Enol complexes of these ligands can be readily obtained by the addition of base to solutions containing metal salts (see section 2.1), but the possibility that ligands of this type can coordinate in the keto form has not previously been examined in detail.

Diamantis[1] has reported a complex analysing for the stoichiometry $(IPBH)_2CuCl_2.2H_2O$, but was unable to decide if acetone was condensed with N-benzoylhydrazine or simply present as acetone of crystallization since it could be isolated from the complex as the 2,4-dinitrophenylhydrazone. This problem has been resolved by examination of complexes containing other anions. Thus, $(IPBH)_2Cu(ClO_4)_2$ was found to be anhydrous, so that the acetone present in this molecule can only be in the condensed form. Further, the chloride complex was found to slowly lose weight on continued drying in vacuo over P_2O_5, a monohydrate being obtained. The propionylhydrazine complex, $(IPPH)_2CuCl_2.0.5H_2O$ was also prepared.

The indication of the stoichiometry of these complexes that the ligand is coordinated in the keto form was further substantiated by examination of the infra-red spectra in the region 4,000 - 2,500 cm^{-1}. In this range, IPBH shows the first absorption band at 3210 cm^{-1} (table 6.1) which may be ascribed to the single N-H stretching vibration expected for secondary amines[2] and amides.[3] The first absorption in the spectrum of $(IPBH)_2Cu(ClO_4)_2$ occurs at 3340 cm^{-1}, showing a shift to higher wavenumbers compared with the free ligand. This shift may have its origin in a reduction of hydrogen bonding in the complex, although it has been noted that the N-H stretching vibration does not vary greatly in the spectra of secondary amines and their complexes.[2] Possibly differences in lattice forces may account for this effect. $(IPBH)_2CuCl_2.H_2O$ also shows a sharp band at 3380 cm^{-1}, although the presence of water complicates interpretation of the spectrum in this region.

TABLE 6.1. INFRARED SPECTRA OF IPBH AND $(IPBH)_2Cu(ClO_4)_2$ IN THE RANGE 4,000 - 2,900 cm^{-1}.

	BAND MAXIMA (cm^{-1})
IPBH	3210 (s), 3080 (sh), 3020 (s), 2930 (sh)
$(IPBH)_2Cu(ClO_4)_2$	3340 (s), 3080 (m), 3020 (m), 2930 (m).

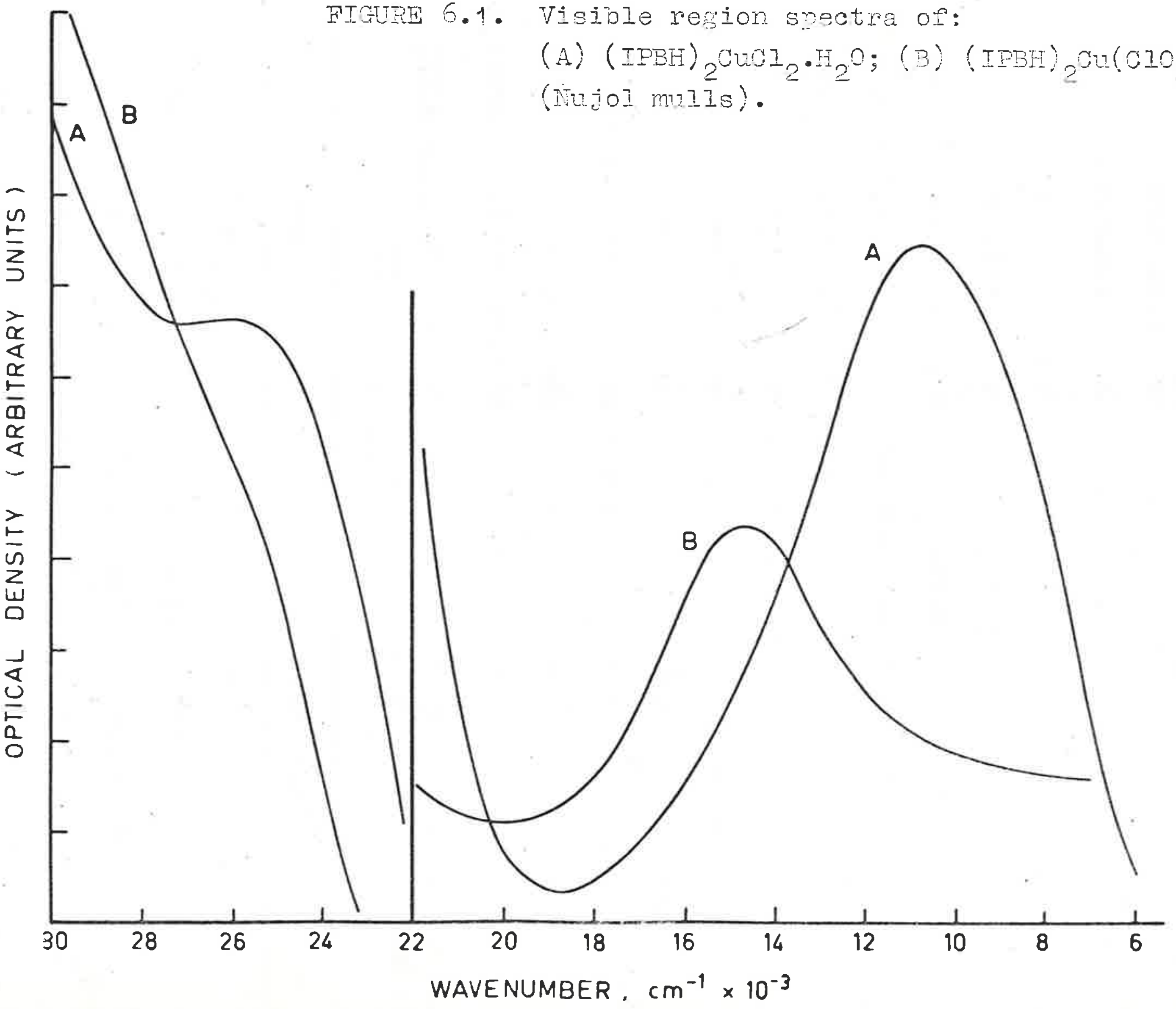
The enol complex $(IPBH)_2Cu$ does not show a band near 3210 cm^{-1}, further supporting its assignment as the N-H stretching vibration (section 7.1). An attempt to support this assignment by examination of the keto N-deutero compounds proved unsuccessful; repeated recrystallization of the ligand or perchlorate complex from D_2O resulted only in partial deuteration as determined by the appearance of weak absorption in the 2400 cm^{-1} region. No significant variation in the N-H stretching region was observed. The remaining bands in this region may be ascribed to C-H stretching vibrations.

(6.2) VISIBLE REGION SPECTRA OF KETO BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE)COPPER(II) COMPLEXES.

Some interesting variations in the visible region spectra of the keto bis-IP complexes are indicative that the environment of the copper(II) ion is not identical in complexes containing different anions. The solid state apectra of $(IPBH)_2Cu(ClO_4)_2$ and $(IPBH)_2CuCl_2 \cdot H_2O$ are shown in figure 6.1, demonstrating a considerable difference which is also apparent in the colours of these compounds (the former is pale green and the latter yellow-green).

Considering the perchlorate complex, the band maximum at 14,600 cm^{-1} indicates that IPBH occupies a position below BH in the spectrochemical series (c.f. $(BH)_2Cu(ClO_4)_2$, table 5.1). The spectrum of this complex differs greatly from that of the halide complexes. The monohydrate chloride

FIGURE 6.1. Visible region spectra of:
(A) $(IPBH)_2CuCl_2.H_2O$; (B) $(IPBH)_2Cu(ClO_4)_2$
(Nujol mulls).



complex shows a large shift to the red, with the maximum of the slightly asymmetrical band at 10,700 cm^{-1}, which would suggest apical coordination of either chloride ions on water molecules. A further difference, however, is the appearance of a band at about 26,000 cm^{-1} which is not observed in the spectrum of the perchlorate complex, although there is possibly a slight inflexion in this region (figure 6.1, curve B). The presence of this band would account for the yellow colouration of the chloride complex.

$(IPBH)_2CuCl_2.2H_2O$ also shows a well-defined band in the 26,000 cm^{-1} region (table 6.2). The spectrum of this complex is very similar to that of the monohydrate except that the 10,800 cm^{-1} band shows a definite shoulder on the infrared side, at approximately 8,700 cm^{-1}. Thus it would appear that at least the more easily lost water molecule

<u>TABLE 6.2</u>. ABSORPTION SPECTRA OF SOLID KETO BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE)COPPER(II) COMPLEXES IN THE REGION 30,000 - 6,000 cm^{-1}.

COMPLEX	MAXIMUM (cm^{-1})
$(IPBH)_2Cu(ClO_4)_2$	14,600
$(IPBH)_2CuCl_2.H_2O$	25,800 (sh); 10,700
$(IPBH)_2CuCl_2.2H_2O$	25,600 (sh); 10,900; ~8,600 (sh)
$(IPBH)_2CuBr_2.2H_2O$	~24,100 (sh); 10,800; ~8,700 (sh)
$(IPPH)_2CuCl_2.0.5H_2O$	24,600 (sh); 10,400.

is apically coordinated in the dihydrate.

Replacement of chloride by bromide, i.e. in (IPBH)$_2$CuBr$_2$.2H$_2$O, would appear to have negligible effect on the spectrum in the near infrared region (table 6.2, see also figure 6.2). However, the 25,600 cm^{-1} band of the chloride shifts to 24,100 cm^{-1} in the bromide complex, suggesting that the halogen is coordinated to the copper(II) ion in these complexes.

It is interesting to compare the spectra of the tetrachloro- and tetrabromocopper(II) ions which are known to have tetrahedral structures, distorted towards square planar.[4,5] Band positions reported for these ions are listed in table 6.3. Bands in the near infra red with ε = 100 - 200 have been ascribed to d-d transitions and the more intense bands at higher energies to charge transfer processes.[8,9,10] Further bands in the near infrared region have been attributed to d-d transitions.[11]

TABLE 6.3. ABSORPTION SPECTRA OF CuCl$_4^{2-}$ AND CuBr$_4^{2-}$ IN THE VISIBLE REGION. (cm^{-1}, ε).

CuCl$_4^{2-}$ (nitromethane)[6] 27,800 (4000); 23,000 (sh; 11,200 (88).
CuBr$_4^{2-}$ (acetonitrile)[7] 28,600 (6300); 23,600 (sh) (1,300);
18,900 (2,000); 16,400 (1,300); 9,100 (160).
(R$_4$N)$_2$CuBr$_4$ (solid)[8] 29,400; 23,600; 19,000; 16,900; 9,100.

(IPBH)$_2$CuCl$_2$.2H$_2$O thus shows similar regions of absorption to the CuCl$_4^{2-}$ ion, suggesting perhaps that the compound might be formulated as $((IPBH)_4Cu)CuCl_4.4H_2O$ with IPBH acting as a monodentate group. This possibility must be considered unlikely, however, since the mull spectrum of this complex indicated that the extinction of the 26,000 cm^{-1} band was approximately three times that of the 11,000 cm^{-1} band, whereas the ratio of extinctions in the $CuCl_4^{2-}$ ion is some 30:1 or more (table 6.3).

Similar remarks apply to the bromide complex, but in this case the absence of strong bands at 19,000 and 17,000 cm^{-1} is additional evidence that this complex does not contain $CuBr_4^{2-}$. The complex was found to be reasonably soluble in acetone (the chloride complex was almost insoluble) hence the extinction coefficients from the solution spectrum (figure 6.2) definitely preclude a formulation containing $CuBr_4^{2-}$. However, two weak bands observed at 17,800 cm^{-1} and 15,200 cm^{-1} may indicate the presence of a small quantity of $CuBr_4^{2-}$ in solution; these bands were not observed in the solid state spectrum. The acetone solution was found to be somewhat unstable, the colour slowly changing from yellow-green to yellow, observable in the spectrum as a general decrease in extinction, more rapid in the 24,000 cm^{-1} region than in the near infrared. The spectrum was thus measured as rapidly as possible after dissolving the complex, and the intensity ratio of 3.4:1, being still larger than the 2.5:1 ratio observed in the mull, indicates that the complex had not appreciably decomposed. These figures also

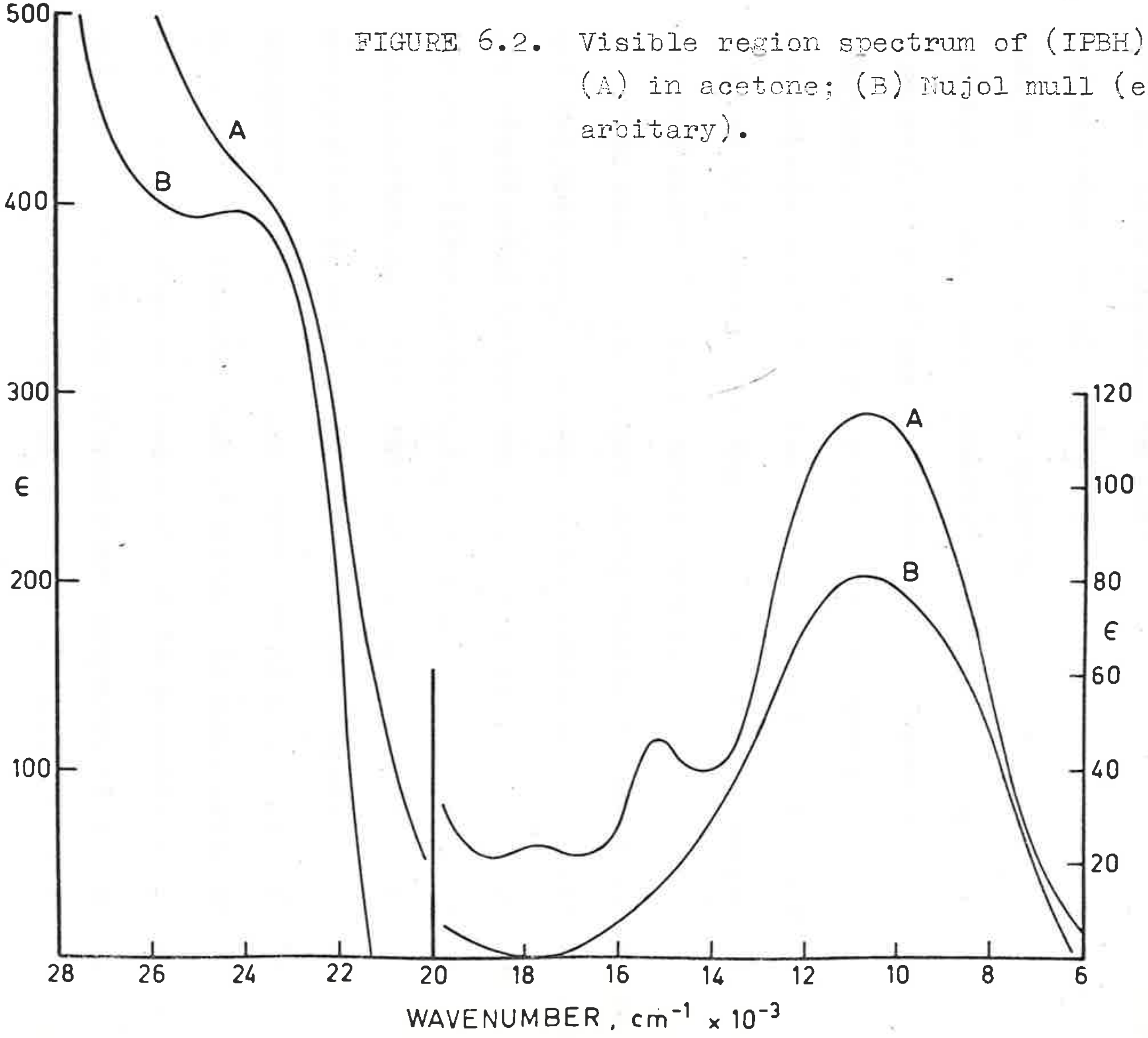


FIGURE 6.2. Visible region spectrum of $(IPBH)_2CuBr_2 \cdot 2H_2O$: (A) in acetone; (B) Nujol mull (extinction arbitary).

serve to demonstrate the inaccuracy in comparing band intensities from the mull spectra, but indicate that they can be used as a rough guide.

The slow decrease in extinction with time was probably due to reduction of copper(II) to copper(I). It was found that preparations of the chloride and bromide complexes carried out from warm solutions gave impure products, a slow evolution of gas occurring. Apart from oxidation of hydrazine, there is the possibility of bromination of the solvent accompanied by reduction of the copper(II) in the case of the bromide, as has been observed for copper(II) bromide alone in methyl ethyl ketone.[12]

The results discussed above indicate that both halide and the more easily removed water molecule of the dihydrates are coordinated to copper(II). In view of the anhydrous nature of $(IPBH)_2Cu(ClO_4)_2$, it is clear that the ligand can function as a bidentate chelating agent since the preparation of this complex from aqueous acetone would undoubtedly result in the formation of a hydrate if the ligand was preferably monodentate. In best agreement with the spectral changes discussed, it is probable that one halide and one water molecule are coordinated above and below the plane of the copper(II) ion, with the second water molecule more firmly held in the crystal lattice by hydrogen bonding.

It is interesting to note that the spectrum of

$BHCuCl_2$ (table 5.3) does not show the 26,000 cm^{-1} band, presumed characteristic of apical coordinated chloride, suggesting that there is little tendency to complete a distorted octahedral arrangement by coordination of chloride. Bands in this region have been observed in the spectra of monoamine complexes of copper(II) bromide with ethylenediamine and related ligands, for which a tetragonal structure in the solid state has been suggested.[13]

The intensity of the d-d band of $(IPBH)_2CuBr_2.2H_2O$ in acetone is considerably greater than that observed for the aqueous solution spectra of the uncondensed acylhydrazine complexes (table 5.1). However, it was observed that as water was replaced by non-aqueous solvent a large variation in the spectrum was produced. For example $(BH)_2CuCl_2$ in 10% aqueous ethanol showed a shift to the red and an increase in extinction coefficient (table 5.2). This compound thus behaves similarly to bis-ethylenediaminecopper(II) dichloride in aqueous ethanol, for which apical coordination of ethanol was originally suggested to be responsible.[14] A more plausible explanation has since been put forward,[15] viz. the formation of ion pairs in ethanol with apical coordination of the anion. It would thus appear probable that this process occurs in the halide complexes of IPBH; apical coordination of bromide would account for the high extinction observed in acetone solution. Bands in the vicinity of 26,000 cm^{-1} may then be ascribed to a forbidden metal-halide transition. The intensities of these bands are too low for them to be ascribed to a pure charge transfer process and they are unlikely to be d-d transitions in view of the large separation form the 11,000 cm^{-1} band. This assignment would explain the shift in comparing the bromide complex with the chloride complex. The d-d transition is not affected, but the near ultraviolet band moves to lower energy as expected for the more easily oxidised bromide ion.[16]

(6.3) KETO POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE COMPLEXES.

The isopropylidene derivatives of the dihydrazide series of ligands also give rise to complexes containing the ligand in the keto form. Apart from OXDH (n = 0), dichloride complexes were obtained containing the ligand and copper in a 1:1 ratio, indicating similar structural possibilities as discussed in relation to the uncondensed ligands (section 5.7).

In view of the spontaneous release of protons observed on formation of the sulphate complexes of OXDH and MADH, it is surprising that no such effect was observed during preparation of the isopropylidene complexes of these ligands. IPOXDH was found to give rise to the complex $IPOXDHCu_2$-$Cl_4.0.5H_2O$, obtained as a yellow powder. The stoichiometry would suggest that copper(II) ions are coordinated to each of the two hydrazide groupings with chloride ions completing a square planar arrangement.

For the remainder of the series, yellow-green complexes were obtained either as mono- or hemihydrates. These complexes are listed in table 6.4. The higher ligands (n = 7,8,10) produced complexes which were precipitated as oils by the addition of excess acetone to aqueous acetone solutions of copper(II) chloride and the ligand. These complexes solidified on removal of the acetone under vacuum.

By varying the recrystallisation conditions, $IPADDHCuCl_2$ (n = 4) was obtained as the yellow-green monohydrate, hemihydrate and anhydrous complex. The existence of yet another blue hydrate was noted - this compound readily dried to constant weight to form the anhydrous complex which rapidly regained the blue colour on exposure to air. In this respect it showed different behaviour to the mono- and hemihydrates which retained their yellow-green colours on exposure. It is possible that the hemihydrate represents a stage in drying between the monohydrate and the anhydrous complex, although the visible spectra (section 6.4) suggests that they could be distinct compounds. From the slow loss of weight on drying to obtain the hemihydrate, it is clear that the water in this complex is differently bound to that in the blue hydrate (which was not characterised).

All of the complexes obtained were either insoluble or only very slightly soluble in acetone, but dissolved readily in water to give blue-green solutions which turned blue on standing. It would appear that the complexes are readily hydrolysed under these conditions, releasing acetone. Supporting evidence for this was obtained by examination of the solution spectra of IPADDHCuCl$_2$.0.5H$_2$O, which will be discussed in the following section.

(6.4) VISIBLE REGION SPECTRA OF KETO POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE COMPLEXES.

In addition to variations in stereochemistry expected as the dihydrazide series of ligands is ascended, the presence of both chloride ions and water molecules which can coordinate in either apical or planar positions complicates interpretation of the visible region spectra of these complexes. In general the spectra of the whole series of complexes are rather similar and closely resemble the spectra of the corresponding monoacylhydrazine complexes (section 6.2). The band positions of the solid complexes are reported in table 6.4.

Apart from IPPMDHCuCl$_2$.0.5H$_2$O and IPSRDHCuCl$_2$.H$_2$O, all the complexes show a band in the vicinity of 26,000 cm^{-1} which probably indicates apical coordination of chloride ions. The absence of this band in the above complexes, coupled with the appearance of a shoulder on the infrared side of the d-d band, would suggest that only water is

TABLE 6.4. ABSORPTION SPECTRA OF SOLID KETO POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE COPPER(II) COMPLEXES.

n	COMPLEX	MAXIMUM (cm^{-1})		
0	IPOXDHCu$_2$Cl$_4$.0.5H$_2$O	26,000 (sh);	12,200	
1	IPMADHCuCl$_2$0.5H$_2$O	25,200 (sh);	10,900	
2	IPSUDHCuCl$_2$.0.5H$_2$O	26,300 (sh);	11,200	
3	IPGLDHCuCl$_2$.H$_2$O	25,400 (sh);	11,800;	9,000 (sh)
4	IPADDHCuCl$_2$.H$_2$O	25,700 (sh);	10,300	
4	IPADDHCuCl$_2$.0.5H$_2$O	26,000 (sh);	10,000	
4	IPADDHCuCl$_2$	27,000 (sh);	13,700	
4	IPADDHCuBr$_2$.0.5H$_2$O	23,400 (sh);	10,000	
5	IPPMDHCuCl$_2$.0.5H$_2$O	-	11,800;	7,600 (sh)
6	IPSRDHCuCl$_2$.H$_2$O	-	11,500;	8,000 (sh)
7	IPAZDHCuCl$_2$.H$_2$O	25,000 (sh);	11,400;	9,600 (sh) (?)
8	IPSBDHCuCl$_2$.H$_2$O	25,500 (sh);	10,500	
10	IPDDDHCuCl$_2$.H$_2$O	25,500 (sh);	10,400	

apically bound. The length of the methylene chain would appear to be sufficient to enable coordination of both hydrazide groups to the one metal ion in these complexes, thus it is probable that the ligands are quadridentate. The reappearance of the 26,000 cm^{-1} band in the next three complexes of the series (n = 7, 8, 10) and the absence of a shoulder towards the infrared (there is possibly a shoulder at about 9,600 cm^{-1} in $IPAZDHCuCl_2 \cdot H_2O$, although the spectrum was not sufficiently well resolved in this region to enable positive identification) would indicate that chloride is coordinated apically in these complexes of potentially quadridentate ligands. The water molecule here could be hydrogen bonded in the crystal lattice or may occupy the second apical position.

The situation becomes more difficult to assess for the lower members, where polymeric, dimeric and tridentate structures are possible. If both hydrazide groups of IPOXDH are coordinated to separate copper(II) ions as suggested in the previous section, the appearance of the 26,000 cm^{-1} band would indicate that a tetragonal configuration is achieved by apical coordination of the chloride ions occupying planar positions to neighbouring copper(II) ions in the crystal lattice. The slightly higher energy of the d-d band (12,200 cm^{-1}) could indicate that the water molecule is not held in the coordination sphere.

For the next four complexes (n = 1 - 4), it is unlikely that any are polymeric in view of the abundance of coordinating groups. For n = 1 and 2, models indicate that the length of the methylene chain is insufficient to enable a tridentate structure to be formed. In these complexes it is possible that only one hydrazide group is coordinated, the other two planar positions being occupied by chloride ions. Packing in the crystal lattice may then produce a tetragonal environment of copper(II).

The spectrum of IPGLDHCuCl_2.H_2O shows quite a marked difference from the complexes of adjacent members in the series. A well defined shoulder occurs at about 9,000 cm^{-1} suggesting apically coordinated water. However, the main d-d band has moved slightly to higher energy - this may be significant but could result from poor resolution of the broad bands. These facts may be explained by the formation of a tridentate structure in which one chloride ion in the plane has been replaced by the nitrogen atom of the second hydrazide unit. The ligand field in the plane would then be stronger than N,O,Cl,Cl field of the preceding complex, counteracting the shift of the main band near 26,000 cm^{-1} also indicates apically coordinated chloride.

IPADDHCuCl_2.H_2O, which would be expected to resemble IPGLDHCuCl_2.H_2O, shows no definite shoulder on the infrared side of the main band, although it is clear from figure 6.3 that the broad envelope could contain a band in this region. The maximum occurs at lower energy than observed in IPGLDHCuCl_2.H_2O, thus the spectrum is still consistent with both water and chloride ion being coordinated in the apical positions (compare the effect of changing from the solid to aqueous solution on the spectrum of the uncondensed monoacylhydrazine complexes, table 5.1. A distinct shift

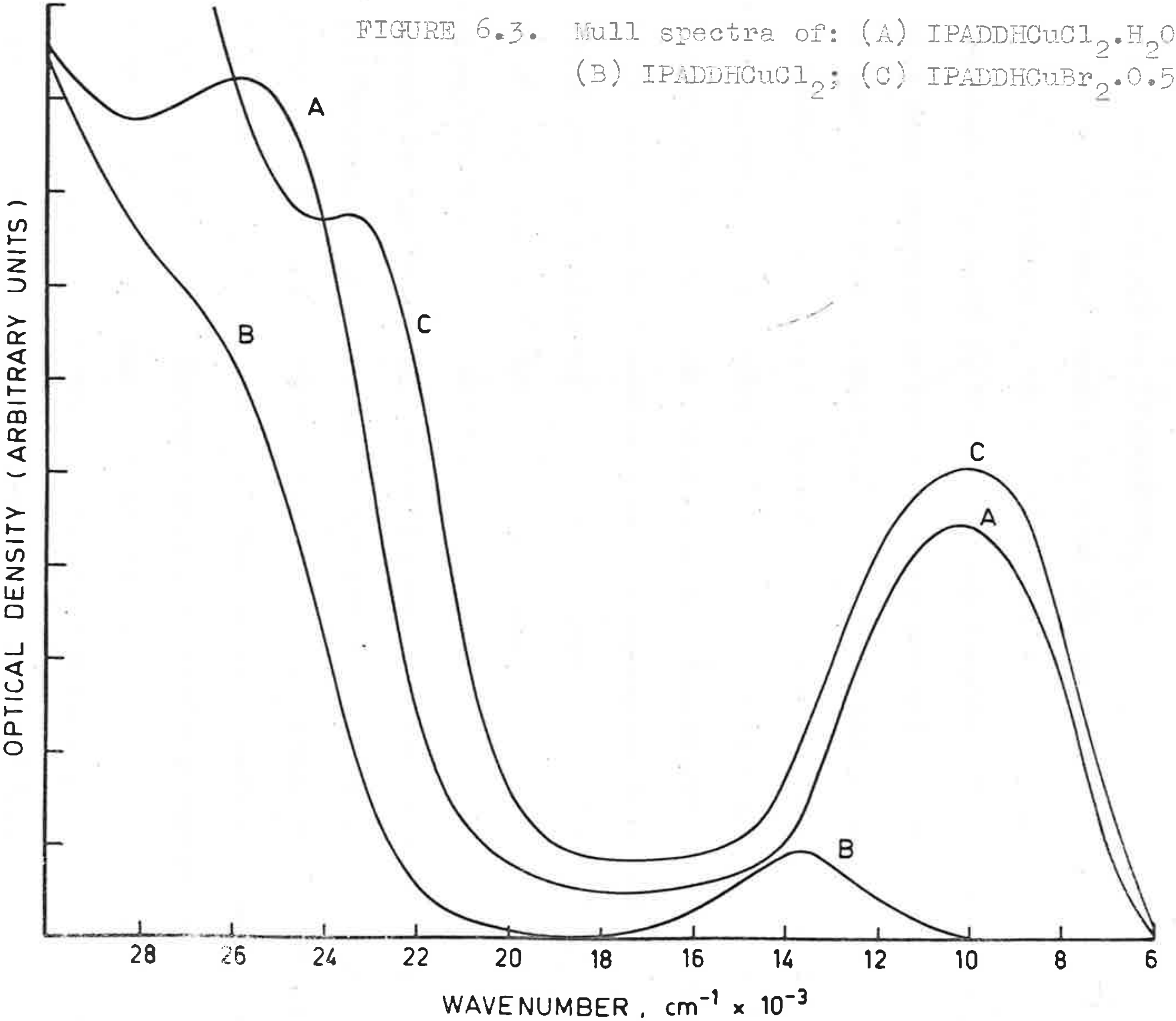


FIGURE 6.3. Mull spectra of: (A) IPADDHCuCl$_2$.H$_2$O; (B) IPADDHCuCl$_2$; (C) IPADDHCuBr$_2$.0.5H$_2$O.

to lower energy is observed but no apparent separation of bands). Further evidence for the effect of apical water on the spectrum is indicated by comparison with the spectrum of anhydrous IPADDHCuCl$_2$ (figure 6.3, curve B), where the d-d band occurs at much higher energy. There is also a difference in the 26,000 cm^{-1} region, where presence of a band in the anhydrous complex is indicated only by a weak shoulder as compared with the well developed band in the monohydrate spectrum. In view of the tendency of the anhydrous complex to revert to a blue hydrate in the atmosphere, it is probable that this complex has a different structure in the solid state from the yellow-green monohydrate. It is possible that water molecules occupy both apical coordination positions in the blue hydrate and being lost on drying, leave chloride ions at larger distances from the copper(II) ion in the anhydrous complex. Unfortunately it cannot be decided from the mull spectrum whether the large difference in intensities in the two regions of absorption is due to weakening of the d-d band or to intensification of the near ultraviolet region. The former possibility may be indicated if the ligand field has little contribution from apically situated chloride ions.

The spectrum of IPADDHCuCl$_2$.0.5H$_2$O is practically identical to that of the monohydrate (table 6.4), both in band positions and intensity ratios (2.2 for the monohydrate and 1.9 for the hemihydrate). This may suggest that the two compounds are distinct since a 50% mixture of the anhydrous complex and monohydrate should produce an observable difference in the spectrum.

A bromide complex, $IPADDHCuBr_2 \cdot 0.5H_2O$, was also prepared. The spectrum of this compound (figure 6.3, curveC) is identical to that of the chloride mono- and hemihydrates in the 10,000 cm^{-1} region. The 26,000 cm^{-1} band in the chlorides has moved to 23,400 cm^{-1} in the bromide, showing a similar effect to that observed in the IPBH complexes. The apical coordination of at least one halide ion is thus indicated.

The possibility that the isopropylidene residues are hydrolysed when the complexes are dissolved in water was remarked on earlier. The spectra of $IPADDHCuCl_2 \cdot 0.5H_2O$ in 80% acetone and in water show a considerable difference (figure 6.4). The appearance of a shoulder about 26,000 cm^{-1} and the large extinction of the d-d band at higher concentrations of acetone would indicate ion pairing, viz. apical coordination of chloride as suggested by the solid state spectrum. Comparison with the aqueous solution spectrum of $ADDHCuCl_2 \cdot 0.5H_2O$ (this is an approximate formulation for reasons which will be discussed below) indicated that this is probably the prevalent species in the aqueous solution of $IPADDHCuCl_2 \cdot 0.5H_2O$. For the uncondensed complex the band maximum occurred at 14,800 cm^{-1}, the solid state spectrum showing the maximum at the same wavenumber (table 6.5). The odour of acetone, detectable over

FIGURE 6.4. Visible region spectrum of IPADDHCuCl$_2$.0.5H$_2$O; (A) in water; (B) in 80% acetone/water.

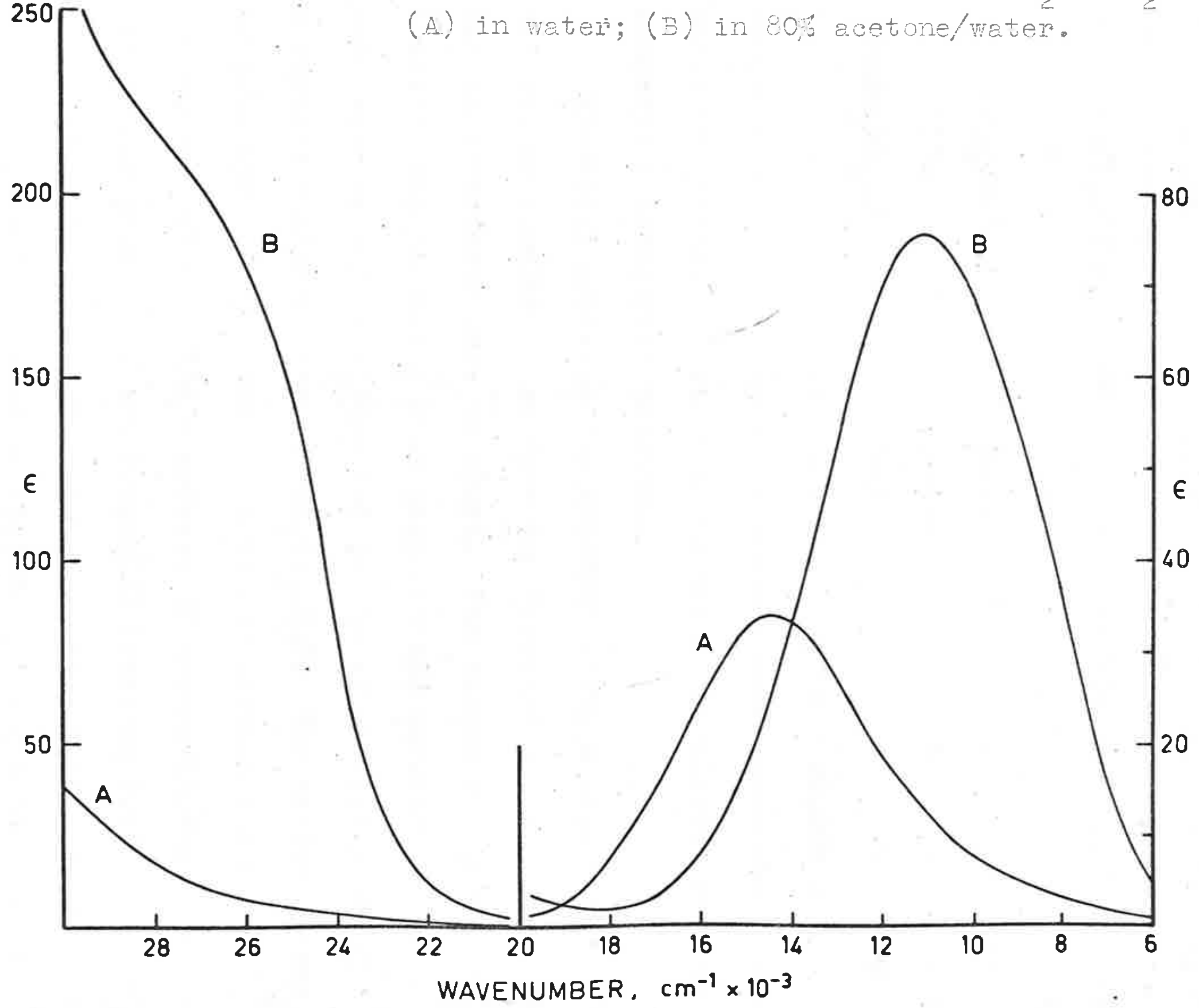


TABLE 6.5. VISIBLE REGION SPECTRA OF ADDH CHLORIDE COMPLEXES.

COMPLEX	MEDIUM	MAXIMUM (cm^{-1}) (ε)	
$IPADDHCuCl_2.0.5H_2O$	80% acetone/water	~26,500 (185);	11,100(76)
"	water	-	14,500 (34)
$ADDHCuCl_2.0.5H_2O$	mull	-	14,800
"	water	-	14,800 (37)
$ADDHCu_2Cl_3.H_2O$	mull	*	15,200

* Broad absorption 30,000 - 20,000 cm^{-1}

concentrated aqueous solution of the IP complexes, further supports a hydrolysis process.

Elemental analyses for $ADDHCuCl_2.0.5H_2O$ were not altogether consistent so that the formulation as a hemihydrate may be considered open to doubt. The reason for the poor analysis was indicated when preparations carried out from warm aqueous solution resulted in the crystallization of a complex analysing for $ADDHCu_2Cl_3.H_2O$. The stoichiometry of this compound suggests that it may contain the $CuCl_3^{2-}$ anion, analogous to the complexes of monoacylhydrazines containing copper(II) and copper(I) (section 2.2). The magnetic moment (table 6.6) is in agreement with this formulation and the visible spectrum (table 6.5) shows a broad band in the region 30,000 - 20,000 cm^{-1}, similar to that observed for $(BH)_2Cu.CuCl_3$ and $(AH)_2Cu.CuCl_3$ (section

5.2). The presence of a band at 15,200 cm^{-1} indicates that the copper(II) is in a similar environment to that in ADDHCuCl$_2$.0.5H$_2$O, although the slightly higher energy may suggest that water is coordinated in the plane of the copper(II) ion, indicating that the ligand behaves as a tridentate chelating agent.

(6.5) MAGNETIC PROPERTIES OF KETO BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE)COPPER(II) AND POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINECOPPER(II) COMPLEXES.

Table 6.6 lists the magnetic moments of the copper(II) complexes of the isopropylidene derivatives of both the monoacylhydrazine and diacyldihydrazine series of ligands. Apart from IPOXDHCu$_2$Cl$_4$.0.5H$_2$O, the magnetic moments lie within the range normally shown by copper(II) complexes.

The subnormal moment of IPOXDHCu$_2$Cl$_4$.0.5H$_2$O, may indicate interaction of the two copper(II) ions in this molecule. This result is not surprising if both ions are bridged by the ligand, when interaction could occur by the superexchange mechanism.

Although the binuclear copper(II) carboxylate complexes show an absorption band in the vicinity of 27,000 cm^{-1}, about the same region as that shown by the keto isopropylidene halide complexes, the possibility of a similar binuclear structure can probably be excluded on magnetic grounds. However, temperature variation studies would be necessary to

TABLE 6.6. MAGNETIC DATA FOR KETO BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE)COPPER(II) AND POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE-COPPER(II) COMPLEXES.

COMPLEX	T(^{o}K)	$10^{6}\chi_{M}$corr.	μ eff.(B.M.)
$(IPBH)_2CuCl_2.H_2O$	291.9	1555	1.91
$(IPBH)_2Cu(ClO_4)_2$	291.8	1575	1.92
$(IPPH)_2CuCl_2.0.5H_2O$	290.7	1544	1.90
$IPOXDHCu_2Cl_4.0.5H_2O$	290.4	1952	1.51[a]
$IPMADHCuCl_2.0.5H_2O$	290.8	1519	1.88
$IPSUDHCuCl_2.0.5H_2O$	290.9	1596	1.94
$IPGLDHCuCl_2.H_2O$	290.8	1492	1.87
$IPADDHCuCl_2.0.5H_2O$	290.7	1519	1.88
$IPADDHCuCl_2$	290.7	1616	1.95
$IPPMDHCuCl_2.0.5H_2O$	290.8	1553	1.91
$IPSRDHCuCl_2.H_2O$	290.8	1608	1.94
$IPAZDHCuCl_2.H_2O$	290.7	1531	1.89
$IPSBDHCuCl_2.H_2O$	290.7	1529	1.89
$IPDDDHCuCl_2.H_2O$	290.8	1728	2.01
$ADDHCuCl_2.0.5H_2O$	290.8	1579	1.92
$ADDHCu.CuCl_3.H_2O$	289.7	1502	1.87[b]

(a) Calculated for two Cu(II).

(b) Calculated for one Cu(II).

verify this conclusion, since Lewis[17] has warned of the danger of using the room temperature moment to discriminate between classes of complexes.

The small variations observed in the diacyldihydrazine series are probably not significant. Many of these complexes had poor packing properties.

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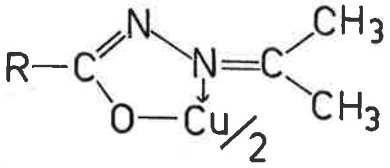
CHAPTER 7.

COPPER(II) COMPLEXES OF N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE AND POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE LIGANDS COORDINATED IN THE ENOL FORM.

(7.1) ENOL BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINO)COPPER(II) COMPLEXES.

Following the procedure adopted for investigation of complexes containing acylhydrazine ligands coordinated in the keto form, complexes containing N-isopropylidene-N'-acylhydrazines coordinated in the enol form were synthesised and studied before examination of the more complicated polymethylene-N,N-isopropylidene-N',N'-diacyldihydrazines. Thus the isopropylidene derivatives of N-benzoyl-, N-acetyl-, and N-propionyl- hydrazines were found to form the neutral complexes $(IPBH)_2Cu$, $(IPAH)_2Cu$ and $(IPPH)_2Cu$ when sodium bicarbonate was added to aqueous acetone solutions of the ligand and copper(II) salts. All three are insoluble in water but readily soluble in organic solvents. $(IPBH)_2Cu$ has been previously reported.

The loss of the secondary amino group hydrogen atom, giving rise to the enol form of the complexed ligand as in (XXVI) was confirmed by infrared spectroscopy. Table 7.1 shows the band positions in the region 4000 - 2900 cm^{-1} for the ligands IPBH and IPPH, and the respective complexes.



(XXVI)

TABLE 7.1. INFRARED BAND POSITIONS OF IPBH, $(IPBH)_2Cu$, IPPH AND $(IPPH)_2Cu$ IN THE REGION 4000 - 2900 cm^{-1} (HEXACHLOROBUTADIENE MULLS).

	BAND MAXIMA (cm^{-1})	
IPBH	3210 (s),	3080 (sh), 3020 (s), 2930 (sh)
$(IPBH)_2Cu$	-	3060 (s), 2990 (s), 2920 (s)
IPPH	3220 (s),	3070 (s), 3000 (s), 2960 (m), 2930 (sh)
$(IPPH)_2Cu$	-	3050 (m), 2990 (s), 2950 (s), 2920 (sh)

The strong band observed at 3210 cm^{-1} for IPBH and at 3220 cm^{-1} for IPPH is absent in the spectra of the corresponding complexes and accordingly may be ascribed to the N-H stretching vibration, which disappears on enolisation of the ligand.

Diamantis[1] has suspected the existence of the corresponding enol complex formed by uncondensed N-benzoylhydrazine, and Albert[2] has noted the formation of a precipitate on attempting to measure the stability constant for the addition of a second molecule of BH to copper(II) by potentiometric titration. However, the complex has not been characterized by these workers. Consequently an attempt was made to prepare it by the addition of sodium hydroxide to solutions containing copper(II) and a large excess of BH. Several such preparations produced precipitates of varying analysis and no solvent was found from which the highly insoluble compound could be recrystallized. Samples in closest agreement with the formulation $(BH)_2Cu$ were obtained as pink, microcrystalline needles from the reaction of $Cu(NH_3)_4 \cdot SO_4 \cdot H_2O$ with BH in sodium acetate solution.

In benzene solution, the enol bis-(N-isopropylidene-N'-acylhydrazino) complexes show absorption spectra in the region 22,000 to 6,000 cm^{-1} consisting of broad bands as shoulders on the low energy side of intense charge transfer bands. These shoulders must undoubtedly result from transitions within the d-shell of copper(II). With maxima in the region of 18,000 cm^{-1} (table 7.2), the spectra of the three complexes are practically identical and illustrate the much increased ligand field strength of the acylhydrazine grouping in this form.

The spectrum of $(IPBH)_2Cu$ in benzene solution is illustrated in figure 7.1 (curve C). Several determinations of this spectrum indicated that the broad shoulder centred at about 18,000 cm^{-1} actually contains two bands, although positive identification of two separate maxima is rendered impossible by the nearness of the charge

FIGURE 7.1. Visible region spectra of: (A) $(BH)_2Cu$ (Nujol mull); (B) $(IPBH)_2Cu$ (Nujol mull); (C) $(IPBH)_2Cu$ in benzene.

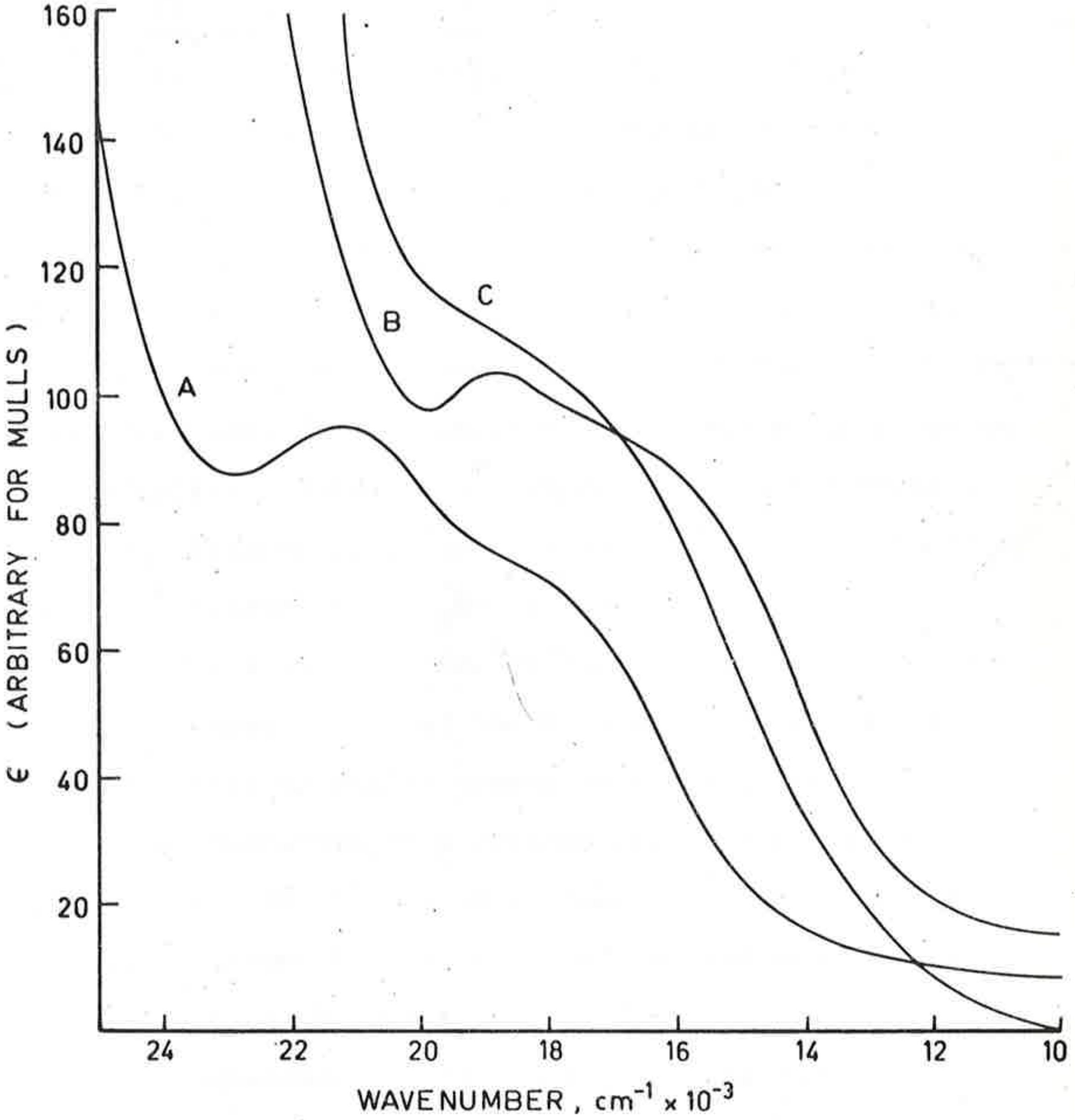


TABLE 7.2. ABSORPTION SPECTRA OF ENOL BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINO) AND BIS-(N-ACYLHYDRAZINO) COPPER(II) COMPLEXES IN THE REGION 22,000 - 6,000 cm^{-1}.

COMPLEX	MEDIUM	MAXIMUM (cm^{-1}) (ε)
$(IPAH)_2Cu$	Benzene	~18,500 (sh) (105)
$(IPPH)_2Cu$	"	~18,600 (sh) (106)
$(IPBH)_2Cu$	"	~18,000 (sh) (104)
"	Mull	18,800, ~16,000 (sh)
$(BH)_2Cu$	"	21,200, ~18,000 (sh)

transfer band. The presence of two bands in this region is definitely indicated, however, by the solid state spectrum (figure 7.1, curve B) and even more convincingly in the spectrum of $(BH)_2Cu$ (figure 7.1, curve A).

Thus the mull spectra of these two complexes show similar characteristics, the main difference being an overall shift to higher energy in the case of $(BH)_2Cu$, which is indicative of a greater ligand field strength for the enol BH ligand. The spectral differences are readily apparent in the colour of the two complexes - $(IPBH)_2Cu$ is olive green while $(BH)_2Cu$ is salmon pink.

The extension of the charge transfer band to lower energy in the case of $(IPBH)_2Cu$ is to be expected in view of the longer conjugated system extending through the ligand molecule. Such a system would conceivably exert a considerable stabilizing influence on the complex in comparison with the corresponding keto complex.

The similarity of the solution spectra of the enol bis-(N-isopropylidene-N'-acylhydrazino) complexes to the spectra of bis-(acetylacetoneiminato)copper(II)^3 and bis-(N-methylacetylacetoneiminato)copper(II)^3 would indicate that the structure of these complexes is similar and presumably the ligands are arranged in the trans configuration. Although the molar extinction coefficients for the IP-acylhydrazine complexes at the maxima (table 7.2) are approximately twice the values for the acim complexes (table 4.5), this fact cannot be taken as evidence for a cis configuration (c.f. Cu(ac$_2$en), table 4.5) since the near proximity of the charge transfer band is undoubtedly responsible for the increased extinction. An estimate of the "true" value for the d-d transition is given in section 7.6.

(7.2) ADDUCTS OF ENOL BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINO)COPPER(II) COMPLEXES.

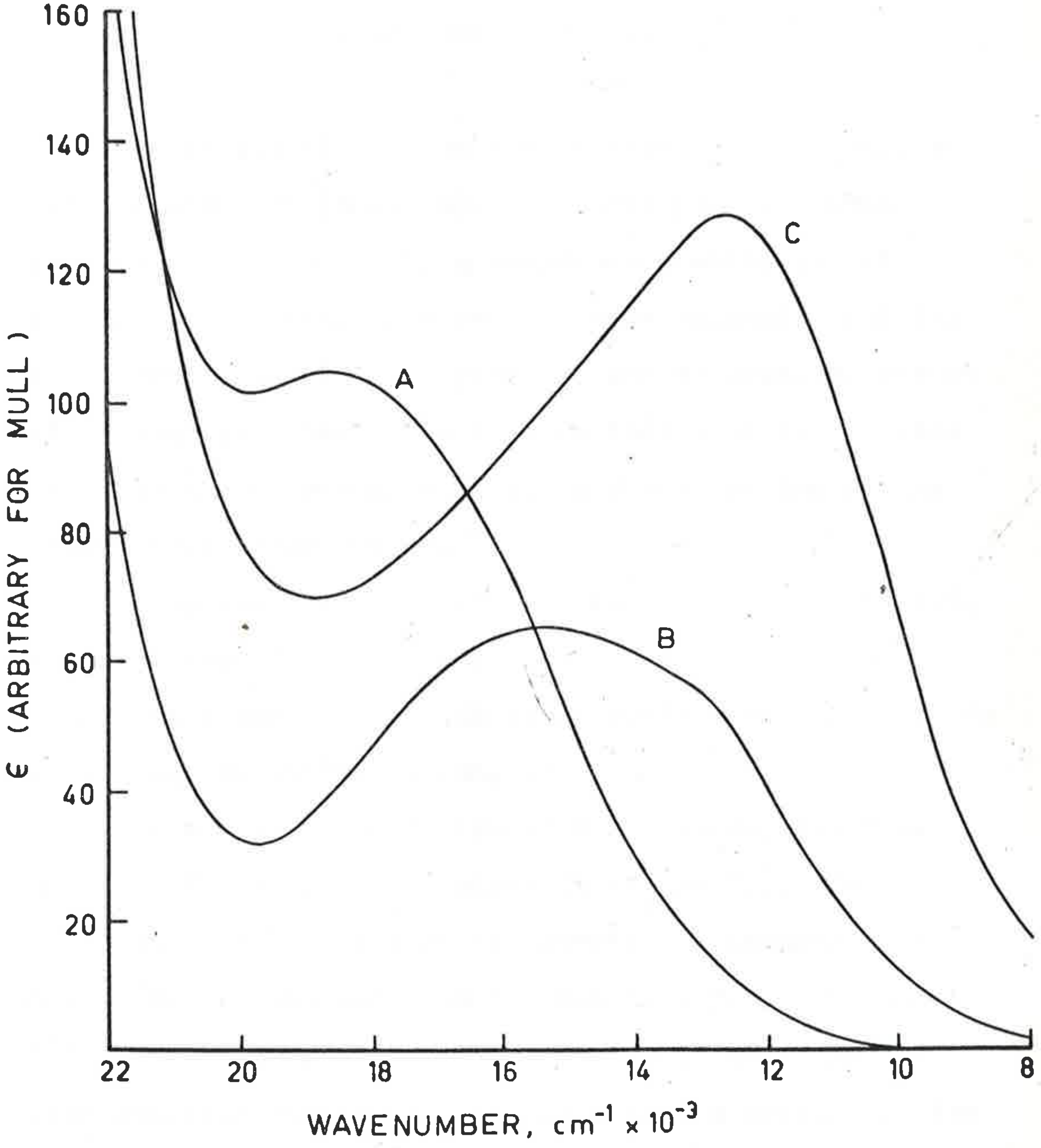
Recrystallization of (IPAH)$_2$Cu and (IPPH)$_2$Cu from aqueous acetone yielded the respective bright green monohydrates, which were also produced when the anhydrous complexes were allowed to stand exposed to the atmosphere. An attempt to prepare (IPBH)$_2$Cu.H$_2$O by precipitation of (IPBH)$_2$Cu from acetone solution with water produced only the anhydrous complex. The complexes $(IPBH)_2Cu(pyridine)_2$, $(IPBH)_2Cu$.2-methylpyridine, and $(IPBH)_2Cu$.4-methylpyridine were obtained by recrystallization from the heterocyclic bases. The green pyridinates were stable in closed containers but readily reverted to the parent complex on exposure to the atmosphere, thus displaying similar behaviour to the adducts of $Cu(acac)_2$ (section 4.5) and indicating that the molecules of base are but weakly bound.

The solid state visible spectrum of $(IPPH)_2Cu.H_2O$ is shown in figure 7.2, curve C; the spectrum of $(IPAH)_2Cu.H_2O$ is similar (table 7.3). The presence of two bands is clearly indicated, and although these bands can be identified in the solution spectrum of $(IPPH)_2Cu.H_2O$ in actone/water (figure 7.2, curve B), the relative intensities of the two bands are reversed. In addition, the broad envelope of the solution spectrum may possibly

TABLE 7.3. ABSORPTION SPECTRA OF THE MONOHYDRATES OF ENOL BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINO) COPPER(II) COMPLEXES IN THE REGION 22,000 - 6,000 cm^{-1}.

COMPLEX	MEDIUM	MAXIMUM (cm^{-1}) (ε)
$(IPAH)_2Cu.H_2O$	Mull	~15,400 (sh); 12,900
$(IPPH)_2Cu.H_2O$	Mull	~15,000 (sh); 12,600
	Benzene	18,600 (sh) (105)
	70% acetone/H_2O	15,400 (66); ~12,800 (sh) (51)

FIGURE 7.2. Visible region spectra of $(IPPH)_2$-Cu.H_2O: (A) in benzene; (B) in 70% acetone/water; (C) Nujol mull.



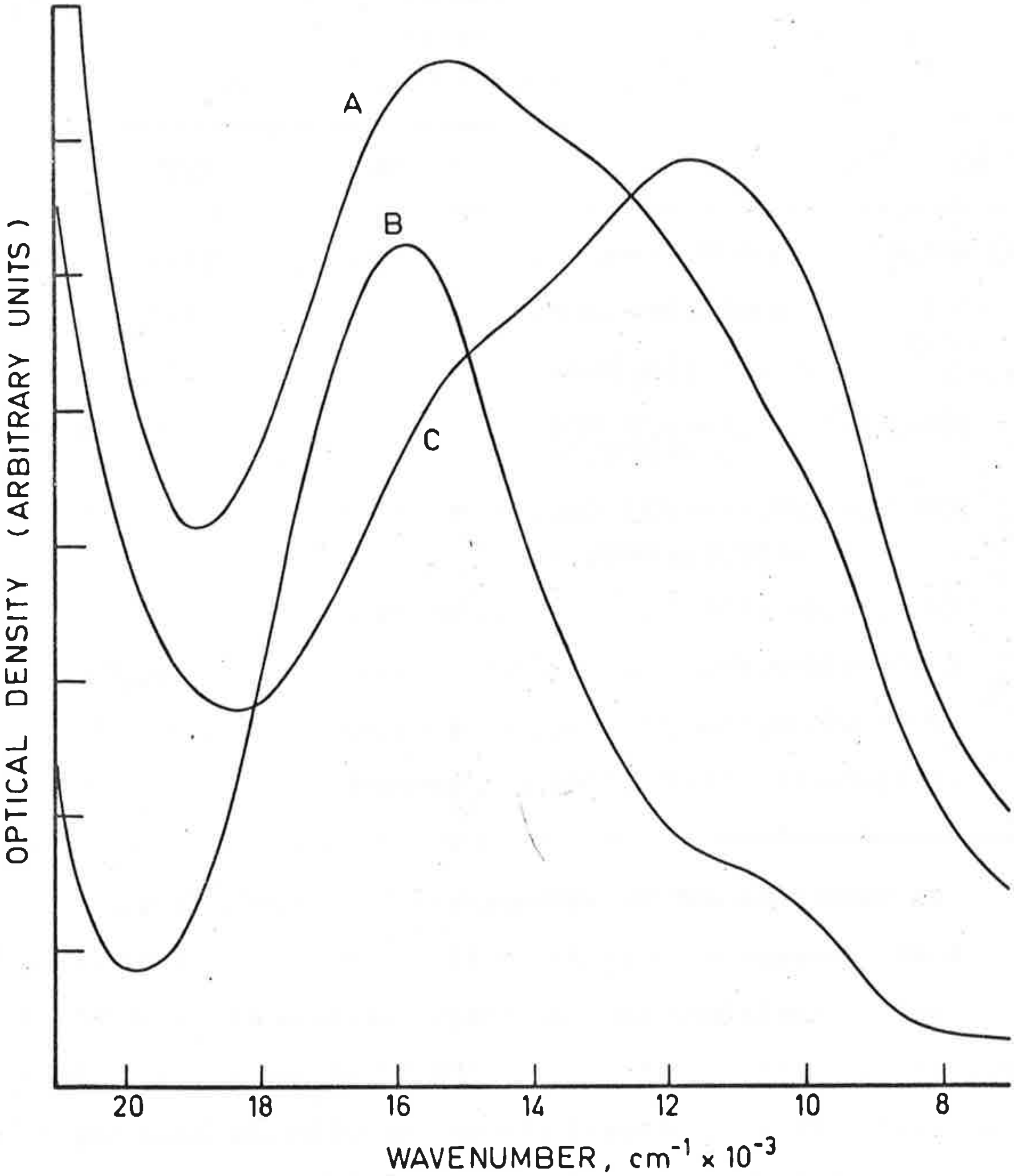
contain a third band at higher energy (approximately 17,500 cm^{-1}) although this is by no means certain. The differences between the solid state and solution spectra may indicate the coordination of a second water molecule in solution.

Figure 7.2 also shows the spectrum of this complex in benzene solution (curve A). The spectrum is almost identical with that of the anhydrous complex in this solvent, indicating loss of the water molecule from the coordination sphere of copper(II) and demonstrating that it is weakly bound. This is also indicated by the ease in which the anhydrous complex is formed on drying the monohydrate under vacuum.

These results can only be interpreted as indicating the presence of five-coordinated copper(II) in the monohydrate complexes, with water coordinated apically to give a square configuration.

The solid state spectra of the heterocyclic base adducts of $(IPBH)_2Cu$ are shown in figure 7.3. In conjunction with the solution spectra in heterocyclic bases (table 7.4, see also figures 7.4, 7.5, 7.6) some information is provided on the number of molecules of base actually coordinated apically to the copper(II) ion in the parent complex. Both in the solid state and in solution large shifts of band maxima to lower energies are apparent on comparison with the parent complex in

FIGURE 7.3. Mull spectra of heterocyclic base adducts of $(IPBH)_2Cu$: (A) $(IPBH)_2Cu.(pyridine)_2$; (B) $(IPBH)_2Cu$.4-methylpyridine; (C) $(IPBH)_2Cu$.2-methylpyridine.



benzene solution. Similar solvent effects are shown by $(IPPH)_2Cu$ in heterocyclic bases (table 7.4).

TABLE 7.4. ABSORPTION SPECTRA OF HETEROCYCLIC BASE ADDUCTS OF $(IPBH)_2Cu$ AND $(IPPH)_2Cu$ IN THE REGION 22,000 - 6,000 cm^{-1}.

COMPLEX	MEDIUM	MAXIMUM (cm^{-1}) (ε)
$(IPBH)_2Cu(py)_2$	Mull	15,300; ~12,600(sh); ~10,000 (sh)
$(IPBH)_2Cu(4\text{-me-py})$	"	15,800; ~10,400(sh)
$(IPBH)_2Cu(2\text{-me-py})$	"	~15,000(sh); 11,700
$(IPBH)_2Cu$	py	15,300(77); ~13,000(sh)(69); ~10,000(sh)(26).
"	4-me-py	15,200(79); ~13,000(sh)(70); ~10,000(sh)(28).
"	2-me-py	~15,400(sh)(70); 13,600(75)
$(IPPH)_2Cu$	py	15,300(74); ~13,000(sh)(65)
"	4-me-py	15,300(77); ~13,000(sh)(69)
"	2-me-py	15,400(sh)(66); 13,600(69).

The similarity of the spectra of the complexes in pyridine and 4-methylpyridine solution is apparent from table 7.4. It will be noted that the positions of the band maxima shown by $(IPBH)_2Cu(py)_2$ in the solid state and in pyridine solution are almost identical, while there is a considerable difference between the solid state spectrum of the mono-4-methylpyridine adduct and the 4-methylpyridine solution spectrum of the parent complex. These observations would indicate that the addition of a second molecule of base in solution (or in the solid state for the bis-pyridine adduct) certainly does have a perturbing effect on the spectrum and results mainly in the appearance of a band at approximately 13,000 cm^{-1}. From the present measurements it cannot be decided whether this is an intensity effect or results from the separation of two near-coincidental bands in the mono-adduct spectrum. However, this effect would indicate that the second molecule of base is actually coordinated to the metal ion and not simply occupying a site in the crystal lattice as suggested by Graddon.[4]

The position of the band at approximately 10,000 cm^{-1} must be considered rather uncertain since, particularly in the solution spectra, it appears only as a slight inflexion on the infrared side of the 13,000 cm^{-1} band. However, its presence in the solid state spectrum of the 4-methylpyridine adduct is definite (figure 7.3), so that the inflexions in the solution spectra should be considered to result from this weaker absorption and not from instrumental errors. The presence of this band could not be positively identified in the spectra of the 2-methylpyridine adduct although it could be easily contained in the absorption envelope, similarly with $(IPPH)_2Cu$ in base solutions.

The solid state spectra of the mono-2-methylpyridine adduct is distinct from that of the mono-4-methylpyridine adduct in that reversal of the relative intensities of the two apparent bands has occurred. This band structure persists in solution in the pure base, indicating little tendency for the formation of a bis-adduct, which is to be expected from the steric effects of the 2-methyl group. The reason for the reversal of band intensities is not readily apparent, but may be associated with the steric effects of the 2-methyl group. That this explanation is dubious, however, may be indicated by the solid state spectrum of $(IPPH)_2Cu.H_2O$ which is remarkably similar to that of $(IPBH)_2Cu$.2-methylpyridine. Such steric effects would be expected to be non-existent in the hydrate complex. Interpretation is also hindered by the fact that it is difficult to decide which of the two bands at 13,000 cm^{-1} and 15,000 cm^{-1} has increased (or decreased) in intensity. Comparison of the solution spectra in 2-methylpyridine and 4-methylpyridine is of little use due to the effects of coordination of a second molecule of base in the case of the 4-methylpyridine adduct.

It is interesting that a bis-pyridinate but only a mono-4-methylpyridinate was obtained by recrystallization of $(IPBH)_2Cu$ from the respective bases, since it would be expected that the greater base strength of 4-methylpyridine would be conducive to the formation of a bis-adduct. Thus it is probable that solubility effects are also important in determining the type of solid adduct which may be deposited from solution, in addition to the effect of base strengths of both the apical and planar coordinated atoms (section 4.5).

(7.3) EQUILIBRIUM CONSTANTS FOR THE COORDINATION OF HETEROCYCLIC BASES TO BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINO)COPPER(II) COMPLEXES.

The solvent effects exhibited by bis-(N-isopropylidene-N'-acylhydrazino)copper(II) complexes make these systems very suitable for spectrophotometric determination of the equilibrium constants for the addition of heterocyclic bases to these complexes. Consequently, the absorption spectra of $(IPBH)_2Cu$ and $(IPPH)_2Cu$ in the region 21,000 - 9,000 cm^{-1} were measured over a range of concentrations of pyridine, 4-methylpyridine, and 2-methylpyridine in benzene solution. The families of curves shown by $(IPBH)_2Cu$ for each of these bases are illustrated in figures 7.4, 7.5 and 7.6. The characteristics of these curves are also shown by the corresponding $(IPPH)_2Cu$ systems.

It will be noted that a single isosbestic point is observed in each system, with all the measured curves passing through this point except for pure pyridine and 4-methylpyridine solutions. This trend was also noted for $(IPPH)_2Cu$. Thus, although the mono-adducts of pyridine and 4-methylpyridine would appear to predominate in

FIGURE 7.4. The spectrum of $(IPBH)_2Cu$ in benzene solution with increasing concentrations of pyridine from (1) pure benzene to (8) pure pyridine. Refer to table 7.5 for pyridine concentrations.

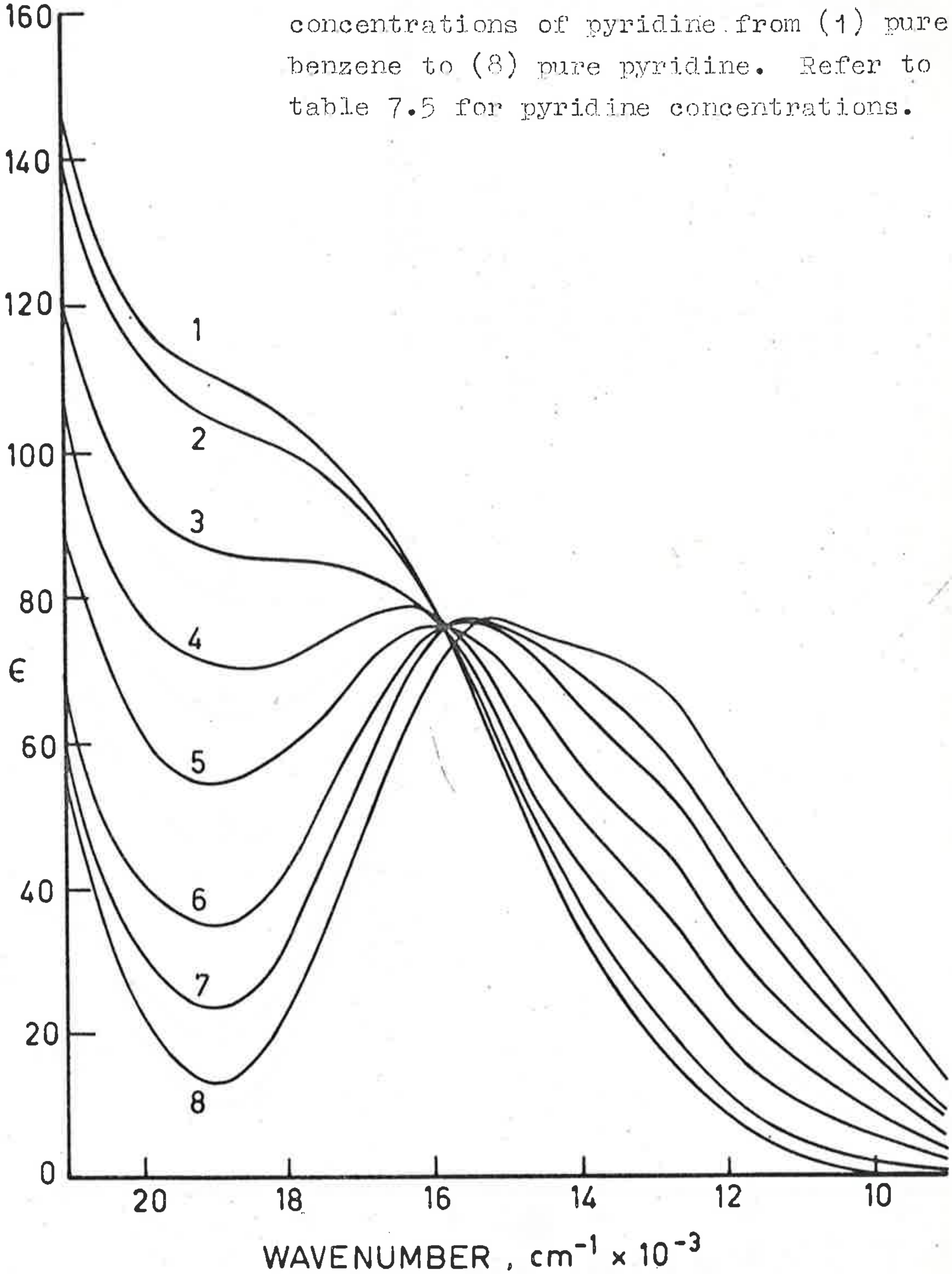


FIGURE 7.5. The spectrum of $(IPBH)_2Cu$ in benzene solution with increasing concentrations of 4-methylpyridine from (1) pure benzene to (7) pure 4-methylpyridine. Refer to table 7.5 for 4-methylpyridine concentrations.

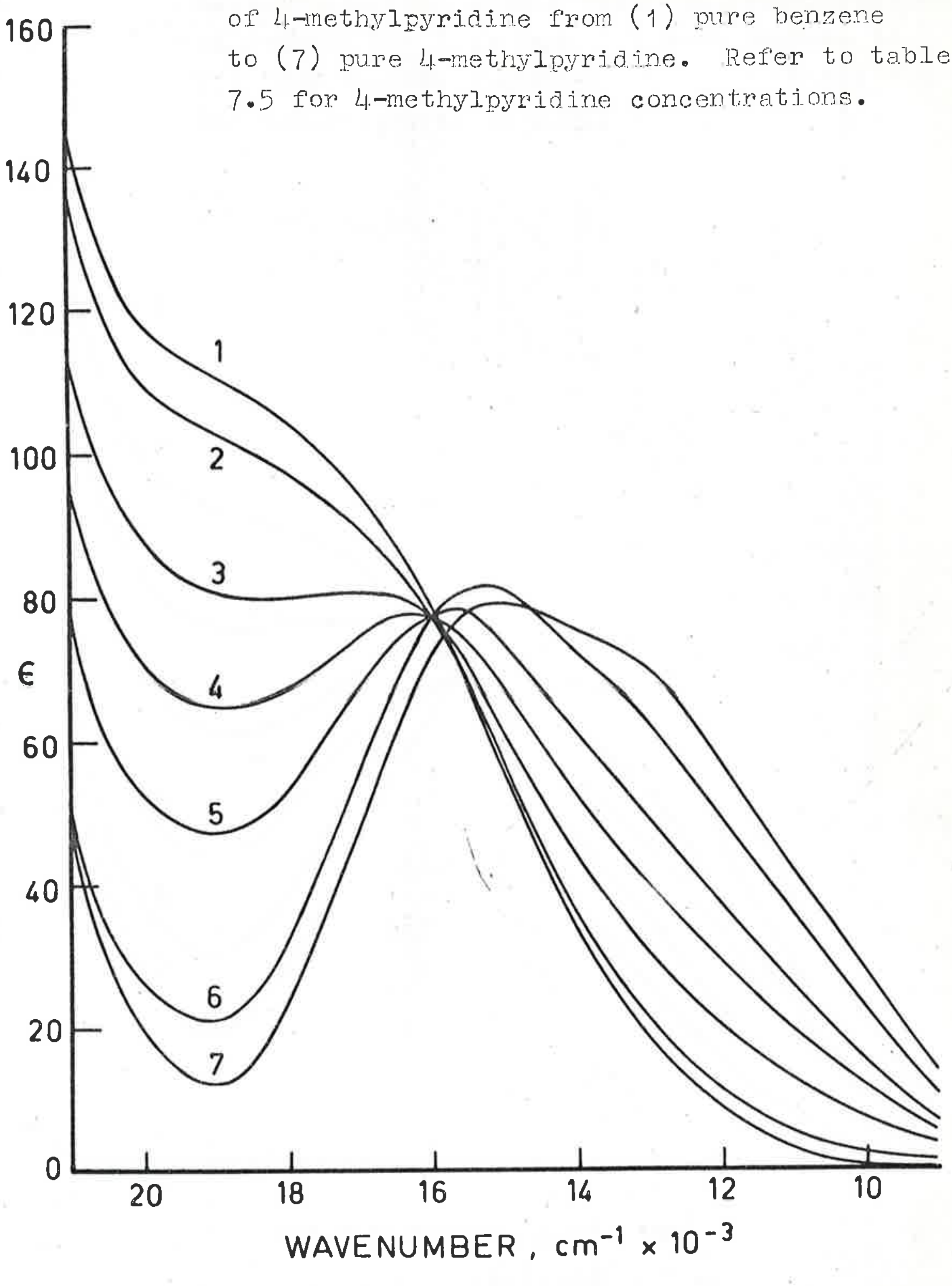
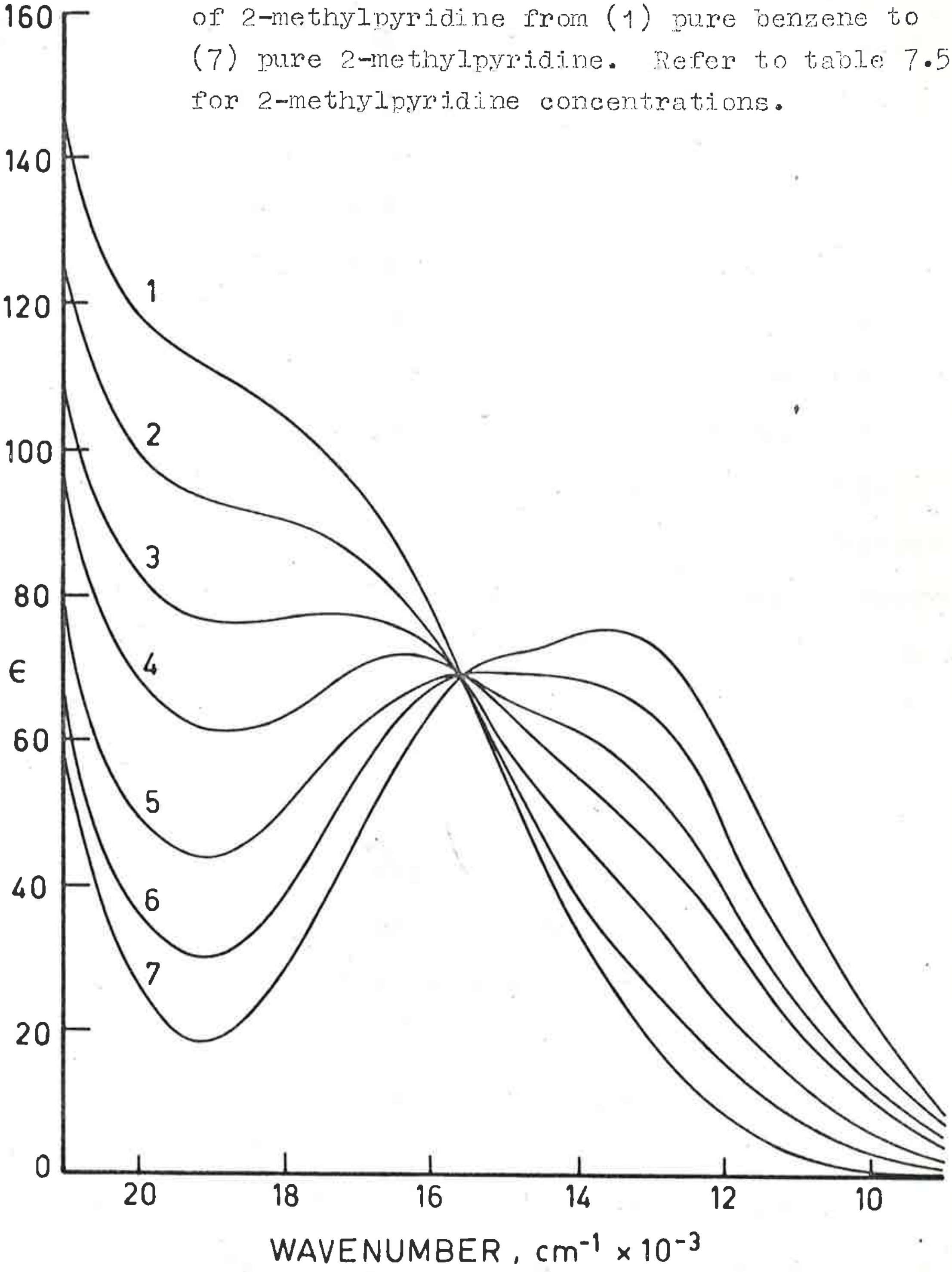


FIGURE 7.6. The spectrum of $(IPBH)_2Cu$ in benzene solution with increasing concentrations of 2-methylpyridine from (1) pure benzene to (7) pure 2-methylpyridine. Refer to table 7.5 for 2-methylpyridine concentrations.



solutions with lower concentrations of base, the presence of bis-adducts in the pure bases is indicated. The 2-methylpyridine systems did not show this effect, so it must be concluded that only the mono-adduct is formed in the pure base.

The small but distinct deviations of the pyridine and 4-methylpyridine solutions is a complicating factor in the calculation of the equilibrium constants. Clearly, the similarity in spectra of the mono- and bis-adducts (as indicated by the mull spectrum of $(IPBH)_2Cu$.4-methylpyridine in comparison with the spectrum in pure base) would make it difficult to determine the concentration of each species for a given concentration of base. However, K_2 would be expected to be much smaller than K_1 (section 4.5) hence the contribution of the bis-pyridinate to the spectrum in solutions containing low concentrations of base should be negligible. It is apparent that contribution from the bis-adduct spectrum becomes noticable only in solutions containing high base concentrations, e.g. in pure pyridine, where the ratio base:complex was approximately 2,000:1.

In calculating formation constants by the method of Graddon and Watton,[4] it was preferred to use values of the extinction coefficient in the region of 19,000 cm^{-1} where the largest spectral changes occur. This procedure should give the most accurate values of K and is based on the decrease in extinction of the parent complex as the adduct is formed. Accordingly the equation relating the concentrations of the species becomes:

$$[\text{Complex}] = [\text{Total Copper}] \times \frac{\varepsilon - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}$$

Where [Complex] is the concentration of the parent complex at equilibrium,

ε is the observed extinction,

ε_0 is the extinction of the parent complex,

ε_∞ is the extinction of the adduct,

and the adduct concentration is determined by difference.

The correct value of ε_∞ is problematical. Walker and Li[5] have determined this value in their measurements by extrapolation of ε to infinite concentration of base, while Graddon and Watton[4] have chosen ε_∞ by trial and error to give the most reproducible values of K. However, the systems for which K was measured by these authors apparently do not show anomalous effects in solutions of the pure bases. Consequently it was decided to use the values of ε shown by the complexes in pure base solutions as ε_∞, since the mull spectrum of $(\text{IPBH})_2\text{Cu.4-methylpyridine}$ indicated that differences between the mono- and bis-adduct spectra should be small in the region of 19,000 cm^{-1}. In view of the large excess of base (2000:1), these values should not be distinguishable from extrapolated values at infinite base concentrations.

The results obtained for $(IPBH)_2Cu$ and $(IPPH)_2Cu$ on the addition of heterocyclic bases in benzene solution are shown in tables 7.5 and 7.6. The reasonable consistency of the values of K for each system indicates that the relationship:

$$K = \frac{[\text{adduct}]}{[\text{Complex}]\quad[\text{base}]}$$

is applicable and corresponds to the formation of mono-adducts in solution. Thus the method of calculation is seen to be reasonable, although the values of K will be subject to a small error resulting from the formation of bis-adducts. This may be apparent in the increased K values shown for the strongest solutions of heterocyclic bases in benzene, at least for the $(IPBH)_2Cu$ systems, although their values would be expected to show the greatest deviation due to experimental error.

For both parent complexes, K follows the trend to be expected from consideration of base strength and the steric effect of the 2-methyl group (section 4.4). Thus K decreases in the order:

4-me-py > py > 2-me-py

paralleling the results previously observed for bis-(acetylacetonato)copper(II) and related complexes.[4] In comparing K for $(IPBH)_2Cu$ and $(IPPH)_2Cu$ with each heterocyclic base, it is apparent that for the latter complex the formation constants are generally lower than

TABLE 7.5. FORMATION CONSTANTS FOR THE REACTION OF HETEROCYCLIC BASES WITH BIS-(N-ISOPROPYLIDENE-N'-BENZOYLHYDRAZINO)COPPER(II) IN BENZENE SOLUTION.

(A). PYRIDINE (at 22°)

	$(\text{PYRIDINE})_{\text{tot.}}$(M)	$\varepsilon_{19,000}$	K (l.mole^{-1})	K_{ave}
(1)	0	110.5	-	
(2)	0.00497	105.1	13.0	
(3)	0.02483	86.6	14.0	
(4)	0.04966	70.7	14.7	14.1±0.4 l.mole^{-1}
(5)	0.09932	54.3	14.2	
(6)	0.2483	34.8	14.4	
(7)	0.4966	23.6	(16.9)	
(8)	pure.	13.1	-	

(B). 4-METHYLPYRIDINE (at 21°)

	$(\text{4-ME-PYRIDINE})_{\text{tot.}}$(M)	$\varepsilon_{19,000}$	K (l.mole^{-1})	
(1)	0	110.5	-	
(2)	0.00410	102.6	23.9	
(3)	0.2050	80.8	23.0	
(4)	0.04099	64.5	22.9	23.2±0.4 l.mole^{-1}
(5)	0.08198	47.5	22.9	
(6)	0.4099	20.8	(25.8)	
(7)	pure	12.2	-	

(C). 2-METHYLPYRIDINE (at 20°)

	$(\text{2-ME-PYRIDINE})_{\text{tot.}}$(M)	$\varepsilon_{19,000}$	K (l.mole^{-1})	
(1)	0	110.5	-	
(2)	0.0812	93.1	2.89	
(3)	0.2031	76.2	2.94	
(4)	0.4061	60.8	2.90	3.0±0.1 l.mole^{-1}
(5)	0.8122	43.6	3.25	
(6)	2.0305	29.7	(3.44)	
(7)	pure	18.2	-	

TABLE 7.6. FORMATION CONSTANTS FOR THE REACTION OF HETEROCYCLIC BASES WITH BIS-(N-ISOPROPYLIDENE-N'-PROPIONYLHYDRAZINO)COPPER(II) IN BENZENE SOLUTION.

(A). PYRIDINE (at 20°)

	(PYRIDINE)$_{tot.}$(M)	$\varepsilon_{19,600}$	K (1.mole^{-1})	K$_{ave}$
(1)	0	103.5	-	
(2)	0.02483	91.9	5.91	
(3)	0.04966	83.4	5.68	
(4)	0.09932	71.3	5.14	5.5±0.3 1.mole^{-1}
(5)	0.2483	50.8	5.30	
(6)	0.4966	34.9	5.64	
(7)	pure	10.2	-	

(B). 4-METHYLPYRIDINE (at 20°)

	(4-ME-PYRIDINE)$_{tot.}$(M)	$\varepsilon_{19,600}$	K (1.mole^{-1})	
(1)	0	103.5	-	
(2)	0.02050	90.6	7.95	
(3)	0.04099	80.5	8.08	8.0±0.1 1.mole^{-1}
(4)	0.08198	66.9	7.87	
(5)	pure	8.95	-	

(C) 2-METHYLPYRIDINE (at 20°)

	(2-ME-PYRIDINE)$_{tot.}$(M)	$\varepsilon_{19,600}$	K (1.mole^{-1})	
(1)	0	103.5	-	
(2)	0.2031	83.7	1.46	
(3)	0.4061	70.8	1.49	1.5±0.04 1.mole^{-1}
(4)	0.8122	54.9	1.57	
(5)	pure	16.6	-	

exhibited by the former complex. Other factors being equal, this difference may be associated with the electron-donating properties of the methyl group of IPPH, resulting in reduction of the effective positive charge of copper(II) in this complex and decreasing the bond strength of the apically attached heterocyclic base.

An apparent anomaly in the behaviour of $(IPPH)_2Cu$ compared with $(IPBH)_2Cu$ is demonstrated in the reluctance of the latter compound to form a solid hydrate, which might be expected to form in the light of the above discussion, since $(IPPH)_2Cu.H_2O$ is easily prepared. Here again, the importance of solubility effects is indicated in determining whether or not a particular adduct may be isolated in the solid state.

(7.4) ENOL POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINO COPPER(II) COMPLEXES.

Following the behaviour exhibited by the N-isopropylidene derivatives of monoacylhydrazine ligand, many of the N,N-diisopropylidene-N',N'-diacyldihydrazine series of ligands were found to give rise to neutral copper(II) complexes. All of the complexes isolated were found to contain a 1:1 ratio of ligand to copper.

The first member of the series, IPOXDH (n = 0) formed the complex IPOXDHCu when reacted with copper(II) chloride in sodium acetate solution. Provided the preparation ratio of ligand:copper was at least 2:1, this complex was obtained as a dark green, finely divided precipitate. Preparation from 1:1 or 0.5:1 ratios yielded complicated products (probably mixtures) containing chloride. The complex was found to be insoluble in all solvents tried, and in view of the geometry of the ligand must be considered to be polymeric in structure.

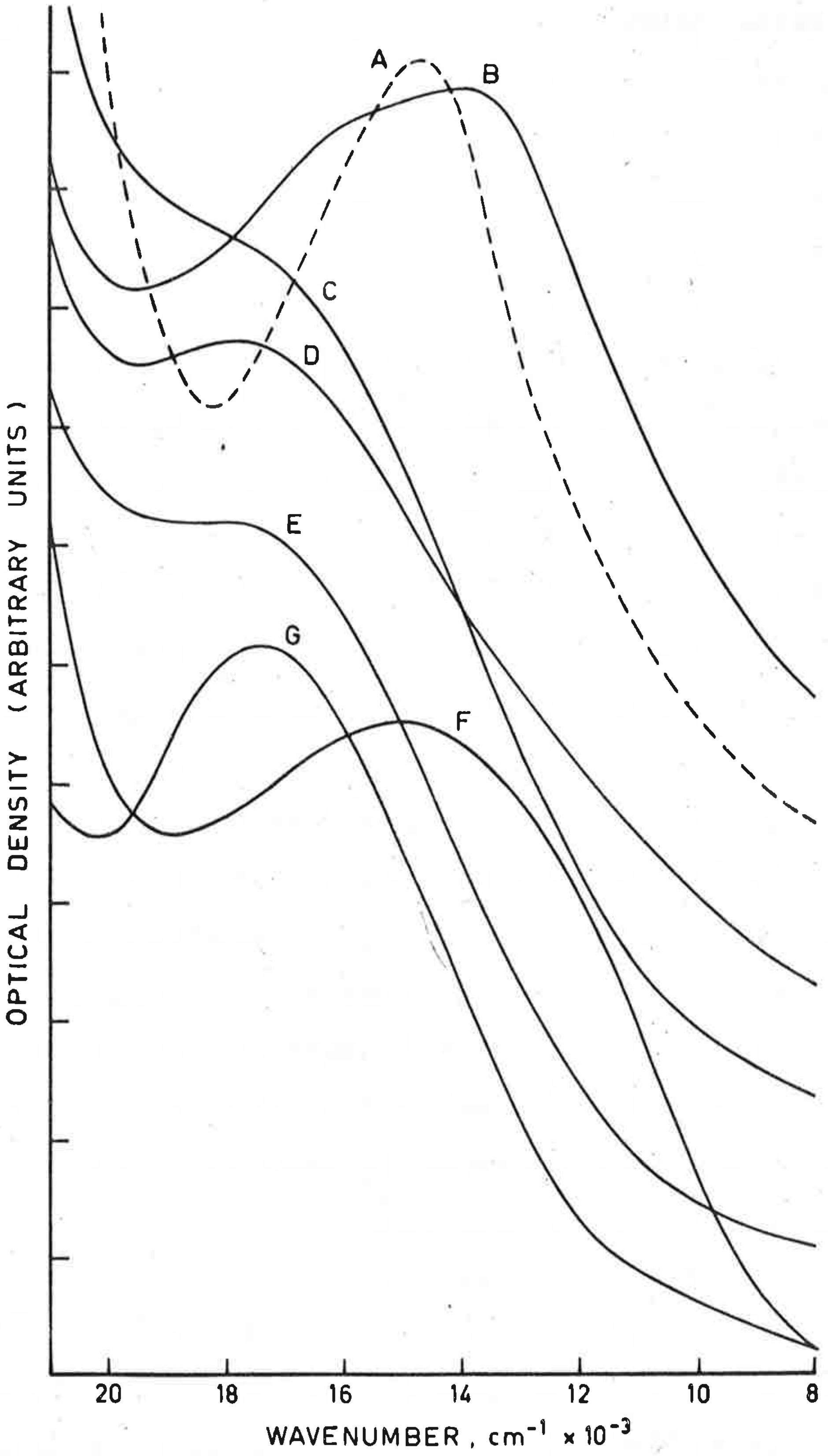
No anion-free complex could be obtained from IPMADH (n = 1) under similar conditions to those above. From n = 2 to 4, bright green complexes of the type $LCu(H_2O)_x$ (where x is greater than 1) were obtained; these compounds dried slowly to the olive green monohydrates. IPPMDHCu (n = 5) was obtained as the olive green anhydrous compound by drying the bright green monohydrate. IPSRDHCu (n = 6) was obtained in the anhydrous state, although the existence of an unstable hydrate was indicated during the preparation.

Attempts to prepare complexes from the higher members (n = 7, 8, 10) were unsuccessful, no anion-free products being obtained. The preparation of a neutral complex from IPSBDH (n = 8) was attempted several times; analyses approximated to a 1:1 formulation but were highly inconsistent. This was probably due to the instability of the complex, which appeared to decompose extensively at 70°.

The solid state visible region spectra of this series of complexes are illustrated in figure 7.7. The similarity of the spectra of $IPGLDHCu.H_2O$, $IPADDHCu.H_2O$, IPPMDHCu and IPSRDHCu to the spectra of the bis-monoacylhydrazino

FIGURE 7.7. Mull spectra of:

(A) IPOXDHCu;
(B) IPSUDHCu.H_2O
(C) IPGLDHCu.H_2O
(D) IPADDHCu.H_2O;
(E) IPPMDHCu;
(F) IPPMDHCu.H_2O;
(G) IPSRDHCu.


A
B
C
D
E
F
G
OPTICAL DENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
8
WAVENUMBER, cm^{-1} × 10^{-3}

complexes (figure 7.1) is apparent, and would indicate that copper(II) exists in a similar environment in both series of complexes. This is born out by the chloroform and pyridine solution spectra (table 7.7, see also figure 7.11), which show very similar band positions and extinction coefficients to $(IPBH)_2Cu$ etc. in benzene and pyridine.

It must be considered unlikely that the water molecule in $IPGLDHCu.H_2O$ and $IPADDHCu.H_2O$ is coordinated apically. Although the close proximity of the intense charge-transfer bands in these spectra prohibit accurate determination of the maxima of the bands due to transitions within the d-shell, it is clear that the presence of a water molecule in these two complexes has very little effect on the spectrum. This is not so for $IPPMDHCu.H_2O$, which shows a broad band centred at lower energy, following the trend shown by $(IPPH)_2Cu.H_2O$ in comparison with the anhydrous complexes.

The presence of water in $IPADDHCu.H_2O$ was confirmed by infrared spectroscopy. The spectra of the ligand and complex in the range 4000 - 2500 cm^{-1} are shown in figure 7.8. The complex shows two broad bands centred at 3,400 and 3,200 cm^{-1}, probably corresponding to the antisymmetric and symmetric stretching vibrations of the water molecule.[6a] $(IPPH)_2Cu.H_2O$, however, shows only a single broad band centred at 3,160 cm^{-1}. It is improbable that the strong band shown by the free ligand at 3,280 cm^{-1} makes any

TABLE 7.7. ABSORPTION SPECTRA OF ENOL POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINO COPPER(II) COMPLEXES IN THE REGION 22,000 - 6,000 cm^{-1}.

COMPLEX	n	MEDIUM	MAXIMUM (cm^{-1}) (ε)
IPOXDHCu	0	mull	14,800
IPSUDHCu.H_2O	2	mull	∼15,700; ∼13,800
IPCLDHCu.H_2O	3	mull	∼17,000
		pyridine	15,100 (86.5); 13,000 (74.0) ∼10,600 (34.5) (?)
IPADDHCu.H_2O	4	mull	∼17,700
		chloroform	∼18,000 (108)
		pyridine	15,300 (75.1); 12,900 (64.0); ∼10,500 (30.2) (?)
IPADDHCu.py	4	mull	14,400; ∼11,500
		chloroform	∼17,700 (105)
		pyridine	15,300 (81.5); 13,000 (72.0); ∼10,200 (30.0) (?)
IPPMDHCu	5	mull	∼17,700
		chloroform	∼17,000 (107)
		pyridine	15,300 (71.1); 13,000 (63.6); ∼10,700 (32.0) (?)
IPPMDHCu.H_2O	5	mull	∼15,100
IPSRDHCu	6	mull	∼17,400
		chloroform	∼17,800 (107)
		pyridine	15,300 (68.9); 12,900 (62.7); ∼10,700 (32.9) (?)

(?) = presence of band uncertain.

FIGURE 7.8. Infrared spectra of: (A) IPADDH; (B) IPADDHCu.H_2O in the region 4,000 - 2,500 cm^{-1} (hexachlorobutadiene mulls).

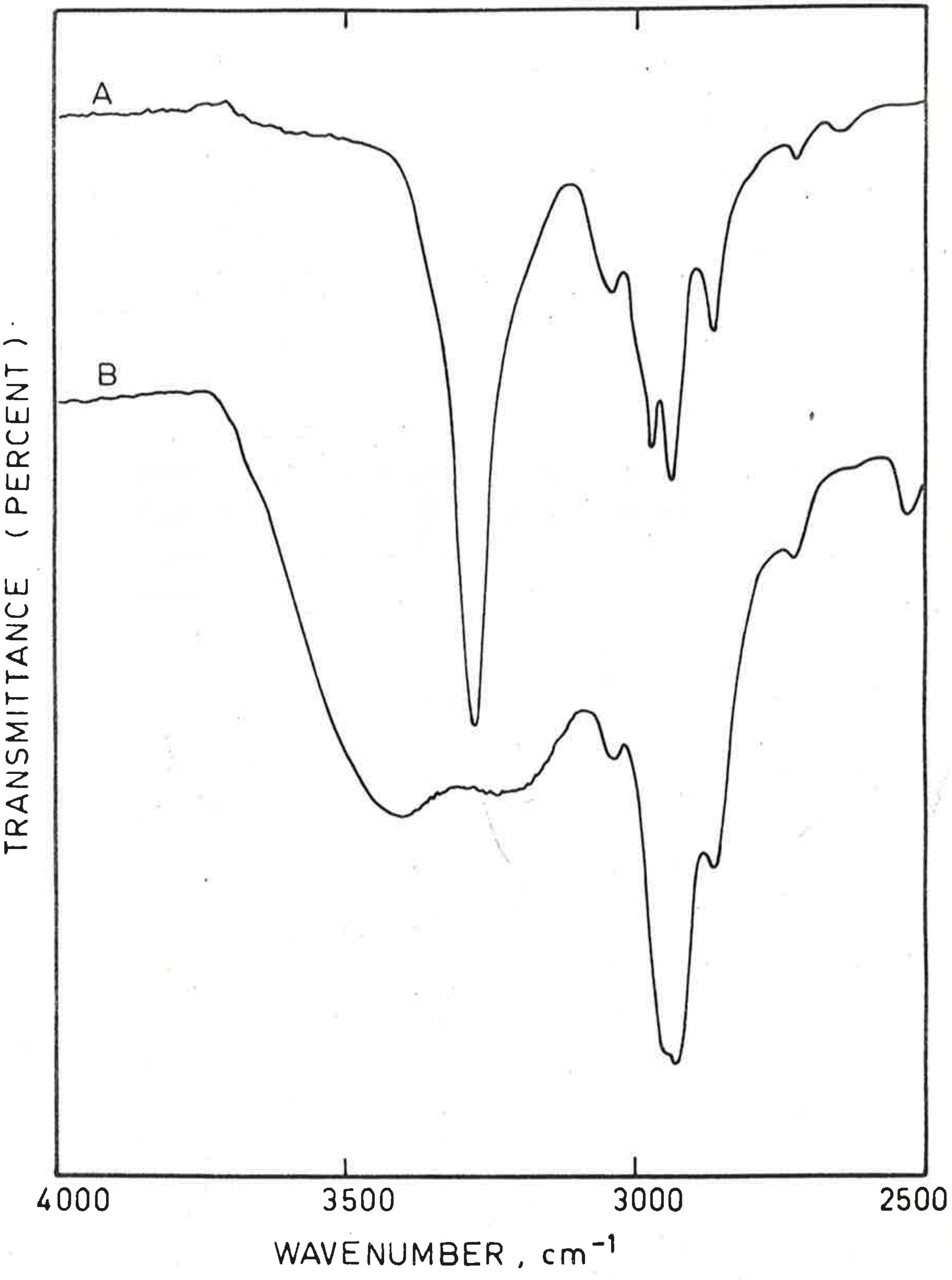
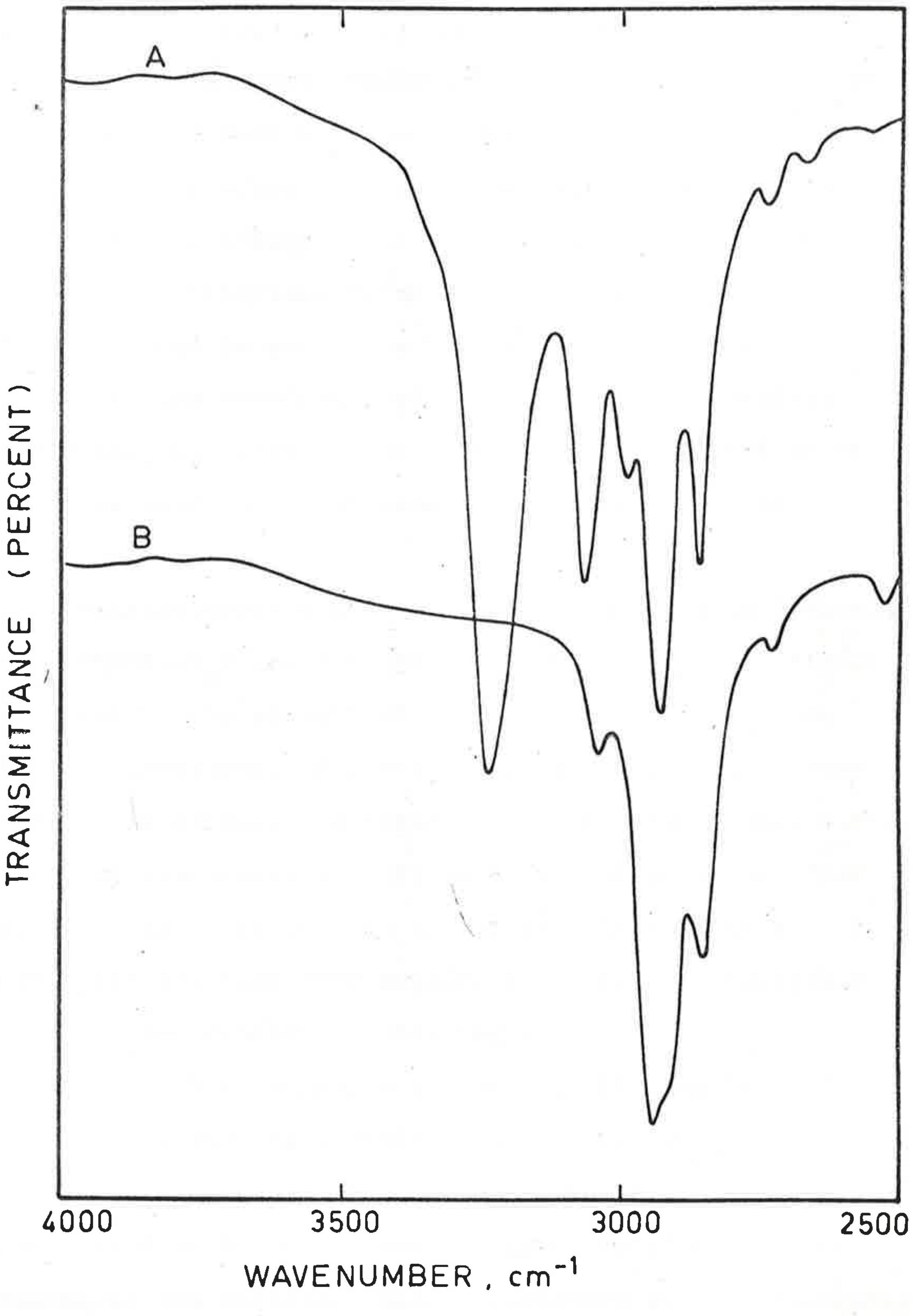

A
B
TRANSMITTANCE (PERCENT)
4000
3500
3000
2500
WAVENUMBER , cm^{-1}

FIGURE 7.9. Infrared spectra of: (A) IPSRDH; (B) IPSRDHCu in the region 4,000 - 2,500 cm^{-1} (hexachlorobutadiene mulls).


A
B
TRANSMITTANCE (PERCENT)
4000
3500
3000
2500
WAVENUMBER , cm^{-1}

contribution to the spectrum of the complex since the corresponding band in IPSRDH is observed to be absent in the anhydrous complex IPSRDHCu (figure 7.9). The 3280 cm^{-1} band in the ligands may accordingly be ascribed to the N-H stretching vibration, and its disappearance in the complexes is confirmatory evidence that the formation of the enol polymethylene-N,N-diisopropylidene-N',N'-diacyldihydrazino complexes occurs by a mechanism identical to that of the bis-(N-isopropylidene-N'-acylhydrazino) complexes, viz. loss of the hydrogen atom situated on the secondary amide nitrogen atom of both acylhydrazine groupings.

Possible arrangements of the ligand atoms in IPGLDHCu.H_2O and IPADDHCu.H_2O are summarised diagramatically in figure 7.10, and may be classified as monomeric, polymeric or dimeric structures. Since it is unlikely that the water molecule is apically coordinated in these complexes, either the third coordination position in the plane is occupied by water, or water is held in the crystal lattice at a sufficient distance form copper(II) to have a negligible effect on the d-orbital splittings.

The monomeric structures, (i) and (ii) of figure 7.10, must be considered unlikely. In (i), coordination of the nitrogen atom of the second hydrazide group would mean that a free $-O^-$ group would have to be present in the complex. Such a structure would undoubtedly

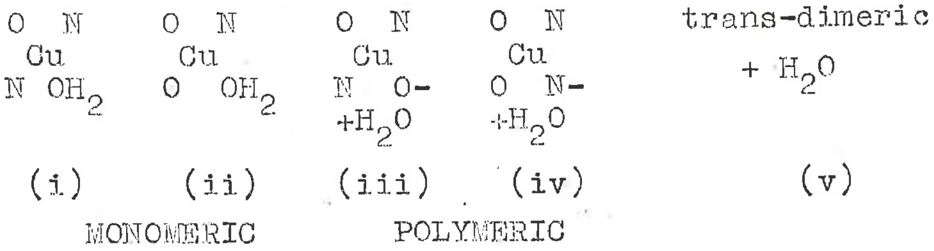


FIGURE 7.10. SCHEMATIC REPRESENTATION OF POSSIBLE COORDINATION MODES IN IPGLDHCu.H_2O and IPADDHCu.H_2O (c.f. FIGURE 1.1).

be unstable, any of the structures (ii) - (v) being more favourable.

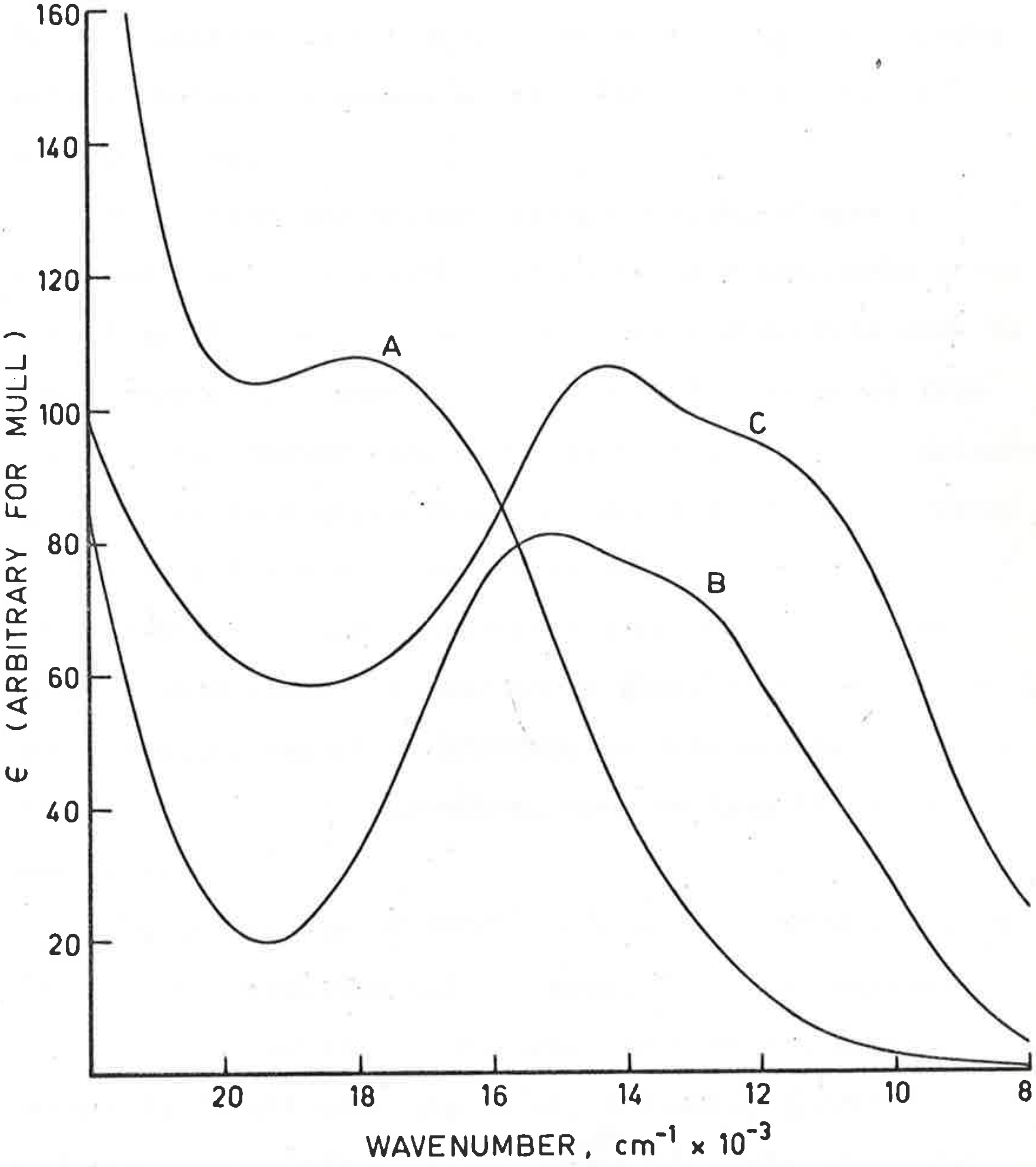
There exists the possibility of coordination of hydroxyl ion in the fourth position, accompanied by protonation of one hydrazide group and producing a free carbonyl group. Such a structure may explain the band position in the visible spectrum and also the presence of two bands (O-H and N-H stretching) in the infrared (figure 7.8). However, bands due to both of these groups are generally observed to be much sharper than is found here[6b] (c.f. spectrum of the ligand). Also, the formation of an apically coordinated monopyridinate (see below) is not accounted for, since this compound contains no water (or hydroxyl group).

Structure (ii) should show a considerable shift of the ligand field bands to lower energy in comparison with the trans bis- bidentate complexes, which is not observed. Structure (iv) is doubtful since the cis configuration should result in increased intensity of the visible bands,[3] which is also not observed in the spectra of these complexes to any significant extent. Thus the trans-polymeric (iii) or trans-dimeric structures are most probable.

On increasing the length of the methylene chain to n = 5 or 6, a cis-quadridentate structure for IPPMDHCu or IPSRDHCu becomes possible (Chapter 1). However, this structure must similarly be excluded on intensity grounds, and structures (iii) or (v) of figure 7.10 are also the most likely structures for these complexes.

The water molecule in IPADDHCu.H_2O can be replaced by pyridine by recrystallization of the complex from this solvent. Figure 7.11, curve C, shows the solid state spectrum of IPADDHCu.py, which is similar to the solution spectrum of this complex in pyridine (curve B). This would indicate apical coordination of pyridine in view of the large shifts observed relative to the monohydrate in chloroform solution (curve A), similar to the shifts observed on apical coordination of bases to the mono-acylhydrazine complexes (c.f. table 7.4). Apical coordination of pyridine in the solid monopyridinate would also lend support to the assignment of structures (iii) or (v) (figure 7.10) for the IPADDH complexes since it is probable that pyridine would replace the water in (i) and (ii), or the nitrogen of the bridging hydrazide group in (iv). Support for the proposed apical coordination of pyridine in IPADDHCu.py is given by the spectrum of this complex in chloroform solution, which is almost identical

FIGURE 7.11. Visible region spectrum of: (A) IPADDHCu.H_2O in chloroform; (B) IPADDHCu.pyridine in pyridine; (C) IPADDHCu.pyridine (Nujol mull).



to that of the monohydrate in this solvent (figure 7.11). Thus weak binding of the pyridine molecule is indicated. In addition, examination of other complexes containing tridentate molecules with pyridine coordinated in the fourth position (section 7.5) indicated that the spectra of such molecules behave as expected for a trans-N,O configuration.

Thus, from the present investigation, either a tridentate polymeric structure containing monomeric units linked by $-O^-$ groups or a trans dimeric structure must be considered most probable for the enol IP complexes from n = 3 to 6. Indeed, the solubility of all these complexes in pyridine (and chloroform from n = 4 to 6) may perhaps indicate that the dimeric structure is a more likely possibility, although a definite conclusion cannot be made on this basis. It should be possible to determine the molecular weight of IPSRDHCu as this complex is readily soluble in chloroform, more so than the other complexes.

The properties of IPOXDHCu (n = 0) and IPSUDHCu.H_2O (n = 2) are significantly different from the remainder of the complexes of this series. Both compounds were insoluble in all solvents tried, including pyridine. Neither complex was obtained in a high state of purity, but a 1:1 formulation is clearly indicated. These properties point to a polymeric structure for both complexes, which also show considerable differences to the higher members of the series in their visible spectra (figure 7.7).

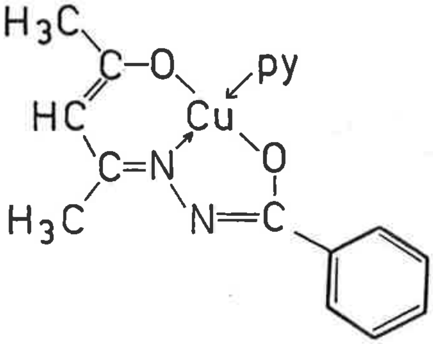
The spectrum of IPSUDHCu.H_2O (curve B) is strongly indicative of apically coordinated water. However the purity of the sample obtained is such that its formulation as a monohydrate is open to some doubt, consequently interpretation of the spectrum is uncertain. It is possible that this complex is polymeric with water molecules occupying apical positions of copper(II).

The anhydrous nature of IPOXDHCu is definitely indicated by the analytical figures. With a single broad band positioned at 14,800 cm^{-1} (figure 7.7, curve A), the ligand field in this complex is considerably less than in the other complexes of the series. Such an effect may result from a strained structure in which the coordinated atoms are twisted slightly out of plane.

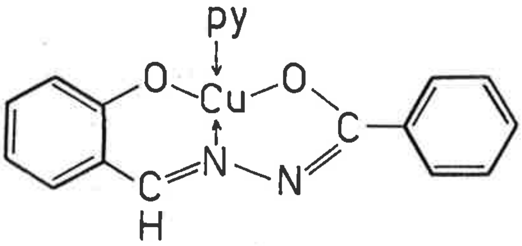
(7.5) COMPLEXES CONTAINING TRIDENTATE N-ACYLHYDRAZINE DERIVATIVES.

As discussed in the previous section, the visible spectrum of IPADDHCu.py suggests that the pyridine molecule in this complex is apically coordinated to copper(II). Since molecular models indicated that a tridentate type structure is possible for complexes of this ligand (Chapter 1), pyridine would be expected to coordinate in the fourth position of the plane. Even if polymeric structures were involved, solution in pyridine could possibly result in de-polymerisation with the formation of stable monomeric monopyridinates.

In order to ascertain the effect on the spectrum of pyridine coordinated in the fourth position of complexes containing tridentate ligands, the monopyridinate complexes of acetylacetonebenzoylhydrazone, ACACBH (XXVII) and salicylaldehydebenzoylhydrazone, SALBH (XXVIII) were examined. The preparation of (XXVIII)[7] and of the ammonia derivative of (XXVII)[8] have been previously reported.



(XXVII)



(XXVIII)

The solid state visible region spectra of these two complexes, together with the 2-methylpyridine derivative of (XXVII), are shown in figure 7.12. Band positions of the solution spectra are listed in table 7.8.

Included in table 7.8 and figure 7.12 is the spectrum of the complex formed by N-isopropylidene-N'-salicoylhydrazine, (IPSALH) a ligand which could possibly coordinate as a tridentate, but in doing so would be expected to form a strained structure. This complex will be discussed below.

FIGURE 7.12. Mull spectra of:

(A) ACACBHCu.pyridine;
(B) ACACBHCu.2-methylpyridine;
(C) SALBHCu.pyridine;
(D) ACACBHCu;
(E) $(TPSALH)_2Cu$.

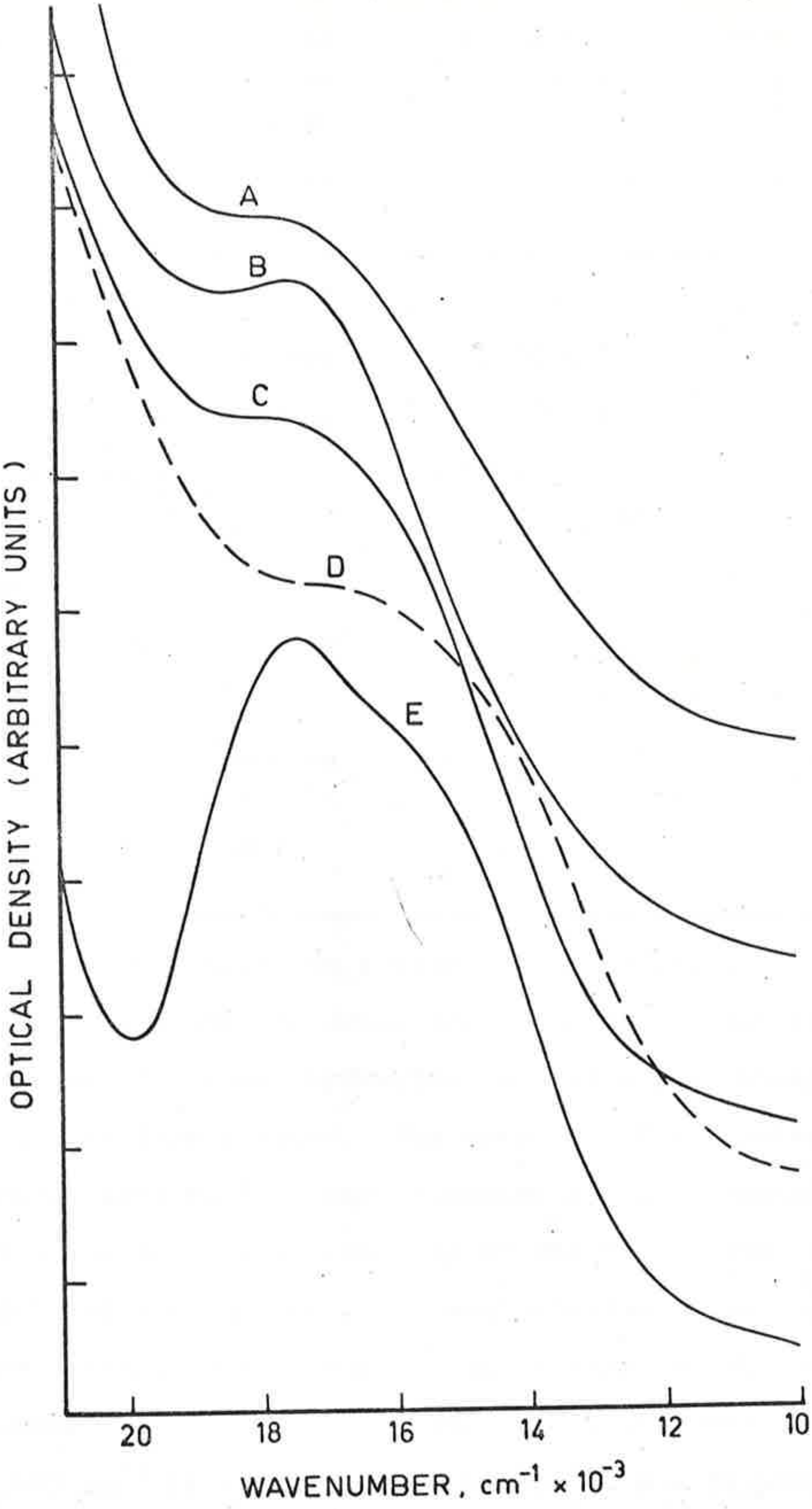

A
B
C
D
E
OPTICAL DENSITY (ARBITRARY UNITS)
20
18
16
14
12
10
WAVENUMBER, cm^{-1} × 10^{-3}

TABLE 7.8. ABSORPTION SPECTRA OF COPPER(II) COMPLEXES CONTAINING TRIDENTATE LIGANDS, IN THE REGION 22,000 - 6,000 cm^{-1}.

COMPLEX	MEDIUM	MAXIMUM (cm^{-1}) (ε)
ACACBHCupy	Mull	~17,500
	Benzene	17,700 (112)
	Pyridine	16,400 (102)
ACACBHCu2-me-py	Mull	~17,400
	2-me-py	17,000 (108)
SALBHCupy	Mull	~17,500
	Pyridine	15,700 (130)
$(IPSALH)_2Cu$	Mull	17,500; ~15,000
	Pyridine	~15,000 (835); ~13,000 (815) ~10,000 (42.4) (sh)
ACACBHCu	Mull	~16,000

It is clear that the spectra of ACACBHCupy, ACACBHCu2-me-py and SALBHCupy are markedly similar to the spectra of the acylhydrazine complexes previously discussed in this chapter. The presence of extensive conjugated systems in these molecules may be expected to result in near-perfect planarity of the fused five- and six-membered ring systems, and are undoubtedly responsible for the intense charge transfer bands observed at low wavenumbers (ACACBHCupy in benzene solution shows bands at 27,500 cm^{-1} (ε = 16,500); 26,600 cm^{-1} (ε = 16,900) and

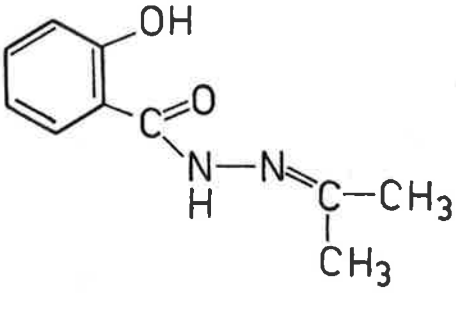
25,000 cm^{-1} (ε = 9,800)). Although bands in the region of 17,500 cm^{-1} are well resolved, it is again impossible to accurately determine the position and extinction due solely to the d-level transitions responsible for these bands.

However, because of their similarity to the spectra of the acylhydrazine complexes discussed in section 7.1, the spectra of the tridentate pyridine complexes must be considered typical of the enol trans-N,O grouping.

In pyridine solution, ACACBHCupy shows a shift of the 17,700 cm^{-1} band to lower energy (table 7.8), but no separation into two or more bands is evident. Thus it would appear that there is a tendency to form pyridinates in solution with molecules of the base coordinated in the apical positions. However, in view of the small shift observed either the apically coordinated pyridine has only a small effect on the spectrum, or else incomplete formation of the pyridinate, even in pure pyridine, is indicated. The latter explanation may be preferred, since rotation of the pyridine molecule in the plane may sterically affect the apical coordination of further molecules. The parent complex shows no tendency to add more than one molecule of pyridine as is evident by the fact that the well-formed crystals from a pyridine solution lost no weight on drying. This supports the idea that it is the reluctance to form adducts which is important, rather than small spectral effects of apically coordinated molecules.

Comparing the mull spectrum of SALBHCupy with the spectrum in pyridine solution (table 7.8), a larger shift was observed than is the the case with ACACBHCupy, although again no separation of the bands was noted. The apparent difference in the extinction coefficients of the two complexes at the respective maxima is probably due to the perturbing effect of the charge transfer bands, which is greater in the case of the salicylaldehyde complex. Similar observations have been noted by Belford and Yeranos.[3] Unfortunately SALBHCupy was found to be unstable in benzene solution, a fine precipitate being slowly deposited, hence the spectrum in this solvent could not be determined. This decomposition was probably due to dissociation of pyridine with formation of the dimeric molecue.[7] ACACBHCupy was found to be quite stable in benzene solution.

The importance of the ideal geometrical arrangement in enabling a ligand to function as a tridentate chelating agent is indicated by the behaviour of IPSALH (XXIX) on complex formation. It is apparent from the structure of



(XXIX)

this ligand that formation of a tridentate complex would involve considerable distortion from the ideal bond angles. Thus it is not surprising that a bis-complex, $(IPSALH)_2Cu$ is formed. That the ligand is only bidentate in this complex is also indicated by the formation of a solid bis-pyridine adduct, which shows the usual spectral effects of apically coordinated pyridine.

The visible region spectrum of $(IPSALH)_2Cu$ (figure 7.12) differs from that shown by bis-(N-isopropylidene-N'-acylhydrazino) complexes in that two distinct bands with maxima at 17,500 cm^{-1} and approximately 15,000 cm^{-1} are clearly indicated. This would suggest that coordination does not occur through the nitrogen and oxygen atoms constituting the acylhydrazine grouping. Of the remaining two ways in which the ligand can function as a bidentate chelating agent, coordination in a manner identical to that shown by salicylaldehyde is indicated by comparison with the spectrum of bis-(salicylaldehydato)copper(II). This complex shows maxima at 17,700 cm^{-1} and approximately 14,500 cm^{-1} in chloroform solution.[3] Unfortunately $(IPSALH)_2Cu$ was found to be insoluble in benzene or chloroform, hence it cannot be ascertained if the observed solid state spectrum persists in solution. Thus comparison with the spectrum of bis-(salicylaldehydato)copper(II) may not be conclusive, since axial coordination of ligand atoms in the solid state in a coordinated acylhydrazine type structure may produce a spectrum similar to that observed.

Although salicylaldehydebenzoylhydrazone readily loses two protons on complex formation in alkaline solution, there is evidence that the protonated ligand may also form complexes. Reaction with copper(II) chloride in cold ethanolic solution produced a mixture of green and red complexes. On boiling this mixture in ethanol, conversion to the red complex was effected. The formulation of this complex as SALBHCuCl.0.5H_2O was indicated by analysis, and it is evident that one proton is retained by the ligand. Presumably the proton which is lost comes from the phenolic-OH group, since the acylhydrazine grouping is capable of forming stable complexes when coordinated in the keto form. If the tridentate configuration of the ligand is maintained in this complex, it is probable that the fourth coordination position is occupied by the chloride ion.

Kubo et al.[7] have found that the pyridine molecule can be removed from SALBHCupy and that the magnetic moment falls from 1.82 B.M. in the pyridine complex to 1.08 B.M. in the "tridentate" complex. This complex belongs to a class of compounds which exhibit subnormal magnetic moments presumed to occur through spin interaction of the superexchange type (see section 4.8). and appears to be the result of a dimeric structure in which two copper(II) ions are bridged by ligand atoms. Such a structure has been verified for acetylacetonemono-(o-hydroxyanil)copper(II).[9]

ACACBHCu2-methylpyridine was observed to slowly lose weight on drying in vacuo at room temperature, the final product obtained corresponding to the formulation ACACBHCu. This complex would appear to belong to the above-mentioned class of complexes since the magnetic moment at room temperature (table 7.9) was found to be subnormal.

TABLE 7.9. MAGNETIC DATA FOR COMPLEXES CONTAINING TRIDENTATE LIGANDS.

COMPLEX	T(°A)	$10^6 \chi'_M$	μeff (B.M)
SALBHCupy	290.2	1399	1.81
ACACBHCupy	289.0	1380	1.79
ACACBHCu	289.0	441.5	1.01

The magnetic moment of SALBHCupy also determined here is in good agreement with the value reported by Kubo et al.[7] A similar value was observed for ACACBHCupy.

The slow loss of 2-methylpyridine from ACACBHCu2-methylpyridine is undoubtedly a manifestation of the hindrance to coordination of the nitrogen atom due to the presence of the 2-methyl group. However no significant difference in the visible spectrum of this complex compared to the corresponding pyridine complex was observed (figure 7.12). Although 2-methylpyridine is apparently more weakly bound than pyridine, any difference in ligand field effect is not detectable in these complexes. It is probable that steric hindrance will be reduced when the molecule is coordinated in the plane of the copper(II) ion compared to the effect on apical coordination, since in the former case the 2-methyl group should project over the plane of the rest of the molecule. In such a case, weaker binding may be associated with a loss of entropy of rotation of the molecule as a whole due to the restricting effects of adjacent ligand atoms.

The visible spectrum of ACACBHCu is shown in figure 7.12. Although similar to the pyridine and 2-methylpyridine derivatives, it appears that a broadening of the shoulder has occurred, caused by a shift in the maximum to lower energy. Such an effect is to be expected on replacement of a coordinated nitrogen atom by an enol oxygen, and is consistent with a dimeric structure containing oxygen bridges between the two copper(II) ions. Thus it is expected that each copper(II) ion will be effectively four-coordinated, the ligand field being that of one nitrogen and three oxygen atoms.

(7.6) GENERAL INTERPRETATION OF THE VISIBLE REGION SPECTRA OF N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE COPPER(II) COMPLEXES.

Before discussing possible assignments of bands in the visible region spectra of N-isopropylidene-N'-acylhydrazine copper(II) complexes, it is important to point out the presence of an absorption band centred at approximately 23,000 cm^{-1} and observed as a weak shoulder on the low energy side of the intense charge transfer band.

Heeding the warning of Jørgensen[10] that weak shoulders may sometimes erroneously appear to be present near the feet of perfect Gaussian curves, it is impossible to state with certainty that the solution spectra of all the N-isopropylidene-N'-acylhydrazino complexes do show the presence of this band. As can be seen from the spectrum of $(IPBH)_2Cu$ in benzene (figure 7.13, curve A) the inflexion at approximately 23,000 cm^{-1} is very weak, but the shoulder at this point is quite obvious in the solid state spectrum (curve B). In the dihydrazide series, IPSRDHCu shows similar absorption, but for the remainder of the complexes the presence of a shoulder in this region is uncertain.

Pyridination does not appear to alter the position of the shoulder (figure 7.13, curve C), although the intensity of absorption in the range 27,000 - 20,000 cm^{-1} is certainly decreased. In this matter $(IPBH)_2Cu$ behaves similarly to the bis-(acetylacetonato) complex;[3] accordingly the view of Belford et al.[3,11] that the 26,000 cm^{-1} band in $Cu(acac)_2$ is likely to be due to a spin-forbidden ligand transition may similarly apply to $(IPBH)_2Cu$.

As remarked earlier in this chapter, any attempt at

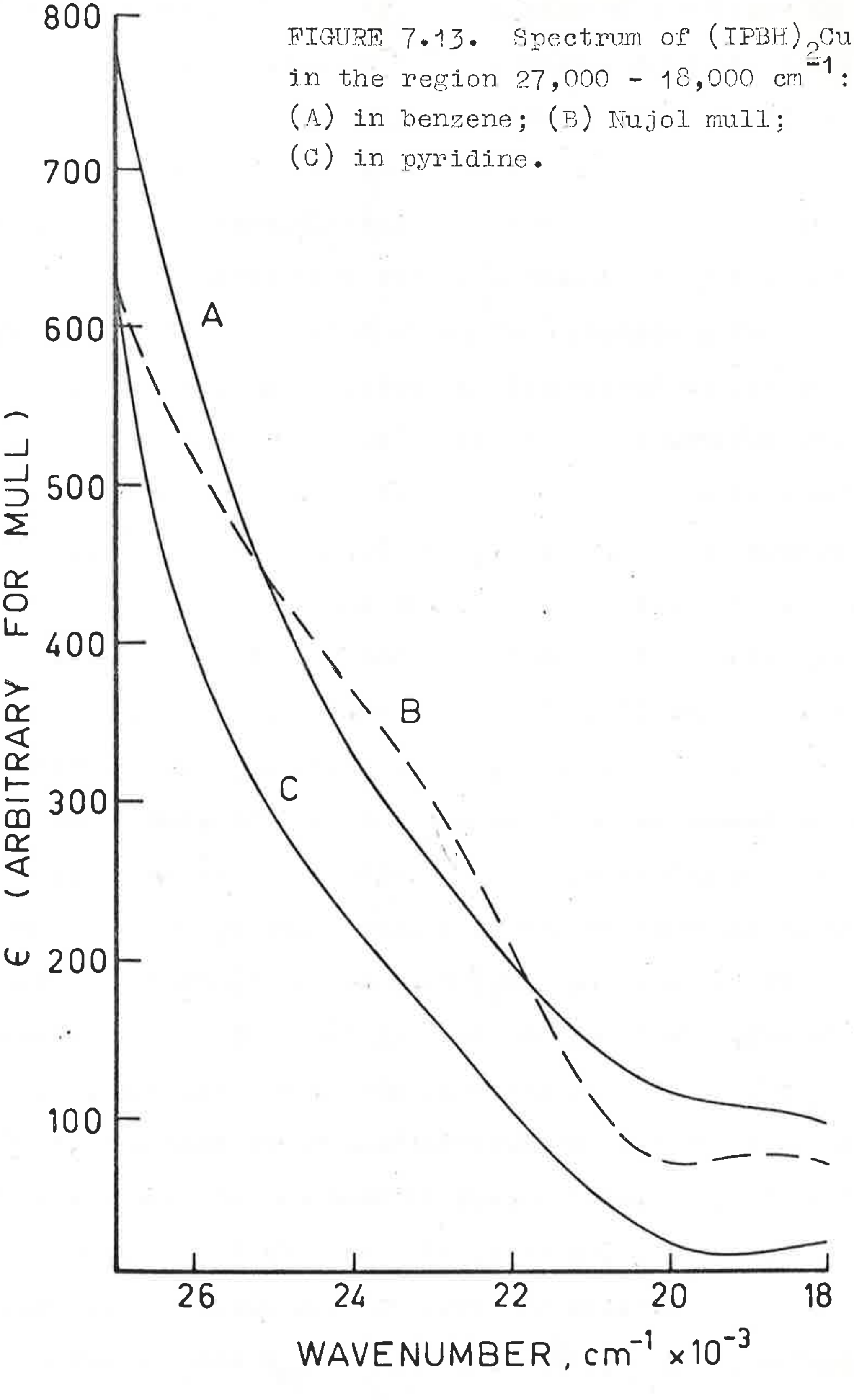


FIGURE 7.13. Spectrum of (IPBH)$_2$Cu in the region 27,000 - 18,000 cm^{-1}: (A) in benzene; (B) Nujol mull; (C) in pyridine.

band assignments for $(IPBH)_2Cu$ and related complexes in the region 20,000 - 10,000 cm^{-1} is hampered by the proximity of the charge transfer band, with its consequential perturbing effects on intensities and positions of the d-d bands. By extrapolation of the charge transfer band, an approximate resolution of the shoulder centred about 18,000 cm^{-1} may be carried out. This procedure for $(IPBH)_2Cu$ in benzene solution is illustrated in figure 7.14, and would indicate that the position of the maximum of the broad band due to the d-d transitions alone is about 16,800 cm^{-1} with an extinction between 60 and 70 $l.mole^{-1}cm^{-1}$. It is clear from the solid state spectrum (figure 7.1) that at least two transitions are contained in this envelope, while a third transition at 13,000 - 14,000 cm^{-1} of lower intensity could also possibly be present.

The effects of pyridination may then be described in terms of an energy level diagram similar to figure 4.3, where the $d_{xy} \rightarrow d_{z^2}$ hole transition may be ascribed to the 18,800 cm^{-1} band (in solid $(IPBH)_2Cu$) which moves to approximately 10,000 cm^{-1} in pyridine solution. Transitions to the degenerate (or nearly degenerate) pair d_{xz}, d_{yz} would be expected to be less affected by pyridination and may be ascribed to the band at approximately 16,000 cm^{-1} in the solid and 15,300 cm^{-1} in pyridine. The band at approximately 13,000 cm^{-1} in pyridine solution could then be ascribed to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. It is unfortunate

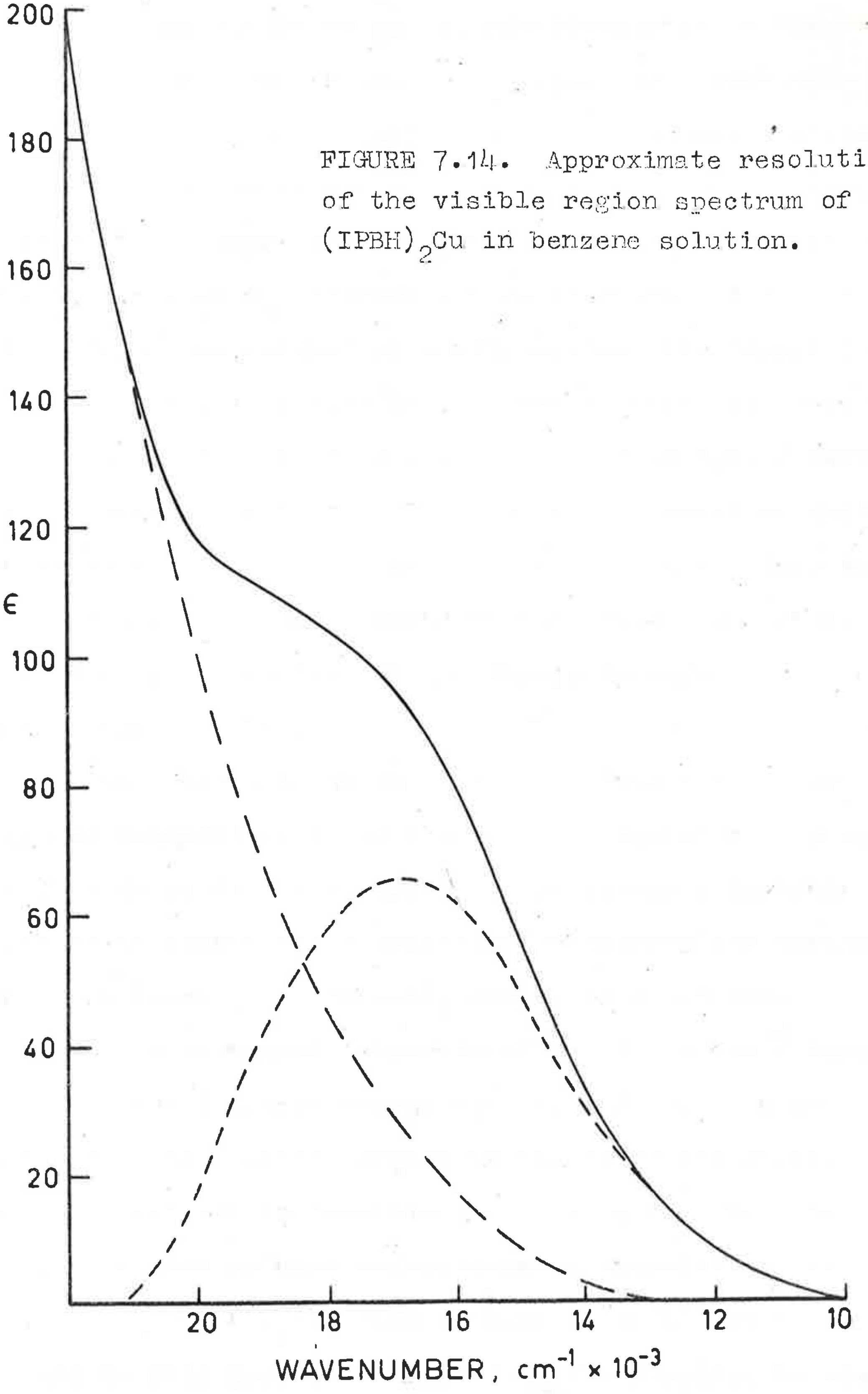


FIGURE 7.14. Approximate resolution of the visible region spectrum of $(IPBH)_2Cu$ in benzene solution.

that this band cannot be positively identified in the solid state or benzene solution spectrum of $(IPBH)_2Cu$. In these spectra it may indeed occur at higher energy since the shift on pyridination will be dependent on the manner in which the energy of the d_{xy} ground state is affected. If the energy of d_{xy} increases more than that of $d_{x^2-y^2}$ on tending to an octahedral configuration, the transition between these levels will be observed to shift to lower energy, although the shift will be less than that observed for the other transitions. The net effect would be that all transitions move to lower energy on pyridination. Such an effect may also be produced by the evident reduction in intensity of the tail of the charge transfer band in pyridine solution.

If the intensity of the broad envelope containing only d-d transitions is in the range indicated by figure 7.14, it is evident that pyridination causes a general increase in intensity as predicted by Belford and Yeranos[3] for the $Cu(acac)_2$ and $Cu(sal)_2$ series of complexes. Although the increased intensity of the 13,000 cm^{-1} band relative to the higher energy band of $(IPBH)_2Cu$ in 2-methylpyridine solution cannot be unambiguously explained (section 7.2), it is possible that this effect is caused by the coincidence or near coincidence of transitions from d_{xy} to $d_{x^2-y^2}$ and d_{z^2}, since no band at 10,000 cm^{-1} was evident in this spectrum. This is to be expected in view of the weaker coordinating properties of 2-methylpyridine (section 7.3) i.e. the d_{z^2} orbital should be less affected in this solvent than in pyridine or 4-methylpyridine.

(7.7) MAGNETIC PROPERTIES OF ENOL BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE) AND POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE COPPER(II) COMPLEXES

Table 7.10 lists magnetic data for the solid enol complexes of the isopropylidene derivatives of the mono-acylhydrazine and diacyldihydrazine series of ligands. Apart from IPOXDHCu, the magnetic moments of all complexes at room temperature were found to lie in the range normally observed for copper(II) complexes. In the monohydrazine series, apical coordination of water or heterocyclic bases produced no significant variation compared with the parent complexes.

For IPOXDHCu, the moment of 1.23 B.M. at room temperature is subnormal. Although direct interaction between pairs of copper(II) ions (as in the alkanoate type complexes) cannot be ruled out, it is possible that interaction of the superexchange type occurs between neighbouring ions via the π-electron system of the ligand. This type of interaction may indeed be expected if the complex has a linear polymeric structure as suggested by its insolubility and the geometry of the ligand.

TABLE 7.10. MAGNETIC DATA FOR ENOL BIS-(N-ISOPROPYLIDENE-N'-ACYLHYDRAZINO) AND POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINO COPPER(II) COMPLEXES.

COMPLEX	T($^{\circ}$A)	$10^6\chi'_M$	μeff. (B.M.)
(IPBH)$_2$Cu	293.6	1431	1.84
(IPAH)$_2$Cu	293.6	1437	1.85
(IPPH)$_2$Cu	290.9	1415	1.82
(IPBH)$_2$Cu.py$_2$	292.0	1485	1.87
(IPBH)$_2$Cu.4-me-py	292.0	1457	1.85
(IPBH)$_2$Cu.2-me-py	292.0	1517	1.89
(IPAH)$_2$Cu.H_2O	293.6	1490	1.88
(IPPH)$_2$Cu.H_2O	292.5	1467	1.86
IPOXDHCu	292.5	638	1.23
IPSUDHCu.H_2O	292.9	1554	1.92
IPGLDHCu.H_2O	292.6	1571	1.93
IPADDHCu.H_2O	292.8	1444	1.85
IPPMDHCu	292.6	1454	1.85
IPPMDHCu.H_2O	292.7	1488	1.87
IPSRDHCu	292.7	1439	1.84

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CHAPTER 8.

CONCLUSIONS

Ligands containing one N-acylhydrazine grouping were found to give rise to bis- cationic copper(II) complexes containing the ligands in the keto form, coordinated through the terminal amino group nitrogen atom and the keto carbonyl oxygen atom forming five-membered rings. This conclusion was based on the geometry of the ligand, the stoichiometry of the complexes, and the position which the ligand occupies in the spectrochemical series. Preparative indications that copper(II) can expand its coordination number to five (or possibly six) by the addition of water molecules or further molecules of ligand to the bis- complexes were confirmed by examination of their spectra in the visible and infrared regions. The visible spectra show shifts of the band maxima to lower wavenumbers, frequently accompanied by the appearance of a separate band on the infrared side of the main band. Such effects were seen to be analogous to the "pentammine" effect in the copper(II) ammonia system.

Preparations from N-benzoylhydrazine carried out in alkaline solution produced a neutral bis complex which could not be purified because of its insolubility. When condensed with acetone the ligands also gave rise to neutral complexes which were readily soluble in organic solvents. The visible spectra of these complexes showed pronounced shifts to lower energies in heterocyclic base solution, indicating coordination in the apical positions. Equilibrium constants determined spectrophotometrically for this process indicated that coordination of only one molecule of base was mainly responsible for the effect on the spectra; evidence was presented that coordination of a second molecule of base may also occur in solution and in the solid state. The equilibrium constants for the addition of pyridine and 4-methylpyridine showed variations to be expected from the presence of the electron-donating methyl group; in 2-methylpyridine a marked reduction of K was ascribed to steric hindrance to coordination by the methyl group in this position. Consistent differences in K between the benzoyl- and propionyl- complexes for the three heterocyclic bases may be associated with a reduction of the effective positive charge of copper(II) in the case of the latter complex.

It was ascertained that the polymethylene-N,N-diacyldihydrazine series of ligands similarly produced cationic keto and neutral enol complexes. While the higher members of the series (n greater than 2) generally formed complexes containing one molecule of the ligand and one copper(II) ion, oxalyldihydrazine (n = 0) and malonyldihydrazine (n = 1) showed a distinct difference in behaviour as would be expected from the geometry of these ligands. When reacted with copper(II) in neutral aqueous solution, spontaneous release of hydrogen ions occurred on the formation of complexes approximating to the composition $L_2Cu_3X_2.xH_2O$ ($X = Cl^-$, $\frac{1}{2}SO_4^{2-}$). These complexes would appear to be trinuclear, with the ligands coordinated in the enol form. When dissolved in acid, the oxalyldihydrazine complexes formed $OXDHCuX_2.0.5H_2O$, which could be polymeric, but coordination of anions or water molecules would appear likely, producing monomers.

Further differences in the behaviour of OXDH to the remainder of the ligands were evident in both the keto and enol diisopropylidene series of complexes. In the keto form, IPOXDH produced the complex $IPOXDHCu_2Cl_4.0.5H_2O$ in which the ligand is probably bis-bidentate, with chloride ions occupying the third and fourth coordination positions of the copper(II) ions. The enol complex IPOXDHCu was presumed to be polymeric; this was indicated by its insolubility and subnormal magnetic moment.

For the remainder of the series coordinated in the keto form, no distinct variations in the visible spectra were observed to indicate a change from tridentate to quadridentate configurations. From n = 2 to 6, $LCuSO_4.$-0.5(or 1)H_2O complexes were obtained for which a bis-bidentate dimeric structure containing apically coordinated water molecules must be considered likely. The anhydrous complexes (n = 7, 8, 10) probably contain both N-acylhydrazine groups coordinated to the one metal ion; this structure was indicated to be unstable by the preferential formation of $L_3Cu_2X_4$ complexes, isolated as the perchlorates.

All except two of the keto diisopropylidene complexes (n = 5, 6) of the type $LCuCl_2.0.5(or\ 1)H_2O$ showed, in addition to the main d-d band, a further band in the vicinity of 26,000 cm^{-1} presumed to result from apical coordination of chloride ions. The abundance of coordinating groups would make a polymeric structure seem unlikely for any of these complexes. It was suggested that the lower members (n = 1, 2) may contain the ligands coordinated by only one N-acylhydrazine grouping, or by three ligand atoms to form a tridentate structure (n = 3,4). Probably a quadridentate configuration occurs for the higher members (n = 5 - 8, 10). Evidence was found that acetone is readily hydrolysed from these complexes in aqueous solution.

The enol diisopropylidene complexes (n = 2 - 4) were isolated as the hydrates, $LCu.xH_2O$, which dried to the monohydrates. With the possible exception of the n = 2 complex, the water molecule would appear not to be coordinated in the apical positions. The pronounced similarity of the visible spectra of these complexes (and the anhydrous n = 5, 6 complexes) to the spectra of the bis-(N-isopropylidene-N'-acylhydrazino) complexes suggested that the ligand field was similar, i.e. a trans-N,O,N,O arrangement. A bis-bidentate dimeric structure, with the water molecule held in the crystal lattice, was suggested for these complexes. This was further indicated by the formation of an apically coordinated monopyridinate (n = 4) and monohydrate (n = 5) (as suggested by the spectra of these compounds). Coordination of pyridine in the plane of the copper(II) ion was seen to be unlikely in view of the normal trans-N,O,N,O spectra shown by complexes of tridentate ligands containing pyridine in the fourth position.

Finally, in evaluating the usefulness of visible region spectra as an indication of the stereochemistry of complexes formed by the diacyldihydrazine ligands, it must be remarked that the complexity of the systems is such that a definite assignment of configuration is not possible in many instances. The tendency of copper(II) to expand its coordination number to five or six is frequently a complicating factor which, however, may often be detected by the spectral changes.

CHAPTER 9

EXPERIMENTAL.

(9.1) PREPARATION OF LIGANDS.

MONOACYLHYDRAZINE LIGANDS.

N-acylhydrazines were prepared by refluxing the ethyl esters of the corresponding acids with hydrazine hydrate for several hours, followed by recrystallisation from ethanol or water. The compounds were characterised by their melting or boiling points:

N-benzoylhydrazine, M.P. 112° (from ethanol) (lit.[1] 112.5°)
N-acetylhydrazine, M.P. 66° (from ethanol) (lit.[2] 67°)
N-propionylhydrazine, B.P. 130°_{18mm} (lit.[3] 130°_{16mm})
N-salicoylhydrazine M.P. 146° (from water) (lit.[4] 146.5°)

N-isopropylidene-N'-acylhydrazines were prepared by recrystallization of the corresponding N-acylhydrazines from acetone.

N-isopropylidene-N'-benzoylhydrazine, M.P. 142° (lit.[5] 142°)
N-isopropylidene-N'-acetylhydrazine, M.P. 137° (lit.[2] 137°)
N-isopropylidene-N'-propionylhydrazine, M.P. 101° (lit.[3] 101°)
N-isopropylidene-N'-salicoylhydrazine, M.P. 242° (lit.[6] 243-244°)

DIACYLDIHYDRAZINE LIGANDS.

Polymethylene-N,N-diacyldihydrazines were prepared analogously to N-acylhydrazines[7] and recrystallized twice from water. The purity of these compounds was checked by hydrazine determination (table 9.1).

TABLE 9.1 ANALYSIS OF POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE LIGANDS.

n	LIGAND	FORMULA	$\%N_2H_4$ FOUND	$\%N_2H_4$ CALC.
0	OXDH	$C_2H_6N_4O_2$	54.4	54.3
1	MADH	$C_3H_8N_4O_2$	48.6	48.5
2	SUDH	$C_4H_{10}N_4O_2$	42.8*	43.8
3	GLDH	$C_5H_{12}N_4O_2$	39.7[7]	40.0
4	ADDH	$C_6H_{14}N_4O_2$	36.9	36.8
5	PMDH	$C_7H_{16}N_4O_2$	33.9	34.1
6	SRDH	$C_8H_{18}N_4O_2$	31.5	31.7
7	AZDH	$C_9H_{20}N_4O_2$	29.5	29.6
8	SBDH	$C_{10}H_{22}N_4O_2$	27.6	27.8
10	DDDH	$C_{12}H_{26}N_4O_2$	24.6	24.8

* Recrystallization each time yielded a small quantity of an insoluble compound which may be a cyclisation or polymerisation product.

The following isopropylidene derivatives were prepared for synthetic or infrared purposes by recrystallization of the parent compound from aqueous acetone:

N,N-diisopropylidene-N',N'-oxalyldihydrazine.

Found: N_2H_4, 32.2%; calculated for $C_8H_{14}N_4O_2$: 32.3%.

N,N-diisopropylidene-N',N'-adipoyldihydrazine.

Found: N_2H_4, 25.0%; calculated for $C_{12}H_{22}N_4O_2$: 25.2%.

N,N-diisopropylidene-N',N'-suberyldihydrazine.

Found: N_2H_4, 22.6%; calculated for $C_{14}H_{26}N_4O_2$: 22.7%.

N-salicylidene-N'-benzoylhydrazine was prepared by the reaction of equimolar quantities of salicylaldehyde and N-benzoylhydrazine in ethanol solution. The pale yellow solid was recrystallized from ethanol, M.P. 178° (lit.[8] 182°).

Attempted synthesis of dimethylmalonyldihydrazine.

Diethyl dimethylmalonate was prepared from the di-sodiomalonic ester and methyl iodide,[9] the fraction boiling 196-198° collected (lit[9] 196-196.5°$_{753mm}$).

Diethyl dimethylmalonate (62g) was refluxed with hydrazine hydrate (40g) in n-butanol (40 ml) for 24 hours. The excess solvent was removed by distillation under reduced pressure and the solid residue recrystallized from ethanol, (white prisms, M.P. 253°).

Although the required product has been reported to be obtained from the reaction of the ester with hydrazine hydrate in ethanol at 120°,[10] the above method of synthesis produced a compound analysing for 4,4-dimethyl-3,5-diketopyrazolidine.

Analysis: Found C, 47.2%; H, 6.25%; N, 21.9%; N_2H_4, 24.8%. Calculated for $C_5H_8N_2O_2$: C, 46.9%; H, 6.29%; N, 21.9%; N_2H_4, 25.0%.

The reaction of substituted malonic esters with hydrazines is a general method of preparation of substituted 3,5-diketopyrazolidines.[11,12] Although many derivatives have been reported, no mention of the melting-point of the 4,4-dimethyl-derivative could be found in the literature. The 4,4-diethyl-[13] and 4,4-dimethyl-2-phenyl-[14] compounds are known. Elderfield[12] reports that the 4,4-dimethyl-derivative shows chemiluminescence when oxidised by hydrogen peroxide but the reference given[15] was unobtainable. No mention of this compound is given in the abstract.

Attempted synthesis of diphenylmalonyldihydrazine.

Diethyl oxomalonate was prepared[16] and refluxed with benzene and concentrated sulphuric acid to obtain diethyl diphenylmalonate.[17] The crude ester was distilled under reduced pressure, the fraction boiling 190-220° at 16mm pressure collected (lit.[17] $180\text{-}200^{\circ}_{9mm}$).

Diethyl diphenylmalonate (40g) was refluxed with excess hydrazine hydrate (20g) for 24 hours. The mixture crystallized on cooling, was collected and recrystallized from water (white needles, M.P. 134°). The compound was found to be diphenylacetylhydrazine (lit.[18] M.P. 135°).

Analysis. Found: C, 74.5%; H, 6.39%; N, 12.3%; N_2H_4, 14.2%. Calculated for $C_{14}H_{14}N_2O$: C, 74.3%; H, 6.23%;

N, 12.4%; N_2H_4, 14.2%. The compound was further characterised by molecular weight determination (depression of freezing point of benzene): found, 216; calculated 226. Hydrolysis by refluxing with strong sodium hydroxide solution followed by acidification and recrystallization of the precipitate from dilute alcohol gave diphenylacetic acid, M.P. 145° (lit.[19] 146°).

(9.2) PURIFICATION OF SOLVENTS.

BENZENE. Thiophene-free benzene was prepared by extraction of A.R. grade solvent with sulphuric acid as recommended by Vogel.[20] After preliminary drying with calcium chloride and then sodium, the benzene was distilled (B.P. 80-81°) and stored over sodium wire.

CHLOROFORM. A.R. grade chloroform was extracted several times with water, dried for 24 hours over anhydrous calcium chloride and distilled with exclusion of moisture[20] (B.P. 61°) shortly before use. The purified solvent was kept under nitrogen in the dark to prevent photochemical decomposition.

ACETONE. A.R. grade acetone was distilled and used without further purification (B.P. 56°).

PYRIDINE. A.R. grade pyridine was refluxed over sodium hydroxide pellets and distilled with exclusion of moisture (B.P. 115°).

2-METHYLPYRIDINE. Fluka pure 2-methylpyridine was distilled with exclusion of moisture (B.P. 129 °).

4-METHYLPYRIDINE. Fluka pure 4-methylpyridine was distilled with exclusion of moisture (B.P. 145°).

(9.3) PHYSICAL MEASUREMENTS.

VISIBLE REGION SPECTRA. Absorption spectra in the range 30,000 - 6,000 cm^{-1} were measured using a Unicam S.P. 700 double-beam recording spectrophotometer. Solution spectra were recorded in matched silica cells. Solid state spectra were obtained by mulling the sample with Nujol and supporting the mull on filter-paper compressed between glass discs. A similar arrangement with Nujol impregnated filter-paper was used in the reference beam to equalise light scattering.[21]

The optical density scale of the instrument was checked with a standard potassium chromate solution in 0.05M KOH measured at 26,700 cm^{-1}. The calculated extinction coefficient showed a deviation of less than 1.6% from the reported value[22] in the 0 - 1.1 optical density range. The deviation was up to 2.6% on the seldomly used (for solution spectra) 0.9 - 2.0 scale. The plotted results showed no detectable variation form Beer's Law.

The wavenumber scale was calibrated using the hydrogen line at 15,237 cm^{-1} after each period of use.

INFRARED SPECTRA were obtained in Nujol and hexachlorobutadiene mulls using a Perkin-Elmer Model 21 instrument fitted with sodium chloride optics.

MAGNETIC MEASUREMENTS. Magnetic moments were determined at room temperature by the Gouy method. The apparatus consisted of a water-cooled Newport four-inch Type A electromagnet fitted with voltage stabilizer, placed beneath a Mettler H16 balance weighing to 0.01 mg. The field strength was controlled manually, a current of 8 amps being used for all measurements. This produced an increase in weight of 34.45 mg in a sample of 0.5936g of $H_gCo(CNS)_4$, the substance used for calibration.[23] Reproducibility of β was found to be within 0.5%. Diamagnetic corrections were calculated from Pascal's constants.[24]

Reproducibility of the calculated magnetic moment of the more crystalline samples was found to be within 1%. However, many of the complexes reported in this study were obtained as very fine powders which had poor packing properties. Some of these compounds showed variations of up to 4% in successive determinations.

FORMATION CONSTANT MEASUREMENTS. Formation constants for the addition of heterocyclic bases to bis-(N-isopropylidene-N'-benzoylhydrazine)copper(II) and bis-(N-isopropylidene-N'-propionylhydrazine)copper(II) in benzene solution were determined spectrophotometrically at room temperature. For $(IPPH)_2Cu$, stock solution were made up to give a final concentration of approximately 0.006M after dilution of 5ml aliquots to 25ml by the addition of the heterocyclic base and further benzene. The limited solubility of $(IPBH)_2Cu$ in benzene made it necessary to weigh out a quantity of the finely powdered substance sufficient to give a final solution of 0.005 - 0.006M. Concentrations of the heterocyclic bases were determined from the published density data[25] extrapolated to the pertinent temperature. Aliquots of benzene solutions of the bases were added to achieve the smaller final concentrations necessary in each series of determinations.

No significant deviation from Beer's Law was observed for either $(IPBH)_2Cu$ or $(IPPH)_2Cu$ in benzene, pyridine, 2-methylpyridine, and 4-methylpyridine solutions down to concentrations in the order of 6×10^{-4}M.

(9.4) ANALYSES.

HYDRAZINE was determined by titration with standard potassium bromate solution in perchloric acid medium, the endpoint being detected by extraction of free bromine into chloroform. With hydrochloric acid, the normally used medium,[26,27] the bromine colour was masked by the strong yellow colour of the $CuCl_4^{2-}$ anion when the complexes were titrated. Perchloric acid was previously found to give good results.[28] Isopropylidene complexes were warmed nearly to boiling with very dilute perchloric acid for a few minutes to expel acetone, which otherwise caused fading of the endpoint. This was done prior to the addition of an equal volume of 70% $HClO_4$, since boiling the sample in strong $HClO_4$ resulted in a low hydrazine figure.

Malonyldihydrazine was titrated with standard potassium iodate solution since bromination of malonic acid interferes with the bromate method.[7] Hydrazine in the complexes of this ligand could not be determined since copper(II) interferes with the iodate method.[28]

COPPER(II) was estimated iodometrically after removal of the organic material by oxidation with sulphuric and nitric acids.

CHLORIDE was determined as AgCl after the removal of hydrazine by oxidation with hydrogen peroxide in alkaline solution.

CARBON, HYDROGEN AND NITROGEN analyses were carried out by the Australian Microanalytical Service, Melbourne.

(9.5) DRYING OF COMPLEXES.

The complexes were dried to constant weight in vacuo over phosphorus pentoxide at room temperature, unless otherwise specified.

(9.6) KETO N-ACYLHYDRAZINE COMPLEXES.

The following complexes (i) - (viii) have been previously reported. Complexes (i) - (v) were prepared by reaction of the ligand and metal salt in the stoichiometric proportions in aqueous solution and allowing the solutions to crystallize. The composition of the complexes (iv) - (viii) has been previously established.[28]

(i) Bis-(N-benzoylhydrazine)copper(II) sulphate dihydrate[29,30]

The complex was obtained as fine blue needles which were air dried to constant weight.

Analysis. Found: N_2H_4, 13.6%; Cu, 13.8%. Calc. for $(C_7H_8N_2O)_2CuSO_4.2H_2O$: N_2H_4, 13.7%; Cu, 13.6%.

(ii) Bis-(N-benzoylhydrazine)copper(II) sulphate[7]

The dihydrate was ground and dried to constant weight in vacuo over P_2O_5.

Analysis. Found: N_2H_4, 14.8%; Cu, 14.6%. Calc. for $(C_7H_8N_2O)_2CuSO_4$: N_2H_4, 14.9%; Cu, 14.7%.

(iii) Bis-(N-acetylhydrazine)copper(II) sulphate[7]

The complex was obtained as blue plates.

Analysis. Found: N_2H_4, 20.6%; Cu, 20.5%. Calc. for $(C_2H_6N_2O)_2CuSO_4$: N_2H_4, 20.8%; Cu, 20.7%.

(iv) N-Benzoylhydrazinedichlorocopper(II)[28, 31]

The complex crystallised as well formed blue needles from strong hydrochloric acid solution.[28]

(v) Bis-(N-benzoylhydrazine)copper(II) dichloride[28]

The tetrahydrate crystallized in blue plates which effloresced on drying to the pale blue anhydrous complex. The addition of dilute sodium chloride solution was found to aid crystallisation. The preparation must be carried out in ice cold solution to prevent partial reduction of copper(II).

(vi) Bis-(N-benzoylhydrazine)copper(II) trichlorocopper(I)[28]

The dark green (almost black) complex was obtained from hot ethanolic solutions containing BH and $CuCl_2.2H_2O$ in a 2:1 molar ratio.

(vii) Bis-(N-benzoylhydrazine)copper(II) dichloride tri(copper(I chloride)[28]

Green needles were obtained from hot aqueous solutions containing BH and $CuCl_2.2H_2O$ in a 1:2 molar ratio.

(viii) Bis-(N-acetylhydrazine)copper(II) trichlorocopper(I)[28]

Bright green plates were obtained from the reaction of AH and $CuCl_2.2H_2O$ in a 2:1 molar ratio in hot ethanol.

(ix) Tris-(N-benzoylhydrazine)copper(II) dichloride.

$CuCl_2.2H_2O$ (0.85g.) was dissolved in water (5ml), cooled in ice, and added to a solution of BH (2.04g.) in water (10ml), cooled to just before the point of crystallization. The solution was placed in the refrigerator and the first crop of pale blue-green prisms collected, air dried, ground up and washed with ether. The complex became pale green in colour on drying.

Analysis. Found: C,46.4%; H, 4.51%; N, 14.9%; N_2H_4, 17.4%; Cu, 11.8% Calc. for $(C_7H_8N_2O)_3CuCl_2$: C, 46.4%; H, 4.45%; N, 15.5%; N_2H_4, 17.7%; Cu, 11.7%.

(x) Tetrakis-(N-benzoylhydrazine)copper(II) dichloride.

$CuCl_2.2H_2O$ (0.85g.) was dissolved in water (10ml), cooled in ice, and added to a solution of BH (2.72g.) in water (20 ml). The solution was cooled in the refrigerator overnight and the pale blue crystals collected, air dried, ground, washed with ether, and dried.

Analysis. Found: C, 49.1%; H, 4.68%; N, 16.2%; N_2H_4, 18.7%; Cu, 9.55%. Calc. for $(C_7H_8N_2O)_4CuCl_2$: C, 49.5%; H, 4.74%; N, 16.5%; N_2H_4, 18.9%; Cu, 9.36%.

(xi) Bis-(N-benzoylhydrazine)copper(II) perchlorate

$Cu(ClO_4)_2.6H_2O$ (3.71g) in water (10ml) was added to a warm solution of BH (2.72g) in water (25ml). The deep blue solution crystallized on standing in blue plates. The complex was collected, washed with water and dried.

Analysis. The complex explodes violently on heating, hence C and H analyses could not be determined. Found: N, 10.7%; N_2H_4 12.0%; Cu, 11.9%. Calculated for $(C_7H_8N_2O)_2Cu(ClO_4)_2$: N, 10.5%; N_2H_4, 12.0%; Cu, 11.9%. The complex appeared to be stable to mulling techniques but detonated violently on vigorous percussion. Preparation on a much smaller scale than that used here and extreme caution in handling is therefore recommended.

(xii) Tris-(N-benzoylhydrazine)copper(II) perchlorate.

$Cu(ClO_4)_2.6H_2O$ (1.85g) in water (5ml) was added to a warm solution of benzoylhydrazine (2.72g) in water (10ml). A large quantity of dark green oil was deposited. The mixture was cooled to room temperature and the supernatant decanted from the oil and filtered. The blue filtrate was scratched to initiate crystallization and after standing for 15 minutes with occasional shaking the small pale blue-green crystals were collected, washed once with a small volume of cold water, and dried.

Analysis. Found: C, 37.7%; H, 3.73%; N, 12.1%; N_2H_4, 14.3%; Cu, 9.33%. Calc. for $(C_7H_8N_2O)_3Cu(ClO_4)_2$: C, 37.6%; H, 3.61%; N, 12.5%; N_2H_4, 14.3%; Cu, 9.47%.

(xiii) Attempted preparation of tetrakis-(N-benzoylhydrazine)-copper(II) perchlorate.

The dark green oil produced in the preparation of $(BH)_3Cu(ClO_4)_2$ was dissolved in methanol and precipitated by the addition of ether. On redissolving in methanol, filtering and evaporating to dryness under vacuum the oil solidified when the solvent was removed. Analysis showed the sample to be impure. (Found: Cu, 8.19%. Calc. for $(C_7H_8N_2O)_4Cu(ClO_4)_2$: Cu, 7.87%).

The above sample was redissolved in dry ethanol, filtered, and dry ether added. An oil was precipitated at first but solidified, the pale green solid was collected and washed with ether. Analysis indicated the compound to be impure $(BH)_3Cu(ClO_4)_2$. (Found: N_2H_4, 13.6%. Calc.: N_2H_4, 14.3%).

In a subsequent preparation the oil was taken up in methanol, precipitated with ether and washed twice with small volumes of water. On removing the remaining water under reduced pressure on a warm waterbath the oil solidified, was ground up and washed repeatedly with dry ether. Evaporation of the filtrates yielded appreciable quantities of benzoylhydrazine.

Analysis. Found: N_2H_4, 15.3%. Calculated for $(C_7H_8N_2O)_4Cu(ClO_4)_2$: N_2H_4, 15.9%.

(xiv). Bis-(N-propionylhydrazine)copper(II) sulphate hemihydrate.

$CuSo_4.5H_2O$ (2.50g) was dissolved in water (10ml) and added to a solution of isopropylidenepropionylhydrazine (2.56g) in water (10ml). Methanol was added until the deep blue solution began to crystallize. The complex was filtered off and recrystallized twice by dissolving in water (5ml) and adding methanol dropwise until crystallization commenced. The blue plates were collected, washed with methanol and dried.

Analysis. Found: C, 20.8%; H, 5.2%; N, 15.8%; N_2H_4, 18.8%; Cu, 18.6%. Calc. for $(C_3H_8N_2O)_2CuSO_4.0.5H_2O$: C, 20.9%; H, 4.7%; N, 16.3%; N_2H_4, 18.6%; Cu, 18.4%.

A further reprecipitation gave an identical hydrazine figure.

(9.7) ENOL COMPLEXES OF OXALYL- AND MALONYLDIHYDRAZINES.

(i) Di-μ-(oxalyldihydrazine)tricopper(II) monosulphate pentahydrate.

(a) $CuSO_4.5H_2O$ (2.50g) in water (50ml) was added slowly to oxalic acid dihydrazide (1.18g) in warm water (150ml) with mechanical stirring. The pale blue precipitate was collected by centrifugation and washed three times by centrifugation. The complex was collected on a sinter and sucked as dry as possible. After a preliminary drying for 24 hours in vacuo over $CaCl_2$, the complex was crushed and dried in vacuo over P_2O_5. The complex continued to lose weight over several weeks and had not reached constant weight when analysed, although the daily weight loss was very small.

Analysis. Found: C, 8.44%; H, 3.22%; N, 18.05%, S, 5.58%; N_2H_4, 21.0%; Cu, 31.5%. Calculated for $(C_2H_4N_4O_2)_2Cu_3SO_4.5H_2O$, C, 7.89%; H, 2.98%; N, 18.4%; S, 5.26%; N_2H_4, 21.1%; Cu, 31.3%.

(b) $CuSO_4.5H_2O$ (2.50g) and sodium acetate monohydrate (3.0g) were dissolved in water (50ml) and added slowly to oxalic acid dihydrazide (2.36g) in water (150ml) at 70° with mechanical stirring. The precipitate was treated as in (a). Constant weight was not achieved after drying in vacuo over P_2O_5 for five months.

Analysis. Found: N_2H_4, 21.4%; Cu, 34.2%.

After drying for two months, a sample was removed and dried for 7 days in vacuo over P_2O_5 at 110°. Constant weight was not achieved. Analysis indicated decomposition had occurred.

Analysis. Found: N_2H_4, 15.7%; Cu, 38.3%.

(ii) Reaction of $(OXDH)_2Cu_3SO_4.nH_2O$ with glycine.

The hydrated complex was prepared as in (i)a. After washing and centrifuging, the residue was dissolved with warming in a solution of glycine (10g) in water (60ml). The deep blue solution was filtered while hot and on cooling a blue-green precipitate was deposited. This was collected, washed well with water and ethanol and dried in vacuo over P_2O_5. Constant weight was not achieved after drying for one month.

Analysis. Found: C, 9.72%; H, 3.12%; N, 19.0%; N_2H_4, 22.1%; Cu, 34.1%; corresponding to the ratio - C : H : N : N_2H_4 : Cu = 6 : 23 : 10 : 5 : 4 based on both the C and Cu percentages. This is not in agreement with the stoichiometry of $(C_2H_4N_4O_2)_2Cu_3SO_4.nH_2O$ however the ratio N : N_2H_4 = 2 : 1 indicates that the compound contained no glycine.

(iii) Attempted preparation of Dipotassium bis-(oxalyldihydrazine)copper(II).

Oxalic acid dihydrazide (1.18g) was dissolved in water

(5ml) by the dropwise addition of concentrated KOH solution. $CuSO_4.5H_2O$ (1.25g) in water (5ml) was added producing a deep green solution. On the addition of excess KOH solution a brown-green precipitate was produced and collected by centrifugation. The residue was dissolved in water and reprecipitated with ethanol, collected by centrifugation and the reprecipitation process repeated.

Analysis. The ratio N_2H_4 : Cu was determined by dissolving the precipitate in dilute H_2SO_4 and withdrawing aliquots for analysis. Found: N_2H_4 : Cu = 3.27 : 1, calculated for $K_2(C_2H_4N_4O_2)_2Cu$, N_2H_4 : Cu = 4.00 : 1.

A solution of the complex in water appears to decompose slowly with the evolution of nitrogen. This may account for the low ratio observed.

(iv) Reaction of $K_2(OXDH)_2Cu$ with copper(II) sulphate.

Portion of the precipitate of $K_2(OXDH)_2Cu$ prepared in (iii) was dissolved in water (20ml) and excess $CuSO_4.5H_2O$ solution added slowly with mechanical stirring. After stirring for 30 minutes, the green precipitate formed was centrifuged and washed three times with water.

Analysis. The ratio N_2H_4 : Cu was determined as above. Found: N_2H_4 : Cu = 1.05 : 1.

(v) Reaction of $K_2(OXDH)_2Cu$ with sulphuric acid.

$K_2(OXDH)_2Cu$ solution was prepared as in (iii) but the complex was not precipitated. The solution was filtered and dilute H_2SO_4 added dropwise with mechanical stirring until the pH dropped to 6.4. The green precipitate formed was collected and washed by centrifugation.

Analysis. The ratio N_2H_4 : Cu was found to be 1.72 : 1.

(vi) Di-μ-(oxalyldihydrazine)tricopper(II) dichloride (hydrated).

OXDH (0.600g) was dissolved in water (150ml). Three solutions, each containing $CuCl_2.2H_2O$ (0.433g) in water (20ml) (i.e. OXDH : Cu = 1 : 0.5) were prepared and added dropwise to the OXDH solution with mechanical stirring. After addition of the first 0.5 equivalent the blue solution contained no precipitate. A further 0.5 equivalent produced a slight precipitate, and complete precipitation occurred during addition of the third 0.5 equivalent. The blue precipitate was collected and washed by centrifugation, then dissolved in water with the dropwise addition of dilute sulphuric acid. The ratio N_2H_4 : Cu : Cl was determined on aliquots of this solution (chloride was determined by potentiometric titration with standard $AgNO_3$ solution).

Found: N_2H_4 : Cu : Cl = 4.02 : 3 : 1.98.
Calculated for $(OXDH)_2Cu_3Cl_2.nH_2O$: N_2H_4 : Cu : Cl = 4.00 : 3.00 : 2.00.

The pH of the solution was observed to fall from 5.85 to 1.81 during the preparation.

(vii) Reaction of Malonyldihydrazine with copper(II) sulphate in Sodium Acetate Solution.

$CuSO_4.5H_2O$ (2.50g) and sodium acetate monohydrate (3.0g) were dissolved in water (40ml) and added dropwise to a solution of MADH (1.32g) in water (100ml) with mechanical stirring. The blue precipitate formed was collected and washed three times with water by centrifugation then transferred to a sintered filter and washed with ethanol. After a preliminary drying over $CaCl_2$ the complex was ground and dried in vacuo over P_2O_5. Constant weight was not achieved after drying for twelve weeks.

Analysis. Found: C, 14.3%; H, 2.75%; N, 15.9%; S, 5.99%; Cu, 32.6% corresponding to the ratio C : N : S : Cu = 7.0 : 6.7 : 1.1 : 3.0. Calculated ratio for $(C_3H_6N_4O_2)_2Cu_3SO_4$: C : N : S : Cu = 6.00 : 8.00 : 1.00 : 3.00.

The poor analysis can only be taken as an indication that the above complex is probably the major constituent of the sample.

(9.8) KETO POLYMETHYLENE-N,N-DIACYLDIHYDRAZINE COMPLEXES.

(i) Oxalyldihydrazinecopper(II) sulphate hemihydrate.

Hydrated $(OXDH)_2Cu_3SO_4$ was prepared as in 9.7 (i)(b). After washing twice with water, the precipitate was dissolved in water (15ml) with the dropwise addition of 10% H_2SO_4. The solution was filtered and began to crystallize immediately. After standing for one hour with occasional shaking, the fine blue-green crystals were collected, washed with a small volume of 1M H_2SO_4, then with ethanol, and dried.

Analysis. Found: C, 8.39%; H, 2.66%; N, 19.0%; S, 11.0%; N_2H_4, 22.0% Cu, 22.3%. Calculated for $C_2H_6N_4O_2CuSO_4.0.5H_2O$: C, 8.38%; H, 2.46%; N, 19.5%; S, 11.2%; N_2H_4, 22.4%; Cu, 22.2%.

(ii) Oxalyldihydrazinecopper(II) chloride hemihydrate.

$(OXDH)_2Cu_3Cl_2.nH_2O$ was prepared as in 9.7(vi). After washing once with water and centrifuging, the damp residue was dissolved by the dropwise addition of 5M HCl and the solution rapidly filtered through a fine sinter. The complex began to crystallize immediately. After standing for one hour, the fine blue crystals were collected and washed with a small volume of 1M HCl then with ethanol, and dried.

Analysis. Found: C, 9.59%; H, 2.70%; N, 21.5%; N_2H_4, 24.7%; Cu, 24.6%; Cl, 28.0%. Calculated for $C_2H_6N_4O_2CuCl_2.0.5H_2O$: C, 9.18%; H, 2.70%; N, 21.4%; N_2H_4, 24.5%; Cu, 24.3%; Cl, 27.1%.

(iii) Tetra-μ-(malonyldihydrazine)pentacopper(II) trisulphate.

The precipitate freshly prepared as in 9.7(vii) was slurried with water (10ml) and 10% H_2SO_4 added dropwise until the formation of a dark blue oil was complete. The oil was transferred to a beaker containing methanol and solidified on stirring. The dark blue powder was collected, washed with methanol and dried, when the colour changed to dark green. Constant weight was achieved after drying for four weeks.

Analysis. Found: C, 12.5%, H, 2.81%; N, 18.3%; S, 8.48%; Cu, 28.3%. Calculated for $(C_3H_7N_4O_2)_4Cu_5(SO_4)_3$: C, 12.7%; H, 2.49%; N, 19.7%; S, 8.47%; Cu, 28.0%.

The complex appears to be anhydrous, which may indicate that sulphate is coordinated to the terminal copper(II) ions. Alternatively, the presence of up to four water molecules may be expected. The analyses would then indicate the presence of some impurity, which is not surprising considering the probable nature of the compound.

(iv) Succinyldihydrazinecopper(II) sulphate hemihydrate.

$CuSO_4.5H_2O$ (2.50g) in water (10ml) was added to SUDH (1.46g) in water (10ml). The deep blue solution was filtered and crystallized on seeding.

Analysis. Found: C, 15.5%; H, 3.49%; N, 17.9%; N_2H_4, 20.4%; Cu, 20.1%. Calculated for $C_4H_{10}N_4O_2CuSO_4.0.5H_2O$: C, 15.3%; H, 3.52%; N, 17.8%; N_2H_4 20.4%; Cu, 20.2%.

(v) Glutaryldihydrazinecopper(II) sulphate monohydrate.

$CuSO_4.5H_2O$ (1.25g) in water (10ml) was added to GLDH (0.80g) in water (25ml). The deep blue solution crystallized in fine needles which were collected, washed with water and dried.

Analysis. Found: C, 17.9%; H, 4.67%; N, 16.9%; N_2H_4, 19.2%; Cu, 19.0%. Calculated for $C_5H_{12}N_4O_2CuSO_4.H_2O$: C, 17.8%; H, 4.18%; N, 16.6%; N_2H_4, 19.0%; Cu, 18.8%.

(vi) Adipoyldihydrazinecopper(II) sulphate hemihydrate.

$CuSO_4.5H_2O$ (5.00g) in water (15ml) was added to a warm solution of ADDH (3.48g) in water (25ml). On cooling, the complex crystallized and was recrystallized from water. The deep blue crystals effloresced to a pale blue powder on drying.

Analysis. Found: C, 20.8%; H, 4.92%; N, 15.8%; N_2H_4, 18.6%; Cu, 18.6%. Calculated for $C_6H_{14}N_4O_2CuSO_4.0.5H_2O$: C, 21.0%; H, 4.41%; N, 16.4%; N_2H_4, 18.7%; Cu, 18.6%.

Loss of weight on drying: Found: H_2O, 17.6%. Calculated loss for $4H_2O$: 17.4%, thus the complex crystallized as the 4.5 hydrate.

(vii) Adipoyldihydrazinecopper(II) chloride hemihydrate.

$CuCl_2.2H_2O$ (1.70g) and NaCl (0.5g) were dissolved together in water (10ml) and the solution cooled in ice then added to ADDH (1.74g) in water (20ml) cooled to 10°. The deep blue solution was cooled in ice and seeded. The crystals were collected, washed with a small volume of cold water and dried.

Analysis. Found: C, 22.9%; H, 4.68%; N, 17.7%; N_2H_4, 20.7%; Cu, 20.3%. Calculated for $C_6H_{14}N_4O_2CuCl_2.0.5H_2O$:

C, 22.7%; H, 4.52%; N, 17.6%; N_2H_4, 20.2%; Cu, 20.0%.

(viii) Adipoyldihydrazinecopper(II) trichlorocopper(I) monohydrate.

$CuCl_2.2H_2O$ (3.40g) in water (10ml) and ADDH (1.74g) in water (20ml) were heated and mixed. A vigorous evolution of gas occurred. The dark green solution was heated to boiling and allowed to cool, when dark green crystals were deposited. These were collected, washed with water and ethanol then dried.

Analysis. Found: C, 16.8%; H, 3.82%; N, 12.4%; Cl, 25.0%; Cu, 29.8%. Calculated for $C_6H_{14}N_4O_2Cu_2Cl_3.H_2O$: C, 16.9%; H, 3.79%; N, 13.2%; Cl, 25.0%; Cu, 29.9%.

(ix) Attempted preparation of adipoyldihydrazinecopper(II) perchlorate.

$Cu(ClO_4)_2.6H_2O$ (3.71g) was dissolved in water (10ml) and ADDH (1.74g) added and dissolved with gentle warming. The deep blue solution was filtered and placed in the refrigerator. On seeding, the complex slowly crystallized.

The complex detonated violently on being crushed in preparation for drying. Further examination of this complex is not recommended.

(x) Pimeloyldihydrazinecopper(II) sulphate hemihydrate.

$CuSO_4.5H_2O$ (1.25g) in water (10ml) was added to PMDH (0.94g) in water (20ml). The solution began to crystallize immediately. The fine blue needles were collected, washed with water and dried.

Analysis. Found: C,23.5%; H, 4.68%; N, 15.7%; N_2H_4, 18.1%; Cu, 17.8%. Calculated for $C_7H_{16}N_4O_2CuSO_4.0.5H_2O$: C, 23.6%; H, 4.80%; N, 15.7%; N_2H_4, 18.0%; Cu, 17.8%.

(xi) Suberoyldihydrazinecopper(II) sulphate hemihydrate.

$CuSO_4.5H_2O$ (2.50g) in warm water (10ml) was added to a warm solution of SRDH (2.02g) in water (35ml). The complex crystallized in fine blue needles on cooling overnight in the refrigerator, was collected and washed with water.

Analysis. Found: C,26.3%; H, 5.08%; N, 15.2%; N_2H_4, 17.5%; Cu, 17.1%. Calculated for $C_8H_{18}N_4O_2CuSO_4.0.5H_2O$: C, 25.9%; H, 5.05%; N, 15.1%; N_2H_4, 17.3%; Cu, 17.1%.

(xii) Pimeloyldihydrazinecopper(II) perchlorate (?) and suberoyldihydrazinecopper(II) perchlorate (?).

These complexes were obtained as fine blue needles from 1:1 molar ratios of reactants in aqueous solution. They were not characterised in view of their possibly dangerous nature.

(xiii) Azelaoyldihydrazinecopper(II) sulphate.

$CuSO_4.5H_2O$ (1.25g) in water (20ml) was added to AZDH (1.08g) in water (300ml). The solution was filtered and methanol (20ml) added. After cooling overnight, the fine blue precipitate was collected, washed with water and methanol, then dried.

Analysis. Found: C, 28.5%; H, 5.21%; N, 14.8%; N_2H_4, 16.9%; Cu, 16.7%. Calculated for $C_9H_{20}N_4O_2CuSO_4$: C, 28.8%; H, 5.35%; N, 14.9%; N_2H_4, 17.1%, Cu, 16.9%.

(xiv) *μ*-Mono-tri-(azelaoyldihydrazine)-dicopper(II) tetraperchlorate.

$Cu(ClO_4)_2 \cdot 6H_2O$ (1.85g) was dissolved in water (10ml) and AZDH (1.08g) added and dissolved, producing a deep blue solution which was filtered and placed overnight in the refrigerator. The small blue needles were collected, washed with water and dried.

Analysis. Found: N_2H_4, 16.3%; Cu, 10.7%. Calculated for $(C_9H_{20}N_4O_2)_3Cu_2(ClO_4)_4$: N_2H_4, 16.4%; Cu, 10.8%.

The complex exploded on heating but was apparently stable to percussion.

(xv) Sebacoyldihydrazinecopper(II) sulphate.

$CuSO_4 \cdot 5H_2O$ (2.50g) in water (30ml) was added to a hot solution of SBDH (2.30g) in water (150ml). The small amount of an immediate green precipitate was removed by filtration and the blue solution cooled in the refrigerator. After three hours the filtration was repeated. A small quantity of crystals was produced when the solution was cooled overnight. These were collected and dried. Methanol (20ml) was added to the filtrate, precipitating a pale blue compound which was collected, washed with water and methanol then dried.

Analysis. Found: C, 30.9%; H, 5.99% N, 13.9%; N_2H_4, 16.3%; Cu, 16.1%. Calculated for $C_{10}H_{22}N_4O_2CuSO_4$: C, 30.8%; H, 5.69%; N, 14.4%; N_2H_4, 16.4%; Cu, 16.3%.

The first crop of crystals was found to be impure. Found: N_2H_4, 17.0%.

(xvi) μ-mono-tri-(sebacoyldihydrazine)-dicopper(II) tetraperchlorate.

$Cu(ClO_4)_2.6H_2O$ (1.85g) was dissolved in water (10ml) and SBDH (1.15g) added. On gentle warming the ligand dissolved and the deep blue solution was filtered. The solution crystallized overnight in the refrigerator. The small blue-green prisms were collected, washed with water and dried.

Analysis. Found: N_2H_4, 15.6%; Cu, 10.4%. Calculated for $(C_{10}H_{22}N_4O_2)_3Cu_2(ClO_4)_4$: N_2H_4, 15.8%; Cu, 10.5%.

The complex exploded on heating but was apparently stable to percussion.

(xvii) Dodecanedioyldihydrazinecopper(II) perchlorate.

$Cu(ClO_4)_2.6H_2O$ (3.71g) was added to DDDH (1.29g) in water (15ml) and the mixture shaken until most of the ligand dissolved. The solution was filtered and overnight deposited clusters of blue crystals and a quantity of a finely divided pale green compound. The supernatant and pale compound were decanted. Washing the blue crystals water each time gave a light blue solution and a small quantity of the pale compound. The complex was collected, washed with ethanol and dried.

Analysis. Found: C, 28.9%; H, 5.73%; N, 10.7%; N_2H_4, 12.5%; Cu, 11.9%. Calculated for $C_{12}H_{26}N_4O_2Cu(ClO_4)_2$: C, 27.7%; H, 5.03%; N, 10.8%; N_2H_4, 12.3%; Cu, 12.1%.

(xviii) μ-Mono-tri-(dodecanedioyldihydrazine)-dicopper(II) tetraperchlorate.

$Cu(ClO_4)_2 \cdot 6H_2O$ (5.57g) in water (30ml) was added to DDDH (3.87g) in water (30ml) and the mixture heated to boiling when the ligand dissolved. The solution was filtered and on cooling deposited a pale blue-green powder. The complex was collected, washed with water and ethanol, then dried.

Analysis. Found: C, 33.0%; H, 6.09%; N, 12.7%; N_2H_4, 14.5%; Cu, 9.71%. Calculated for $(C_{12}H_{26}N_4O_2)_3$-$Cu_2(ClO_4)_4$: C, 33.3%; H, 6.04%; N, 12.9%; N_2H_4, 14.8%; Cu, 9.78%.

(9.9) KETO N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE COMPLEXES.

(i) Bis-(N-isopropylidene-N'-benzoylhydrazine)copper(II) dichloride dihydrate.

The complex has been prepared previously.[30] $CuCl_2 \cdot 2H_2O$ (1.70g) was dissolved in water (10ml) and BH (2.72g) in acetone (40ml) and water (5ml). Both solutions were cooled in ice and mixed. The deep green solution began to crystallize immediately and after chilling for 15 minutes the yellow-green prisms were collected and washed with acetone then air dried.

Analysis. Found: N_2H_4, 12.4%. Calculated for $(C_{10}H_{12}N_2O)_2CuCl_2.2H_2O$: N_2H_4, 12.3%.

(ii) Bis-(N-isopropylidene-N'-benzoylhydrazine)copper(II) dichloride monohydrate.

The dihydrate was ground and dried to constant weight in vacuo over P_2O_5.

Analysis. Found: C, 47.8%; H, 5.45%; N, 11.1%; N_2H_4, 12.7%; Cu, 12.7%. Calculated for $(C_{10}H_{12}N_2O)_2CuCl_2.H_2O$: C, 47.6%; H, 5.19%; N, 11.1%; N_2H_4, 12.7%; Cu, 12.6%.

(iii) Bis-(N-isopropylidine-N'-benzoylhydrazine)copper(II) dibromide dihydrate.

The complex was prepared by an analogous method to $(IPBH)_2CuCl_2.2H_2O$ and air dried.

Analysis. Found: C, 39.1%; H, 4.59%; N, 8.96%; N_2H_4, 10.5%; Cu, 10.3%. Calculated for $(C_{10}H_{12}N_2O)_2CuBr_2.2H_2O$: C, 39.3%; H, 4.61%; N, 9.16%; N_2H_4, 10.5%; Cu, 10.4%.

(iv) Bis-(N-isopropylidene-N'-benzoylhydrazine)copper(II) perchlorate.

$(BH)_2Cu(ClO_4)$ was dissolved in acetone with warming.

The green isopropylidene derivative crystallized rapidly and was redissolved with the dropwise addition of water. The solution was filtered and the complex crystallized on cooling. The complex explodes violently on heating.

Analysis. C and H figures could not be determined. Found: N, 8.82%; N_2H_4, 10.4%; Cu, 10.2%; Calculated for $(C_{10}H_{12}N_2O)_2Cu(ClO_4)_2$: N, 9.01%; N_2H_4, 10.4%; Cu, 10.3%.

(v) Bis-(N-isopropylidene-N'-propionylhydrazine)copper(II) dichloride hemihydrate.

$CuCl_2.2H_2O$ (1.70g) in acetone (25ml) and water (2ml) was cooled in ice and added to IPPH (3.20g) in acetone (50ml) and the mixture chilled. On the addition of acetone (25ml) the complex slowly crystallized. The fine yellow-green needles were collected, washed with acetone and dried.

Analysis. Found: C, 35.9%; H, 6.06%; N, 13.8%; Cu, 16.4%. Calculated for $(C_6H_{12}N_2O)_2CuCl_2.05H_2O$: C, 36.0%; H, 6.30%; N, 14.0%; Cu, 15.9%.

(9.10) KETO POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'--DIACYLDIHYDRAZINE COMPLEXES.

(i) μ-Diisopropylideneoxalyldihydrazine-dicopper(II) tetrachloride hemihydrate.

$CuCl_2.2H_2O$ (1.70g) in acetone (25ml) and water (5ml) was added to IPOXDH (1.98g) in acetone (50ml) and water (10ml). The deep green solution was cooled in ice and acetone (400ml) added. A yellow precipitate slowly formed and was collected after 2 hours, washed with acetone, and dried.

Analysis. Found: C, 18.9%; H, 2.92%; N, 11.8%; N_2H_4, 13.2%; Cu, 26.7%; Cl, 27.0%. Calculated for $C_8H_{14}N_4O_2Cu_2Cl_4.0.5H_2O$: C, 20.2%; H, 3.18%; N, 11.8%; N_2H_4, 13.5%; Cu, 26.7%; Cl, 29.8%.

(ii) Diisopropylidenemalonyldihydrazinecopper(II) dichloride hemihydrate.

$CuCl_2.2H_2O$ (1.70g) in water (5ml) was added to a solution of MADH (1.32g) in acetone (20ml) and water (5ml) at room temperature. The complex was precipitated as an oil on the addition of acetone (180ml) which solidified when the addition of acetone was completed. The complex was dissolved in a mixture of water (10ml) and acetone (5ml) and the solution filtered. On the addition of acetone (90ml) with stirring the complex began to precipitate and after chilling in the refrigerator overnight was collected as small green crystals, washed with acetone and dried.

Analysis. Found: C, 30.2%; H, 5.41%; N, 15.7%; Cu, 17.9%. Calculated for $C_9H_{16}N_4O_2CuCl_2.0.5H_2O$: C, 30.4%; H, 4.82%; N, 15.8%; Cu, 17.9%.

(iii) Diisopropylidenesuccinyldihydrazinecopper(II) dichloride hemihydrate.

$CuCl_2.2H_2O$ (0.85g) in water (5ml) was added to SUDH (1.13g) in water (10ml) and acetone (5ml). On the addition of acetone (50ml) the complex precipitated. Reprecipitation was carried out from a solution of the complex in water (15ml) and acetone (5ml) by the addition of acetone until the solution became cloudy. After cooling overnight in the refrigerator the complex was collected as a bright green coarse powder, washed with acetone and dried.

Analysis. Found: C, 32.4%; H, 5.29%; N, 15.5%; N_2H_4, 17.4%; Cu, 17.2%. Calculated for $C_{10}H_{18}N_4O_2CuCl_2.0.5H_2O$: C, 32.5%; H, 5.18%; N, 15.2%; N_2H_4, 17.3%; Cu, 17.2%.

(iv) Diisopropylideneglutaryldihydrazinecopper(II) dichloride monohydrate.

$CuCl_2.2H_2O$ (0.85g) in water (5ml) and acetone (10ml) was added to GLDH (0.80g) in water (5ml) and acetone (15ml). Light green crystals were deposited on standing, were collected, washed with acetone and dried.

Analysis. Found: C, 33.7%; H, 6.42%; N, 14.1%; N_2H_4, 16.4%; Cu, 16.1%. Calculated for $C_{11}H_{20}N_4O_2CuCl_2.H_2O$: C, 33.6%; H, 5.65%; N, 14.3%; N_2H_4, 16.3%; Cu, 16.2%.

(v) Diisopropylideneadipoyldihydrazinecopper(II) dichloride monohydrate.

$CuCl_2.2H_2O$ (1.70g) in water (5ml) was added to ADDH (1.74g) in acetone (10ml) and water (5ml). The complex crystallized on the addition of acetone (40ml) and was recrystallized by dissolving in water (15ml), filtering and adding acetone until the solution became cloudy. On chilling overnight in the refrigerator the complex crystallized in yellow-green needles, was collected, washed with acetone and dried.

Analysis. Found: C, 36.4%; H, 6.44%; N, 13.8%; N_2H_4, 15.8%; Cl, 17.4%; Cu, 15.4%. Calculated for $C_{12}H_{22}N_4O_2CuCl_2.H_2O$: C, 35.4%; H, 5.95%; N, 13.8%; N_2H_4, 15.8%; Cl, 17.4%; Cu, 15.6%.

The hemihydrate was obtained by dissolving the monohydrate in a small volume of water, then filtering the solution into a large excess of acetone. The yellow green powder was collected, washed with acetone and dried.

Analysis. Found: N_2H_4, 16.2%; Cu, 16.1%. Calculated for $C_{12}H_{22}N_4O_2CuCl_2.0.5H_2O$: N_2H_4, 16.1%; Cu, 16.0%.

The anhydrous complex was prepared by drying the blue hydrate obtained when less acetone was added to precipitate the complex as reported for the recrystallization of the monohydrate. The conditions appeared difficult to reproduce - sometimes a mixture of compounds was obtained. The complex turned yellow-green on drying.

Analysis. Found: N_2H_4, 16.5%; Cu, 16.3%. Calculated for $C_{12}H_{22}N_4O_2CuCl_2$: N_2H_4, 16.5%; Cu, 16.4%.

(vi) Diisopropylideneadipoyldihydrazinecopper(II) dibromide hemihydrate.

$CuBr_2$ (2.23g) in acetone (20ml) and water (5ml) was cooled in ice and added to ADDH (1.74g) in acetone (40ml) and water (15ml) and the solution cooled in ice. The complex crystallized as a fine yellow-green powder, was collected, washed with acetone and dried.

Analysis. Found: C, 30.3%; H, 4.84%; N, 11.3%; N_2H_4, 13.2%, Cu, 13.0%. Calculated for $C_{12}H_{22}N_4O_2CuBr_2$.$0.5H_2O$: C, 29.7%; H, 4.78%; N, 11.6%; N_2H_4, 13.2%; Cu, 13.1%.

(vii) Diisopropylidenepimeloyldihydrazinecopper(II) dichloride hemihydrate.

$CuCl_2.2H_2O$ (1.70g) in water (5ml) was added to PMDH (1.88g) in acetone (30ml) and water (5ml). Acetone (100ml) was added and precipitated the complex as an oil, which solidified on removal of the supernatant and addition of acetone (50ml). The complex was dissolved in acetone (5ml) with the dropwise addition of water and the solution filtered into acetone (100ml) mechanically stirred as the complex precipitated. The pale green complex was collected, washed with acetone and dried.

Analysis. Found: C, 38.6%; H, 6.22%; N, 13.4%; N_2H_4, 15.4%; Cu, 15.4%. Calculated for $C_{13}H_{24}N_4O_2CuCl_2.0.5H_2O$: C, 37.9%; H, 6.12%; N, 13.6%; N_2H_4, 15.6%; Cu, 15.5%.

(viii) Diisopropylidenesuberoyldihydrazinecopper(II) dichloride monohydrate.

SRDH (2.02g) in acetone (50ml) and water (25ml) was dissolved with warming and cooled, when the isopropylidene derivative crystallized. $CuCl_2.2H_2O$ (1.70g) in water (5ml) was added and the ligand dissolved. The complex precipitated on the addition of acetone (250ml), and was redissolved in water (20ml) and acetone (10ml) with gentle warming. On the addition of acetone (200ml) the green complex precipitated, was collected and washed with acetone.

Analysis. Found: C, 40.0%; H, 6.31%; N, 12.9%; N_2H_4, 14.8%; Cu, 14.7%. Calculated for $C_{14}H_{26}N_4O_2CuCl_2.H_2O$: C, 38.7%; H, 6.49%; N, 12.9%; N_2H_4, 14.7%, Cu, 14.6%.

(ix) Diisopropylideneazelaoyldihydrazinecopper(II) dichloride monohydrate.

$CuCl_2.2H_2O$ (1.70g) in water (5ml) was added to AZDH (2.16g) in acetone (25ml) and water (5ml). The complex was precipitated as an oil by the addition of acetone (150ml). The precipitation process was repeated twice by dissolving the oil in acetone (10ml) with the dropwise addition of water followed by acetone (50ml), finally by filtering the solution into a flask, precipitating the oil, decanting the supernatant and removing the remaining solvent by evaporation under reduced pressure. The oil solidified, was ground and the yellow-green complex dried.

Analysis. Found: C, 41.0%; H, 6.73%; N, 12.6%; N_2H_4, 14.5%; Cu, 14.4%. Calculated for $C_{15}H_{28}N_4O_2CuCl_2.H_2O$: C, 40.2%; H, 6.74%; N, 12.5%; N_2H_4, 14.3%; Cu, 14.2%.

(x) Diisopropylidenesebacoyldihydrazinecopper(II) dichloride monohydrate.

$CuCl_2.2H_2O$ (1.70g) in water (5ml) was added to a solution of SBDH (2.30g) in acetone (25ml) and water (15ml) which had been warmed, filtered and cooled to room temperature. Acetone (200ml) was added, precipitating the complex as a green oil. The oil was reprecipitated twice by dissolving it in acetone (10ml) with the dropwise addition of water, filtering the solution and adding acetone (100ml). After decanting the supernatant, the solvent was finally removed from the oil by evaporation under reduced pressure. The oil solidified, was ground and the yellow-green complex dried.

Analysis. Found: C, 41.9%; H, 7.12%; N, 12.1%; N_2H_4, 13.9%; Cu, 13.8%. Calculated for $C_{16}H_{30}N_4O_2CuCl_2.H_2O$: C, 41.5%; H, 6.97%; N, 12.1%; N_2H_4, 13.9%; Cu, 13.7%.

(xi) Diisopropylidenedodecanedioyldihydrazinecopper(II) dichloride monohydrate.

DDDH (2.58g) was dissolved with warming in acetone (20ml) and water (10ml). On cooling to room temperature the isopropylidene derivative crystallized. On the addition of $CuCl_2.2H_2O$ (1.70g) in water (5ml), the ligand dissolved. The complex was precipitated by the addition of acetone (200ml) as a dark green oil. The oil was treated as in the previous preparation and solidified on finally removing the solvent. It was then ground and the yellow-green complex dried.

Analysis. Found: C, 44.6%; H, 7.37%; N, 11.7%; N_2H_4, 13.1%; Cu, 12.8%. Calculated for $C_{18}H_{34}N_4O_2CuCl_2.H_2O$:

C, 44.0%; H, 7.39%; N, 11.4%; N_2H_4, 13.1%; Cu, 12.9%.

(9.11) ENOL N-ISOPROPYLIDENE-N'-ACYLHYDRAZINE COMPLEXES.

(i) Bis-(N-isopropylidene-N'-benzoylhydrazino)copper(II).

The complex was prepared as previously described.[30] $CuCl_2.2H_2O$ (1.71g) in water (15ml) was added to BH (2.72g) in acetone (15ml) and water (25ml). Saturated $NaHCO_3$ solution was added dropwise until effervescence ceased. The precipitate was collected, washed with water and acetone then recrystallized from chloroform and dried. The complex was obtained as olive-green prisms.

Analysis. Found: N_2H_4, 15.4%; Cu, 15.2%. Calculated for $(C_{10}H_{11}N_2O)_2Cu$: N_2H_4, 15.5%; Cu, 15.3%.

(ii) Bis-(N-isopropylidene-N'-benzoylhydrazino)copper(II) dipyridinate.

$(IPBH)_2Cu$ was recrystallized from pyridine. The bright green needles were collected and air dried.

Analysis. Found: C, 62.8%; H, 5.66%; N, 14.7%; N_2H_4, 11.2%. Calculated for $(C_{10}H_{11}N_2O)_2Cu(C_5H_5N)_2$: C, 63.0%; H, 5.64%; N, 14.7%; N_2H_4, 11.2%.

On drying to constant weight in vacuo over P_2O_5, the complex reverted to $(IPBH)_2Cu$.

Analysis. Found: N_2H_4, 15.5%. Calculated: N_2H_4, 15.5%.

(iii) Bis-(N-isopropylidene-N'-benzoylhydrazino)copper(II) mono-2-methylpyridinate.

(IPBH)$_2$Cu was recrystallized from 2-methylpyridine. The bright green needles were collected and air dried.

Analysis. Found: C, 61.6%; H, 5.92%; N, 13.2%; N_2H_4, 12.7%. Calculated for $(C_{10}H_{11}N_2O)_2Cu.C_6H_7N$: C, 61.6%; H, 5.76%; N, 13.8%; N_2H_4, 12.6%.

(iv) Bis-(N-isopropylidine-N'-benzoylhydrazino)copper(II) mono-4-methylpyridinate.

(IPBH)$_2$Cu was recrystallized from 4-methylpyridine. The dark green needles were collected and air dried.

Analysis. Found: C, 61.8%; H, 5.78%; N, 14.3%; N_2H_4, 12.6%. Calculated for $(C_{10}H_{11}N_2O)_2Cu.C_6H_7N$: C, 61.6%; H, 5.76%; N, 13.8%; N_2H_4, 12.6%.

(v) Bis-(N-isopropylidene-N'-acetylhydrazino)copper(II) monohydrate.

The complex was prepared as previously described.[28] $CuSO_4.5H_2O$ (2.50g) in water (10ml) was added to IPAH (2.28g) in water (5ml). Solid $NaHCO_3$ was added until effervescence ceased. The complex was collected, washed with water and recrystallized from acetone. The small green plates were collected and air dried.

Analysis. Found: N_2H_4, 20.8%; Cu, 20.6%. Calculated for $(C_5H_9N_2O)_2Cu.H_2O$: N_2H_4, 20.8%; Cu, 20.7%.

(vi) Bis-(N-isopropylidene-N'-acetylhydrazino)copper(II)

The monohydrate was dried to constant weight in vacuo over P_2O_5 and became dark green in colour.

Analysis. Found: C, 41.2%; H, 6.30%; N, 19.2%; N_2H_4, 22.0%; Cu, 21.6%. Calculated for $(C_5H_9N_2O)_2Cu$: C, 41.5%; H, 6.26%; N, 19.3%; N_2H_4, 22.2%; Cu, 21.9%.

(vii) Bis-(N-isopropylidene-N'-propionylhydrazino)copper(II) monohydrate.

$CuSO_4 \cdot 5H_2O$ (2.50g) in water (20ml) was added to IPPH (2.56g) in acetone (5ml) and water (20ml). Saturated $NaHCO_3$ solution was added until effervescence ceased. The dark green solution was extracted with chloroform. On evaporation of the solvent, a green crystalline mass was obtained which recrystallized from acetone in bright green plates. The complex was collected, washed with acetone and air dried.

Analysis. Found: C, 43.1%; H, 7.01%; N, 16.7%; N_2H_4, 19.3%; Cu, 18.8%; H_2O (as loss of weight), 5.6%. Calculated for $(C_6H_{11}N_2O)_2Cu \cdot H_2O$: C, 42.9%; H, 7.20%; N, 16.7%; N_2H_4, 19.1%; Cu, 18.9%; H_2O, 5.4%.

(viii) Bis-(N-isopropylidene-N'-propionylhydrazino)copper(II).

The monohydrate was dried to constant weight in vacuo over P_2O_5. The crystals became dark green in colour.

Analysis. Found: C, 45.5%; H, 7.12%; N, 17.5%; N_2H_4, 20.2%; Cu, 19.9%. Calculated for $(C_6H_{11}N_2O)_2Cu$:

C, 45.3%; H, 6.98%; N, 17.6%; N_2H_4, 20.2%; Cu, 20.0%.

(9.12) ENOL POLYMETHYLENE-N,N-DIISOPROPYLIDENE-N',N'-DIACYLDIHYDRAZINE COMPLEXES.

(i) Poly-diisopropylideneoxalyldihydrazinocopper(II).

The complex was obtained from a 2:1 ligand : copper preparation ratio. $CuCl_2.2H_2O$ (1.70g) in water (25ml) and sodium acetate monohydrate (5g) in water (25ml) were mixed and added dropwise to IPOXDH (3.96g) in water (100ml) and acetone (25ml) with mechanical stirring. The fine green precipitate was collected by gentle suction on a sintered filter, washed well with 10% acetone in water and finally by centrifugation with pure acetone. The slurry was dried in vacuo over $CaCl_2$ until it caked. It was then ground and dried in vacuo over P_2O_5.

Analysis. Found: C, 34.2%; H, 4.90%; N, 21.4%; N_2H_4, 24.8%; Cu, 24.3%. Calculated for $C_8H_{12}N_4O_2Cu$: C, 37.0%; H, 4.66%; N, 21.6%; N_2H_4, 24.7%; Cu, 24.5%.

(ii) Attempted preparation of Diisopropylidenemalonyldihydrazinocopper(II).

The preparation was attempted under similar conditions to IPOXDHCu, from a 2:1 ratio of ligand to copper. After washing, the blue precipitate was found to contain chloride and the preparation was abandoned.

(iii) Diisopropylidenesuccinyldihydrazinocopper(II) monohydrate.

$CuSO_4.5H_2O$ (2.50g) and sodium acetate monohydrate (4g) in water (80ml) and acetone (10ml) were added dropwise to a filtered solution of SUDH (1.46g) in acetone (10ml) and water (10ml). The pale green solid deposited was collected by centrifugation and washed with water until sulphate-free, finally with acetone, then dried.

Analysis. Found: C, 38.4%; H, 5.59%; N, 18.2%; N_2H_4, 20.2%; Cu, 21.5%. Calculated for $C_{10}H_{16}N_4O_2Cu.H_2O$: C, 39.3%; H, 5.93%; N, 18.3%; N_2H_4, 21.0%; Cu, 20.8%.

(iv) Diisopropylideneglutaryldihydrazinocopper(II) monohydrate.

$CuSO_4.5H_2O$ (2.50g, 0.01 moles) in water (20ml) was added to GLDH (2.40g, 0.015 moles) in water (10ml) and acetone (10ml). Dilute $NaHCO_3$ solution was added with stirring until no more gas was evolved. The complex slowly precipitated, was collected and washed with water by centrifugation, finally with acetone. The bright green powder turned olive-green on drying.

Analysis. Found: C, 41.2%; H, 5.70%, N, 17.2%; N_2H_4. 19.7%; Cu, 21.7%. Calculated for $C_{11}H_{18}N_4O_2Cu.H_2O$: C, 41.3%; H, 6.30%, N, 17.5%; N_2H_4, 20.0%; Cu, 19.9%.

(v) Diisopropylideneadipoyldihydrazinocopper(II) monohydrate.

$CuSO_4.5H_2O$ (2.50g, 0.01 moles) in water (20ml) was added to ADDH (2.61g, 0.015 moles) in acetone (10ml) and water (40ml). $NaHCO_3$ solution was added dropwise until effervescence ceased. The precipitated complex was collected, washed with water and acetone and air dried. The light green complex was dissolved in boiling dioxan, filtered and precipitated with water. It was then collected, washed with water, and acetone. The complex became olive green in colour on drying.

Analysis. Found: C, 43.3%; H, 6.62%; N, 17.1%; N_2H_4, 19.3%; Cu, 19.1%. Calculated for $C_{12}H_{20}N_4O_2Cu.H_2O$: C, 43.2%, H, 6.65%; N, 16.8%; N_2H_4, 19.2%; Cu, 19.1%.

Loss of weight on drying indicates that the complex precipitates from solution as the dihydrate. Found: H_2O, 4.8%. Calculated: 5.1%.

(vi) Diisopropylideneadipoyldihydrazinocopper(II) monopyridinate.

IPADDHCu.H_2O was dissolved in hot pyridine, the solution filtered and allowed to crystallize. The bright green powder was collected and washed with pyridine. The complex became dull green in colour on drying.

Analysis. Found: C, 50.9%; H, 6.41%; N, 17.4%; N_2H_4, 16.0%; Cu, 16.0%. Calculated for $C_{12}H_{20}N_4O_2Cu.C_5H_5N$: C, 51.7%; H, 6.38%; N, 17.7%; N_2H_4, 16.2%; Cu, 16.1%.

(vii) Diisopropylidenepimeloyldihydrazinocopper(II) monohydrate.

$CuSO_4.5H_2O$ (2.50g, 0.01 moles) in water (20ml) was added to PMDH (2.82g, 0.015 moles) in acetone (10ml) and water (40ml). Excess saturated $NaHCO_3$ solution was added and the dark green solution extracted with chloroform. The extract was shaken with anhydrous Na_2SO_4 for 10 minutes, filtered, and the chloroform removed by distillation under reduced pressure. The dark green oil remaining was dissolved in acetone and the complex precipitated by the addition of water, as a bright green powder. This was dried to constant weight then dissolved in dry ethanol, reprecipitated with water and air dried.

Analysis. Found: C, 45.3%; H, 6.98%; N, 16.1%, N_2H_4, 18.6%; Cu, 18.0%. Calculated for $C_{13}H_{22}N_4O_2Cu.H_2O$: C, 44.9%; H, 6.95%; N, 16.1%; N_2H_4, 18.4%; Cu, 18.3%.

(viii) Diisopropylidenepimeloyldihydrazinocopper(II).

$IPPMDHCu.H_2O$ was dried in vacuo over P_2O_5. Constant weight was achieved after several weeks.

Analysis. Found: C, 47.7%; H, 6.74%; N, 16.7%, N_2H_4, 19.3%; Cu, 18.6%. Calculated for $C_{13}H_{22}N_4O_2Cu$: C, 47.3%; H, 6.72%; N, 17.0%; N_2H_4, 19.4%; Cu, 19.3%.

(ix) Diisopropylidenesuberoyldihydrazinocopper(II).

SRDH (3.03g, 0.015 moles) was dissolved in acetone (20ml) and water (50ml) with warming. On cooling the isopropylidene derivative crystallized. $CuSO_4.5H_2O$ (2.50g, 0.01 moles) in water (20ml) was added and most of the ligand dissolved. On the addition of excess $NaHCO_3$ solution a green precipitate was formed. The mixture was extracted with chloroform, the extract dried with anhydrous Na_2SO_4 and the solvent removed leaving a dark oil. On the addition of acetone, most of the oil dissolved, the solution was filtered and a bright green complex precipitated by the addition of water. The complex was collected and air dried. On attempting to reprecipitate the complex from acetone, when solvent was added the complex turned blue-grey in colour and did not dissolve. The complex was collected, washed with acetone and dried.

Analysis. Found: C, 49.2%; H, 6.95%; N, 16.1%; N_2H_4, 18.5%; Cu, 18.2%. Calculated for $C_{14}H_{24}N_4O_2Cu$: C, 48.9%; H, 7.03%; N, 16.3%; N_2H_4, 18.6%; Cu, 18.5%.

(x) Attempted preparation of diisopropylideneazelaoyldihydrazinocopper(II).

Solutions of AZDH in acetone and water gave dark green oils with $Cu(ClO_4)_2.6H_2O$ and $CuCl_2.2H_2O$ solutions on the addition of sodium bicarbonate. After repeated attempts at purification these oils were found to contain perchlorate and chloride respectively. Consequently the preparations were abandoned.

(xi) Attempted preparation of diisopropylidenesebacoyldihydrazinocopper(II).

Several attempts to prepare this complex resulted in the formation of oils or anion-containing solids which showed variable analyses, inconsistent with an conceivable formulation. It is probable that mixtures of complexes were obtained. One sample was found to decompose at approximately 70°, indicating that low stability may also be a factor prohibiting isolation of a pure compound.

(9.13) COMPLEXES CONTAING TRIDENTATE AND RELATED LIGANDS.

(i) Bis-(N-isopropylidene-N'-salicoylhydrazino)copper(II) dipyridinate.

IPSALH (1.92g) was dissolved by the dropwise addition of dilute sodium hydroxide solution to a slurry of the ligand in water (50ml) and acetone (10ml). $Cu(ClO_4)_2.6H_2O$ in water (20ml) was added dropwise with mechanical stirring. The thick green precipitate was collected by centrifugation, washed with water and acetone then dried in vacuo. The crude product was recrystallised from pyridine, forming bright green needles. The complex was collected, washed with ether containing a few drops of pyridine, and air dried.

Analysis. Found: C, 59.1%; H, 5.44%; N, 13.4%; Cu, 10.4%. Calculated for $C_{30}H_{32}N_6O_4Cu$: C, 59.7%; H, 5.34%; N, 13.9%; Cu, 10.5%.

(ii) Bis-(N-isopropylidene-N'-salicoylhydrazino)copper(II).

(IPSALH)$_2$Cu(pyridine)$_2$ was dried to constant weight in vacuo over P_2O_5. The colour of the sample changed to a dull green.

Analysis. Found: C, 53.9%; H, 5.09%; N, 12.3%; Cu, 14.1%. Calculated for $C_{20}H_{22}N_4O_4Cu$: C, 53.9%; H, 4.97%; N, 12.6%; Cu, 14.3%.

(iii) Salicylaldehydebenzoylhydrazonomonopyridinecopper(II).

To SALBH (2.40g) in ethanol (70ml) was added Cu(OAc)$_2$.H_2O (2.00g) in water (75ml) and ethanol (50ml). The thick green precipitate was collected, washed with water and ethanol. The damp precipitate was dissolved in warm pyridine (20ml) and water added until the complex began to crystallize. After warming to redissolve the complex (with the addition of more pyridine) the solution was filtered and crystallized in black (dark green on powdering) prisms.

Analysis. Found: C, 59.8%; H, 4.01%; N, 11.0%; Cu, 16.6%. Calculated for $C_{19}H_{15}N_3O_2Cu$: C, 59.9%; H, 3.97%; N, 11.0%; Cu, 16.7%.

(iv) Acetylacetonebenzoylhydrazonomonopyridinecopper(II).

ACACBH (2.36g) (The oil obtained from dissolving BH in acetylacetone in equimolar proportions$^{32)}$ was dissolved in ethanol (10ml) and water (10ml). The ligand solution was added to $Cu(OAc)_2.H_2O$ (2.00g) and $NaOAc.H_2O$ (4.0g) in water (100ml) and ethanol (10ml). The green precipitate was collected by centrifugation and washed with water and ethanol. The damp precipitate was dissolved in pyridine with warming, the solution filtered; black lustrous prisms were obtained on cooling.

Analysis. Found: C, 56.9%; H, 4.81%; N, 11.4%; Cu, 17.5%. Calculated for $C_{17}H_{17}N_3O_2Cu$: C, 56.9%; H, 4.76%; N, 11.7%; Cu, 17.7%.

(v) Acetylacetonebenzoylhydrazonomono-2-methylpyridine copper(II).

The crude precipitate obtained as in (iv) above was recrystallized from 2-methylpyridine. The complex was obtained as fine olive-green needles which were washed with ether containing a trace of 2-methylpyridine and air dried.

Analysis. Found: C, 57.9%; H, 5.29%; N, 11.3%; Cu, 16.7%. Calculated for $C_{18}H_{19}N_3O_2Cu$: C, 58.0%; H, 5.13%; N, 11.3%; Cu, 17.0%.

(vi) Acetylacetonebenzoylhydrazonocopper(II).

The 2-methylpyridine derivative obtained as in (v) was dried to constant weight in vacuo over P_2O_5. Constant weight was achieved after several weeks.

Analysis. Found: C, 51.1%; H, 4.21%; N, 9.81%; Cu, 22.2%. Calculated for $C_{12}H_{12}N_2O_2Cu$: C, 51.5%;

H, 4.33%; N, 10.0%; Cu, 22.7%.

(vii) Salicylaldehydebenzoylhydrazonomonochlorocopper(II) hemihydrate.

SALBH (1.20g) in ethanol (30ml) was added to $CuCl_2.2H_2O$ (0.85g) in ethanol (10ml). Microscopic examination showed that the complex which crystallized, consisted of a mixture of yellow-green needles and brown spheres. On boiling this mixture with ethanol, a brown precipitate consisting of very fine dark needles was obtained, collected and washed with ethanol.

Analysis. Found: C, 49.3%; H, 3.36%; N, 7.91%; Cu, 18.4%. Calculated for $C_{14}H_{11}N_2O_2ClCu.0.5H_2O$: C, 48.4%; H, 3.46%; N, 8.07%; Cu, 18.3%.

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APPENDIX.

A REVISED INTERPRETATION OF SOLVENT EFFECTS ON THE SPECTRUM OF BIS-(ACETYLACETONATO)COPPER(II).

From an examination of the visible spectrum of bis-(acetylacetonato)copper(II) in a number of solvents ranging from chloroform to piperidine, Belford, Calvin and Belford[1] (B.C.B.) have derived the energy level scheme for positron transitions reproduced in figure 4.2 of Chapter 4. Resolution of the spectra into three Gaussian components was considered to be the most suitable procedure.

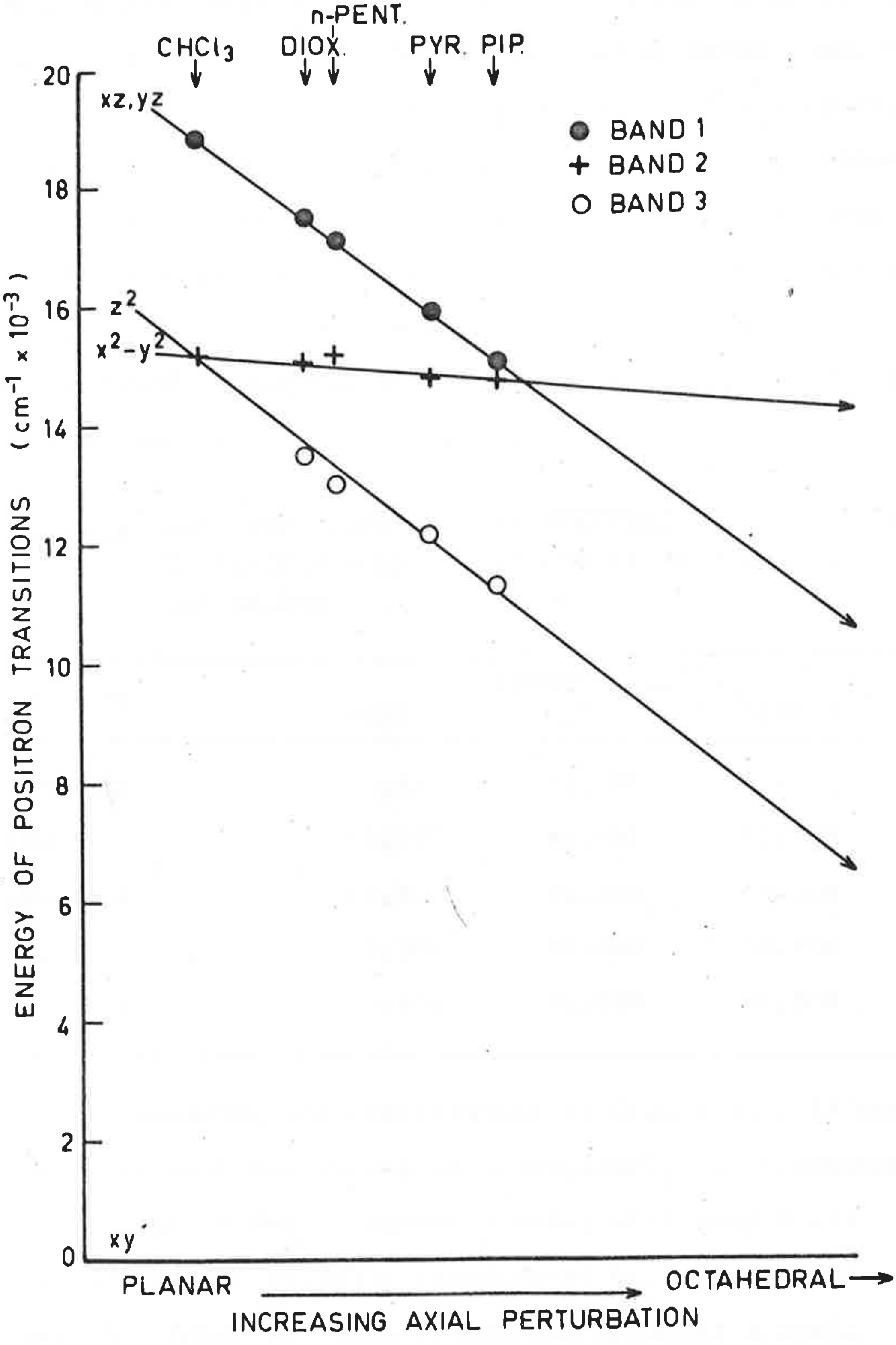
Further examination of the band positions reported by these authors is presented here and would indicate that the B.C.B. scheme does not adequately account for the observed solvent effects, and that the description in terms of three components is incompatible with ligand field theory.

In attempting to describe the variation of the spectrum with increasing coordinating properties of the solvent by graphical representation, it is unfortunate that we have no means of indicating the degree of distortion from a regular octahedral configuration in absolute numerical values. However, the energy of the transitions may be plotted against arbitrary values for the "degree of axial elongation", where extrapolation in either direction must encompass both square planar and regular octahedral configurations.

Such a procedure is shown in figure A.1 for the three

FIGURE A.1.

Empirical energy level diagram for bis-(acetylacetonato)copper(II) resulting from resolution of the visible spectrum in various solvents into three Gaussian components according to Belford, Calvin and Belford.[1]


n-PENT.
CHCl3
DIOX.
PYR.
PIP.
xz,yz
BAND 1
BAND 2
BAND 3
z2
x2-y2
xy
ENERGY OF POSITRON TRANSITIONS (cm-1 x 10-3)
20
18
16
14
12
10
8
6
4
2
0
PLANAR
OCTAHEDRAL
INCREASING AXIAL PERTURBATION

band positions reported by Belford et al. (table A.1). By placing the positions of the highest energy bands (band 1) in chloroform and piperidine an arbitrary distance apart, then plotting band 1 for dioxan, n-pentanol and pyridine on the line joining these points, the positions of bands 2 and 3 lie approximately on straight lines. The order of increasing shift to lower energies is then in the order of the intuitively expected increasing coordinating properties of the solvents.

TABLE A.1. BAND POSITIONS OF BIS-(ACETYLACETONATO)COPPER(II) IN VARIOUS SOLVENTS ACCORDING TO BELFORD, CALVIN AND BELFORD.[1]

SOLVENT	MAXIMUM (cm^{-1}) BAND 1	 BAND 2	 BAND 3
Chloroform	18,810	15,190	-
Dioxan	17,500	15,100	13,500
n-pentanol	17,100	15,200	13,000
Pyridine	15,900	14,800	12,100
Piperidine	15,100	14,800	11,300

In discussing the implications of figure A.1, it must be remarked that the structure of $Cu(acac)_2$ in chloroform should be very close to square planar, with only small perturbation from apically coordinated solvent molecules. It has been observed[2] that chloroform produces a small shift when compared with carbon tetrachloride for other copper(II) complexes, so that coordination of solvent is not completely negligible. Hence the perfectly square planar structure would be expected to have a spectrum consistent with a point just prior to chloroform in figure A.1. The expected crossover between d_{z^2} and $d_{x^2-y^2}$ is then observed (B.C.B. diagram).

The point at which a regular octahedral configuration would occur is more difficult to decide, but must be placed somewhere beyond piperidine. The spectrum in this solvent is clearly not due to the single transition expected in a regular octahedral environment. The point of intersection of band 1 and band 2 is, according to the B.C.B. scheme, expected to occur in a regular octahedral configuration, when the energy of band 3 should be zero in accordance with ligand field theory predictions. The fact that band 3 is observed to have a finite energy of about 11,000 cm^{-1} at this point clearly illustrates that the resolution procedure used by Belford et al. produces band energies which are at variance with the energy level diagram they propose. Further extrapolation of the band energies beyond piperidine cannot produce a situation compatible with the B.C.B. diagram at the regular octahedral configuration, for when band 3 has zero energy, two transitions would still be observed. The only way in which one transition can result is for band 1 to intersect with band 3 at the ground state. This would produce a four-degenerate lower level comprising

d_{xy}, d_{z^2}, d_{x^2} and d_{yz} which is inconceivable on ligand field theory. (The notation here results from the choice of x and y axes as the bisectors of the O-Cu-O bond angles).

In order to clarify the situation, we have adopted the suggestion of Graddon and Schulz[3] and examined the published spectrum of $Cu(acac)_2$ as a consequence of resolution into only two bands. The energy of the maxima were determined by inspection from the spectra reported by Belford et al. and are listed in table A.2 with liberal allowance for the error of this procedure.

TABLE A.2. RESOLUTION OF THE SPECTRA OF BIS-(ACETYLACETONATO)-COPPER(II) IN VARIOUS SOLVENTS INTO TWO COMPONENTS.

SOLVENT	MAXIMUM (cm^{-1}) BAND 1	BAND 2
CHLOROFORM[a]	18,800 ± 500	15,500 ± 500
BENZENE[b]	18,600	14,900
DIOXAN[a]	17,000 ± 500	15,000 ± 500
n-PENTANOL[a]	15,500 ± 500	15,000 ± 1000
PYRIDINE[a]	15,500 ± 500	13,000 ± 1000
PYRIDINE[b]	15,300	12,500
4-METHYLPYRIDINE[b]	15,200	12,500
PIPERIDINE[a]	14,500 ± 500	11,500 ± 1000

(a) Band positions determined by inspection of the spectra reported by Belford et al.[1]

(b) Gaussian analysis by Graddon and Schulz.[3]

The band positions of table A.2 suggest that the solvent effects may best be described by two systems of bands:

(i) Band A decreasing steadily from 18,800 cm^{-1} in chloroform to 11,500 cm^{-1} in piperidine;

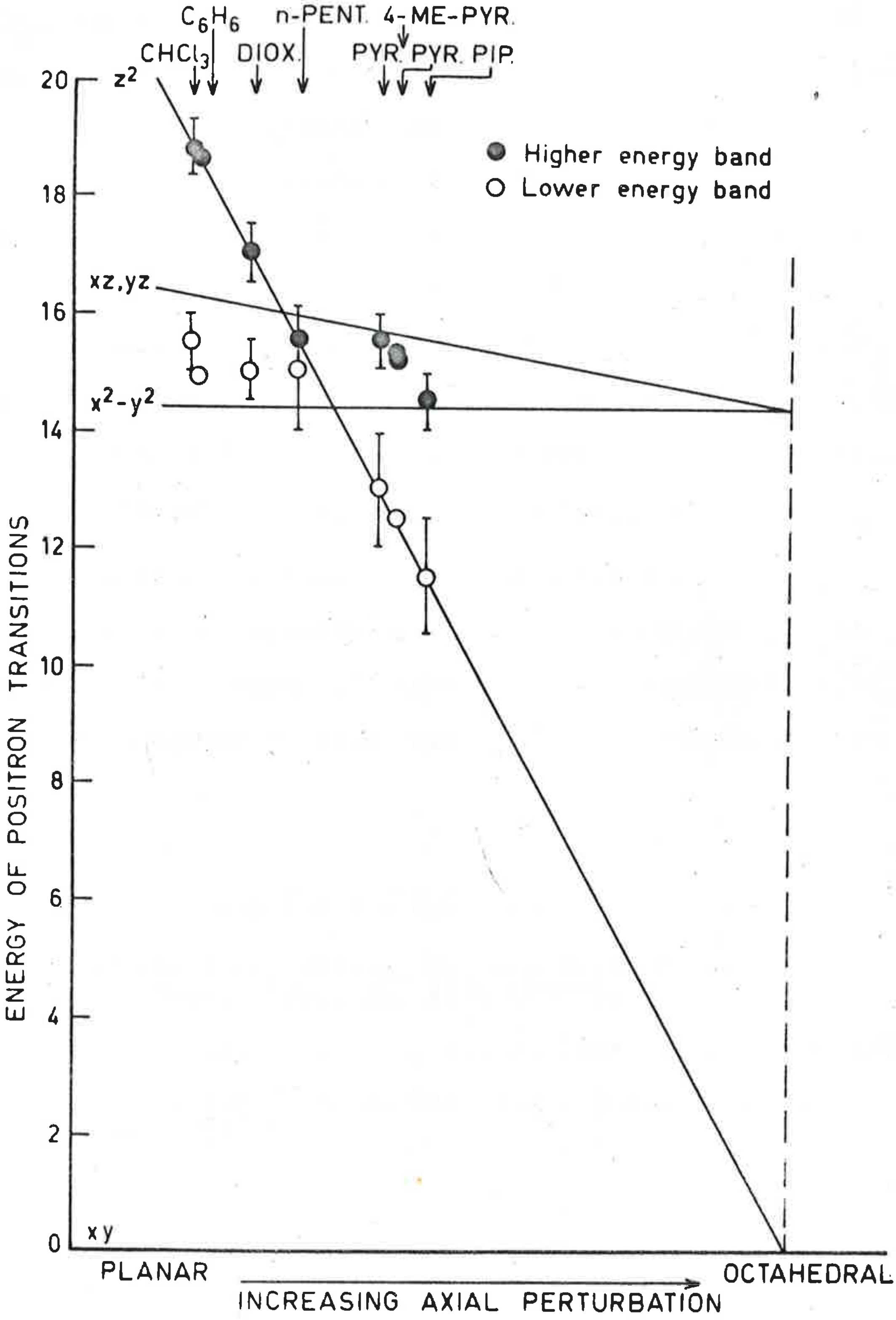
(ii) Band B remaining almost constant at about 15,000 cm^{-1}.

The effect of plotting these band positions in a similar manner to that described above is shown in figure A.2. The energy level scheme thus empirically derived is essentially similar to that proposed by Belford et al. The steep slope of the A series of bands and the intersection of this line with the d_{xy} ground state at an intuitively reasonable position is consistent with its identification as the $xy \rightarrow z^2$ positron transition.

The spread of energies of the B bands (about 2,000 cm^{-1}) may well indicate that the observed maxima are the resultant of two (or three) bands which are nearly coincident. Such a postulate may well be almost impossible to test by Gaussian analysis of the bands in question in view of the broad nature of the bands generally observed in copper(II) spectra; they may be broad because they consist of more than one band. Since the degenerate pair d_{xz}, d_{yz} will be more affected than $d_{x^2-y^2}$ by axial coordination, the assignment of these levels as indicated in figure A.2 is reasonable. These levels have been drawn to converge at the same point

FIGURE A.2.

Empirical energy level diagram for bis-(acetylacetonato)copper(II) resulting from resolution of the visible spectrum in various solvents into two components. Points showing uncertainty were obtained by inspection of the spectra reported by Belford et al.[1]; remaining points from Gaussian analysis reported by Graddon and Schulz.[3]



C6H6
n-PENT.
4-ME-PYR.
CHCl3
DIOX.
PYR.
PYR.
PIP.
z2
xz,yz
x2-y2
xy
● Higher energy band
○ Lower energy band
ENERGY OF POSITRON TRANSITIONS
20
18
16
14
12
10
8
6
4
2
0
PLANAR
OCTAHEDRAL
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as d_z2 and d_{xy} to provide complete agreement with ligand field theory, in that only one transition is to be expected for the regular octahedral configuration. Without resolution of these bands it can only be concluded that they occur within the energy range approximately covered by the area between the two lines.

The main difference in the scheme proposed here and the B.C.B. scheme would appear to be in the extent to which the energy of d_z2 is raised in a square planar configuration. Although the ordering $d_z2 > d_{xz}, d_{yz} > d_{x^2-y^2} > d_{xy}$ (for the coordinate axes used) may not necessarily be generally applicable to the spectra of copper(II) complexes, it is indicated for a number of other complexes besides $Cu(acac)_2$. Further discussion of this aspect is presented in section 4.3.

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