COORDINATION CHEMISTRY OF GUANIDINE DERIVATIVES

by

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To Annie.

ABSTRACT

This thesis describes an investigation of the coordination chemistry of 1-cyanoguanidine (cnge), 1-carbamoylguanidine (clge) and 1-amidino-O-ethylurea (aOeu). Various copper(II) complexes of these analogous molecules were synthesised and characterised using mainly X-ray crystallographic and spectroscopic (infrared and UV-visible) techniques.

Only bis (cnge) complexes were observed for copper(II) ions. The monodentate cnge ligands coordinated the copper(II) via their nitrile nitrogen atoms which were located in trans equatorial positions of the copper(II) ions's tetragonally distorted octahedral coordination sphere. Comparison of the infrared spectra of the complexes with that of cnge indicated that the spectra were highly diagnostic of coordination to the copper(II) ion.

Clge exhibited amphoteric properties; the neutral, anionic and cationic derivatives formed complexes with the copper(II) ion. Whereas the former pair gave bis chelate complexes, the latter derivatives acted merely as a cation and was remote from the copper(II) ion's coordination sphere. Complexation of the neutral molecule resulted in a proton transfer from a terminal amine group to a central nitrogen atom permitting chelation via an imine nitrogen atom and a carbonyl oxygen atom to give a square planar CuN_2O_2 chromophore.

The structural ramifications of this tautomeric shift were near identical to those observed upon cation formation which occurred by protonation of the central nitrogen atom of the uncoordinated neutral molecule. Unequivocal structural data could not be obtained for the complex of the anionic derivative. Spectroscopic analysis indicated, however, that chelation occurred via two imine nitrogen atoms to give a square planar CuN_4 chromophore.

Ethanolysis of cnge was effected in the presence of copper(II) ions and ethanol producing complexes of aOeu with a metal:ligand ratio of 1:1 or 1:2. In both complexes the ligand(s) chelated the copper(II) ion via two imine nitrogen atoms. The former complex, a dimer, exhibited a square pyramidal CuN_2X_3 chromophore (X=Cl,Br) whilst the latter complex was a bis chelate with a square planar CuN_4 chromophore.

Monitoring the UV-visible and infrared spectra of ethanol solutions containing copper(II) chloride and cnge, indicated the presence of a plethora of reactions. However, it was concluded that initially mono and/or bis(cnge)copper(II) complexes, of low stability, were present in equilibrium with the reactants. Subsequently, ethanolysis of coordinated cnge occurred producing mono(aOeu)copper(II) complexes. Series first order kinetics approximated to those of the ethanolysis reaction. The ethanolysis process was then repeated to give the final product a bis(cnge)copper(II) complex.

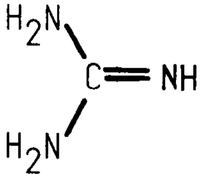
CONTENTS

C H A P T E R   O N E

INTRODUCTION

1.1 General Introduction

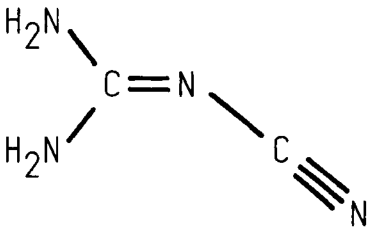
Molecules with a nitrogen to carbon ratio of 1:1 or greater, including guanidine (1.1) and its derivatives, are extensively employed in the modern chemicals industry. Typical of this type of compound are cyanamide (1.2) and 1-cyanoguanidine (1.3).



1.1

$H_2N{-}C{\equiv}N$

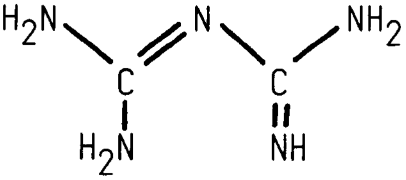
1.2

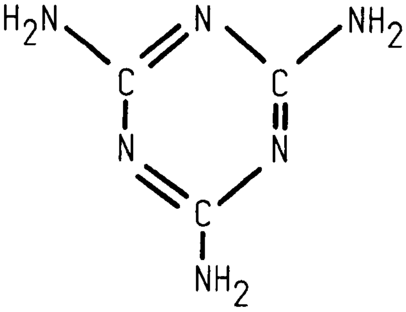


1.3

Cyanamide is mainly used as the precursor to 1-cyanoguanidine but has been utilized as a fertilizer, a weedkiller and in the treatment of alcoholics.[1]

1-Cyanoguanidine will form a myriad of polymers and resins, and is sometimes used to enhance their flow or fire retardent properties. Other applications are in the preparation of guanidine salts, biguanide (1.4) and a host of nitrogen heterocycles such as melamine (1.5).[1]





Presented in this thesis are the results of an investigation into the coordination chemistry of 1-cyanoguanidine, 1-carbamoylguanidine and 1-amidino-O-ethylurea. Single crystal X-ray diffraction and spectroscopic (i.r. and UV-visible) data are reported for various copper(II) complexes containing these ligands.

There follows a series of sections introducing each of the ligands, the properties of copper(II) complexes and the main experimental techniques.

1.2 The Chemistry of 1-Cyanoguanidine

1-Cyanoguanidine* (cnge) is the dimer of cyanamide and was first observed by Beilstein and Geuther[2] during the evaporation of an aqueous solution of cyanamide. It is manufactured on an industrial scale by heating an alkaline solution (pH 8-9) of cyanamide (25%) at 80°C for 2 hours.[1] The material is also formed when cyanamide is kept in a molten state at 48°C for 48 hours.[3]

Cnge is a white solid melting at 208-211°C. It is available at 97% purity and can be readily recrystallised from water. It is moderately soluble in ethanol and sparingly soluble in acetone.

The crystal and molecular structures of cnge have been investigated by single crystal X-ray and neutron diffraction methods.[4,5,6,7] The positions of the hydrogen atoms have been accurately determined and they show that cnge adopts a 'diamino' form (1.3a) rather than

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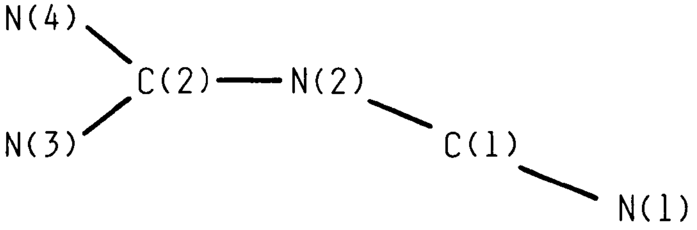
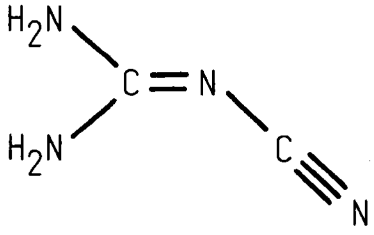
* Also known by its pseudonym dicyandiamide.

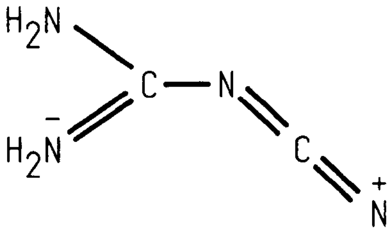
'an imino-amino' form typified by 1.6.



Numbering scheme for 1-cyanoguanidine



1.3a



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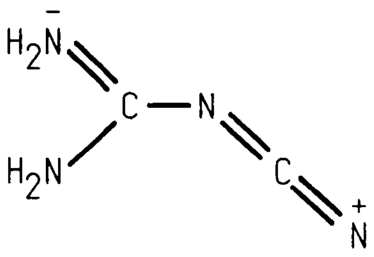
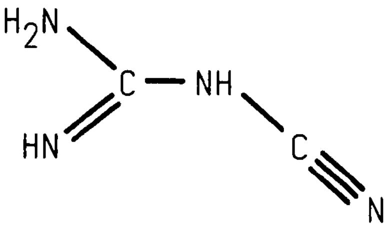


1.3c



1.6

The results of ab initio molecular orbital calculations also indicate that form 1.3a is the energetically most favourable.[8]

The cnge molecule, including the hydrogen atoms, is planar and bond lengths and angles reveal extensive electron delocalisation throughout the C-N skeleton. This implies that form 1.3a does not completely describe the electron distribution about the cnge molecule and that other forms such as 1.3b and 1.3c must be considered to contribute to the overall electronic structure.

From its molecular and electronic structures it can be inferred that cnge could act as a ligand to metal ions. It could ligate via the donation of the lone pairs of electrons on the nitrile or imino nitrogens, N(1) and N(2) respectively. Bonding to metal ions is not possible through either of the amino nitrogens, N(3) or N(4), as each nitrogen is sp^2 hybridised, evidenced by the amino hydrogen atoms lying in the same plane as the C-N skeleton. Hence the lone pair of electrons on the nitrogen atom is delocalised and not available for donation.

Cnge has the potential to act as a monodentate ligand bonding to the metal ion via either N(1) or N(2) or a bidentate ligand bridging two metal ions by using both N(1) and N(2) as donors (Figure 1.1).

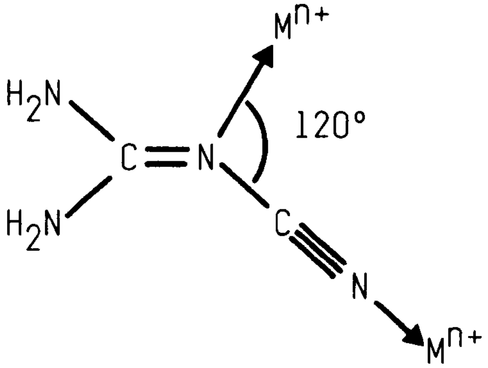


FIGURE 1.1 Possible donor atoms of 1-cyanoguanidine

It would, however, seem unlikely that cnge could chelate a metal ion via N(1) and N(2); the geometry of the N(1)-C(1)-N(2)-C(2) fragment is such that the vectors along which the lone pairs of N(1) and N(2) lie are in the same plane at an angle of ~120° to each other.

A hydrogen transfer between nitrogens within the cnge molecule, as observed on coordination of other ligands (e.g. biguanide), could produce several tautomers similar to form 1.6 which might coordinate via N(1), N(3) or N(4).

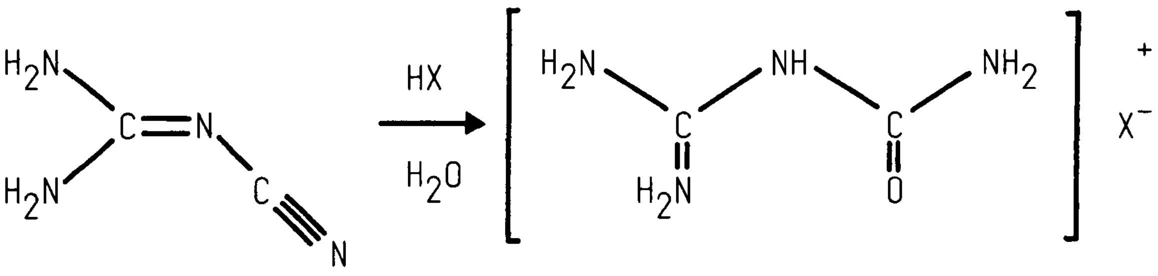
A readily accessible property of metal-cnge complexes which could distinguish between the various possible modes of cnge coordination, is their vibrational spectra. The infrared spectrum of cnge has been investigated by Jones and Orville-Thomas.[9] They assigned many of the absorption bands to vibrations of cnge that could prove to be diagnostic of coordination to a metal ion.

In this work, single crystal X-ray diffraction methods have been used to determine the structure of a copper(II)-cnge complex and a correlation with the infrared spectrum has been attempted.

1.3 **The Chemistry of 1-Carbamoylguanidine**

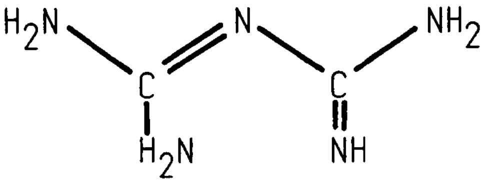
Although 1-cyanoguanidine has been deprotonated to give $M^+[cnge]^-$ type compounds,[10] the protonated form $[cngeH]^+$ has not been observed.

In acidic aqueous solution cnge is not protonated but is hydrolised to give the acid salt of 1-carbamoylguanidine ([clgeH]X). The hydrolysis was noted as early as 1862 by Haag,[11] since when, 1-carbamoylguanidine has been referred to in the literature by several pseudonyms.* It is possible to deprotonate $[clgeH]^+$ to give the neutral 1-carbamoylguanidine molecule (clge) and removal of another proton produces the anionic 1-carbamoylguanidine moiety ($[clge]^-$). With the possibility of several ionic forms and a wide variety of nomenclature, the literature is often difficult to follow, however, $[clgeH]^+$ and $[clge]^-$ are most commonly encountered with little mention made of clge.

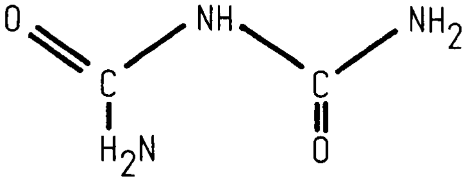


cnge [clgeH]X

1-Carbamoylguanidine is analogous to biguanide (bg, 1.4) and biuret (bu, 1.7).



1.4



1.7

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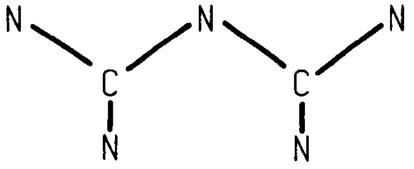
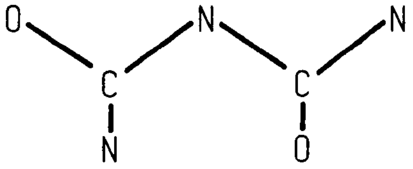
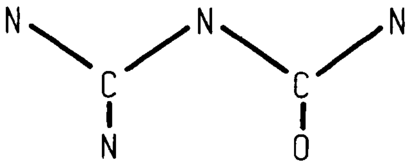
* Most common pseudonym is guanylurea.

Biguanide is known in neutral[12] (bg), cationic[13,14] ($[bgH]^+$), dicationic[13] ($[bgH_2]^{2+}$), and anionic[15] ($[bg]^-$) forms, whilst biuret is known in neutral[16,17] (bu), and anionic[18] ($[bu]^{2-}$) forms.

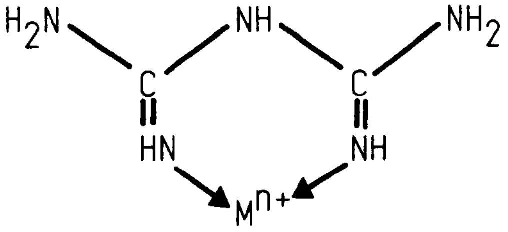
Consideration of the C-N-O skeletons of clge, bg and bu shows clge to be structurally intermediate between bg and bu.


bg


bu


clge

Both bg and bu coordinate metal ions; this is the basis of the 'biuret test' which is used in the detection of peptide linkages.[19,20] Bg chelates via two imino nitrogens[21] (1.8), whilst bu chelates via two carbonyl oxygens[22] (1.9) or acts as a monodentate ligand coordinating via one carbonyl oxygen[23] (1.10).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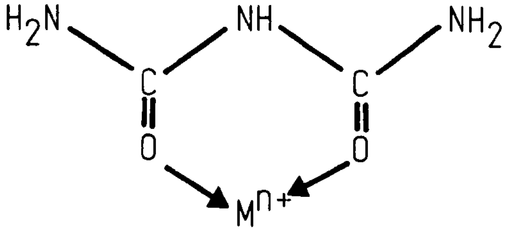
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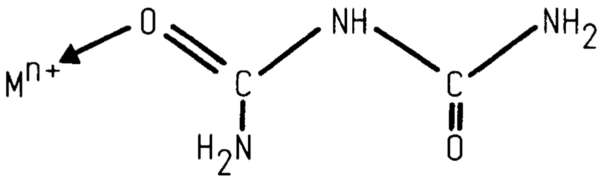


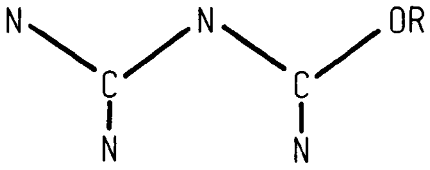
1.10

It must be noted that to facilitate chelation a hydrogen shift occurs for bg and a conformational change occurs for bu. Thus, just considering the coordination properties of the clge molecule only, several possibilities for both tautomers and coordination modes can be envisaged. If the other ionic forms of clge are also considered then a plethora of structures can be imagined.

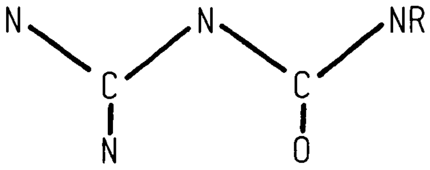
By analogy to previous investigations of the chemistry of coordinated bg and bu, X-ray crystallography and vibrational spectroscopy are the two techniques which have been employed in this study to establish the coordination properties of clge compounds.

1.4 The Chemistry of 1-Amidino-O-Alkylureas

1-Cyanoguanidine is subject to solvolysis by water to produce 1-carbamoylguanidine as described in Section 1.3. It is also known that solvolysis of cnge can be effected by alcohols in the presence of copper(II) salts.[24,25,26] Although this reaction has been known for many years, the exact identity of the products is unknown. Copper(II) complexes of 1-amidino-O-alkylureas (aOau) and 1-amidino-3-alkylureas (a3au) have both been proposed as the products of the reaction. Recent chemical evidence[27] favours the formation of aOau rather than a3au, but no data is available to indicate how the ligand is attached to the transition metal. Consideration of the C-N-O skeletons of aOau and a3au implies coordination modes that are comparable to bg, for aOau, and to clge, for a3au.



aOau



a3au

Despite the availability of these results in the literature, it has been recently reported, on the basis of a study of the reaction of cnge with copper(II) salts in refluxing ethanol, that solvolysis did not occur, the products being described as copper(II)-cnge complexes.[28]

In this study X-ray diffraction methods have been used to determine the identity of the products and the mode of coordination of the ligands.

The kinetics and mechanisms of the alcoholysis of cnge in the presence of copper(II) salts have not been studied. Structural details of complexes that can be isolated from a reaction mixture are obviously of value in determining the species present in solution. Techniques which examine the solution state are, however, much more effective. Consequently, in situ infrared and

UV-visible spectroscopic methods have been used to examine this reaction.

1.5 Chemistry of the Copper(II) Ion

1.5.1 Simple copper(II) compounds

Copper (Cu) (electronic configuration (Ar)$3d^{10}4s^1$) is known with oxidation states I, II, III and IV. Most common are oxidation states I to III with IV being known for a single hexafluoro complex.[29]

Under normal conditions copper(II) compounds are favoured. Thus copper(I) is fairly readily oxidised to copper(II) whilst further oxidation to copper(III) is more difficult.

Copper(II) compounds have been exclusively studied in this thesis.

A large number of simple copper(II) salts can be formed which are predominantly water soluble and often crystallize as hydrates. The best known salt, $CuSO_4.5H_2O$ (blue vitriol), is widely used in industry for electroplating, as a fungicide for crops (Bordeaux mixture) and as an algicide for water treatment. Indeed, the latter property of copper was unknowingly utilized in ancient Persia where, by law, drinking water had to be stored in bright copper vessels.

The aqueous solutions are blue in colour due to the formation of the $[Cu(H_2O)_6]^{2+}$ ion and are prone to slight hydrolysis. Unless stabilised by small amounts of acid they will deposit basic salts.

1.5.2 Copper(II) Complexes

Copper(II) will form complexes with mono and multidentate ligands, particularly those with nitrogen or oxygen ligating atoms. Coordination numbers of four, five and six predominate, but regular geometries are rare. The vast majority of complexes are coloured with colours of purple-blue-green-yellow being frequently found. Varying either the coordination number or the type of ligand results in a colour change. Copper(II) complexes also exhibit paramagnetic properties corresponding to one unpaired electron or less.

To account for the irregular geometries and interpret the spectral and magnetic properties, it is necessary to consider the ground and excited electronic states of the copper(II) ion in a variety of environments.

The copper(II) ion has a $3d^9$ outer electronic configuration. The unpaired electron present has an orbital angular momentum quantum number (l) of 2 and as there is only one unpaired electron the total orbital angular momentum (L) is 2, implying a D spectroscopic state. The total spin angular momentum (S) is $\frac{1}{2}$ and therefore the spin multiplicity, given by 2S+1, is 2. Hence, the free copper(II) has a ^2D state.

To examine how the spectroscopic state is affected by coordination, it is first necessary to examine the symmetry properties of the d orbitals in crystal fields of varying symmetry. The relative energy levels of the d orbitals must then be determined and then the spectroscopic states may be evaluated by filling the orbitals with the nine d electrons of copper(II).

The principles of this analysis are easily demonstrated by firstly considering the copper(II) ion in an octahedral environment and then tetragonally elongating the octahedron to produce coordination symmetries closely related to the structures determined in this thesis.

In an octahedral (O_h) environment, the energy of the d orbitals is increased and they are split into two groups (Figure 1.2). The d_{z^2} and $d_{x^2-y^2}$ are increased in energy more than the d_{xy}, d_{xz} and d_{yz} as the former pair point directly at the ligands, whilst the latter trio point between the ligands. It can be shown that the

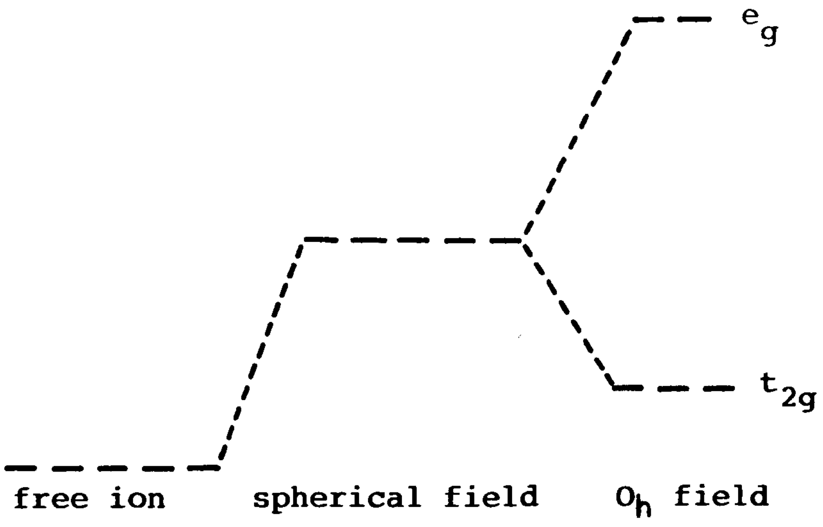
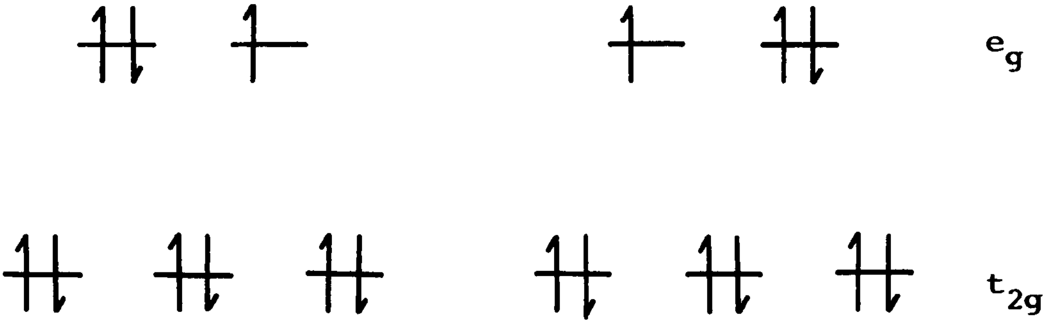
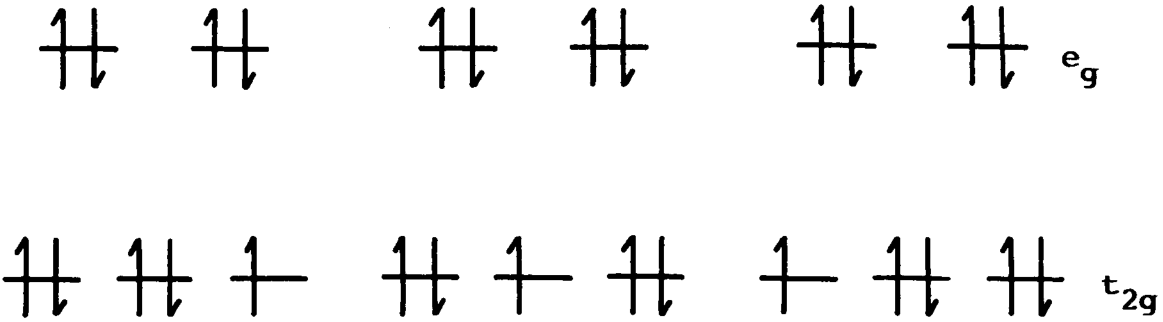


FIGURE 1.2 The splitting of the d orbitals in an O_h crystal field

d_{z^2} and $d_{x^2-y^2}$ have e_g symmetry, whilst the d_{xy}, d_{xz} and d_{yz} have t_{2g} symmetry. If the d orbitals are now filled with nine electrons then the ground state can be established as shown below:-



There are two possible ground state arrangements with spin multiplicity 2 and, therefore, the ground state is ^2E_g. By a transition of one electron from the t_{2g} to e_g orbitals, the excited state can be determined as shown below:-



There are three possible excited state arrangements with spin multiplicity 2 and therefore the excited state is $^2T_{2g}$.

It can now be seen that the symmetry of the state is the same as the symmetry of the orbital which contains the one unpaired electron.

The irregular geometries that are found for virtually all copper(II) complexes can be primarily ascribed to the Jahn-Teller effect.

The Jahn-Teller Theorem states that a molecule in a degenerate electronic state will be unstable and will undergo geometrical distortion that lowers its symmetry and splits the degenerate electronic state.

The copper(II) ion in a regular O_h field has been shown to exist in a degenerate ground state ^2E_g, hence this moiety is expected to be unstable and distortion from a regular geometry should occur. The nature of the distortion is most easily understood by considering complex formation from the ligands' point of view.

As well as the splitting of the d orbitals of the free metal ion by the ligands, there is a corresponding repulsion of the ligands by the d electrons. If the d orbitals are unsymmetrically occupied, as is the case with the d^9 system of copper(II), then the repulsions are unsymmetrical and some of the ligands will be prevented from approaching the metal ion as closely as others, resulting in distortions from regular O_h geometry. The effect will be greatest in those orbitals which point directly at the ligands. Hence, if the d_{z^2} orbital contains one more electron than the $d_{x^2-y^2}$ then the resulting distortion is an elongation of the octahedron along the z-axis. However, if the $d_{x^2-y^2}$ has the extra electron then elongation along x and y results.

The most commonly observed geometry of the complexed copper(II) ion is that caused by elongation of the octahedron along the z-axis giving rise to the so-called tetragonally elongated octahedron.

The two axial ligands of a metal ion in a tetragonally elongated O_h stereochemistry have been described as 'semi-coordinated' implying that they are only weakly bonded to the metal ion.[30] As a measure of the magnitude of this tetragonal distortion, the concept of the tetragonality (T) of a complex has been defined as the ratio of the short equatorial (R_S) to long axial (R_L) metal to ligand bond distances.

$$\text{Hence,} \qquad T = \frac{R_S}{R_L}$$

If the value of T lies in the ranges ~0.90–~0.75 or ~0.66–~0.56, the geometries are considered to be tetragonally distorted O_h or square coplanar stereochemistries respectively. A value of 1.0 corresponds to a regular O_h geometry.

The concept of tetragonality is used where appropriate in the description of the copper(II) structures discussed in this work.

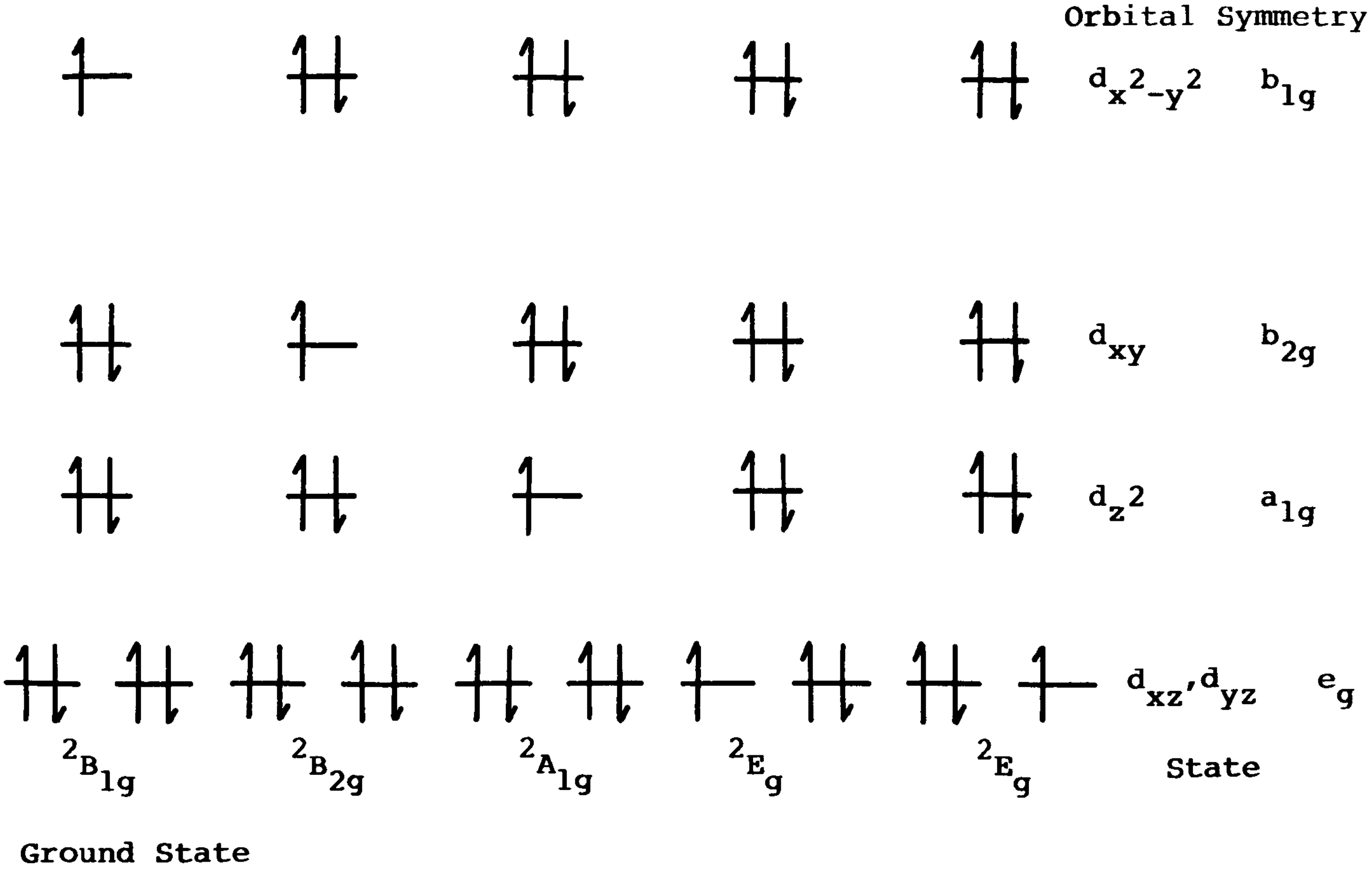
Tetragonal distortion of the O_h environment by axial elongation with results in the symmetry point group D_{4h}, in which the d orbitals have the following symmetry:-

d_{z^2} :- a_{1g} $d_{x^2-y^2}$:- b_{1g}

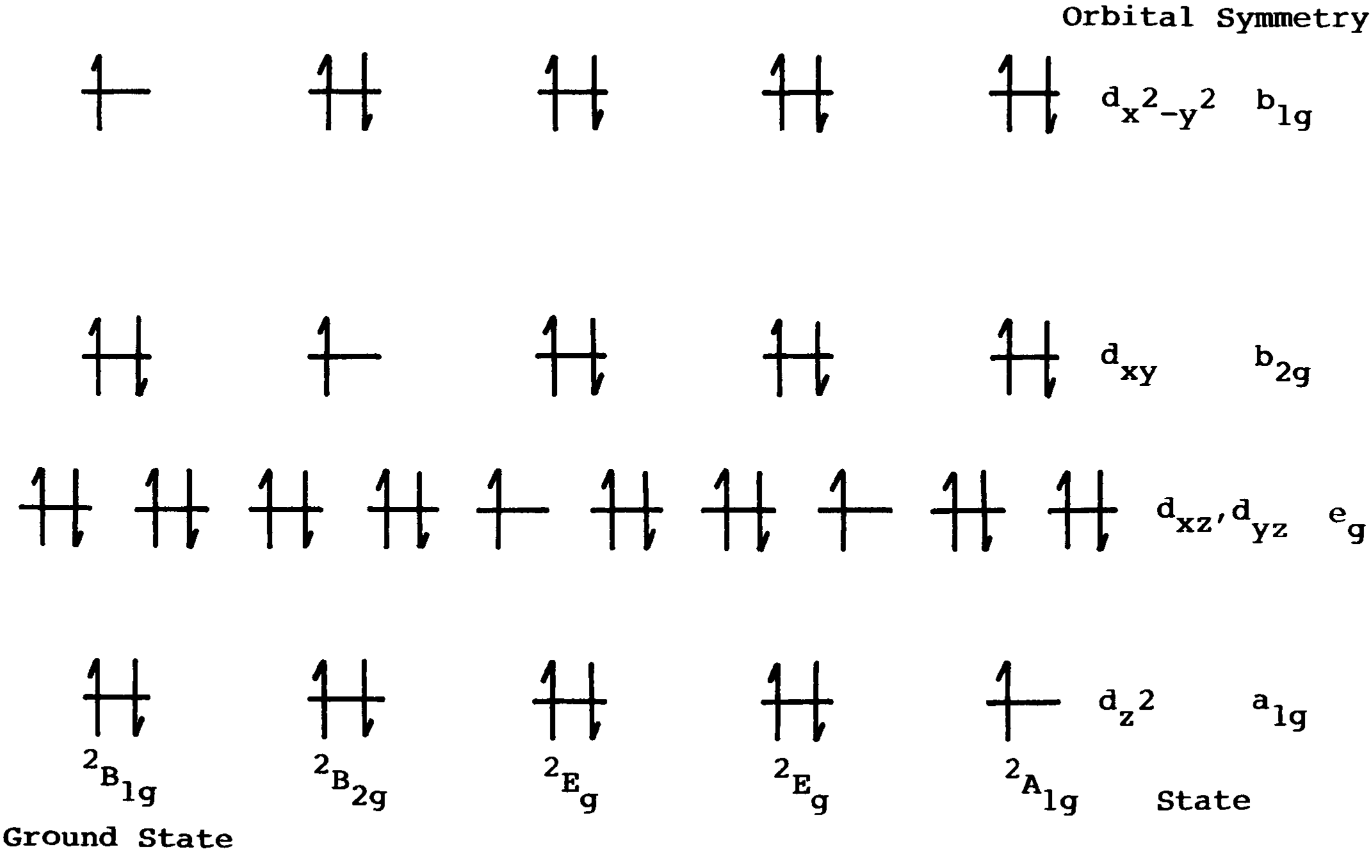
d_{xy} :- b_{2g} $d_{xz,yz}$:- e_g

By consideration of the relative repulsions between the d orbitals and the ligands, it is found that tetragonal elongation further splits the energies of the d orbitals, the $d_{x^2-y^2}$ and d_{xy} levels being destabilized and the d_{z^2}, d_{xz} and d_{yz} levels being stabilized relative to the O_h levels[30] (Figure 1.3).

For a tetragonal O_h coordination geometry, the five possible arrangements of the nine d electrons are shown below, together with the derived states.



For square planar coordination geometry the procedure can be repeated.

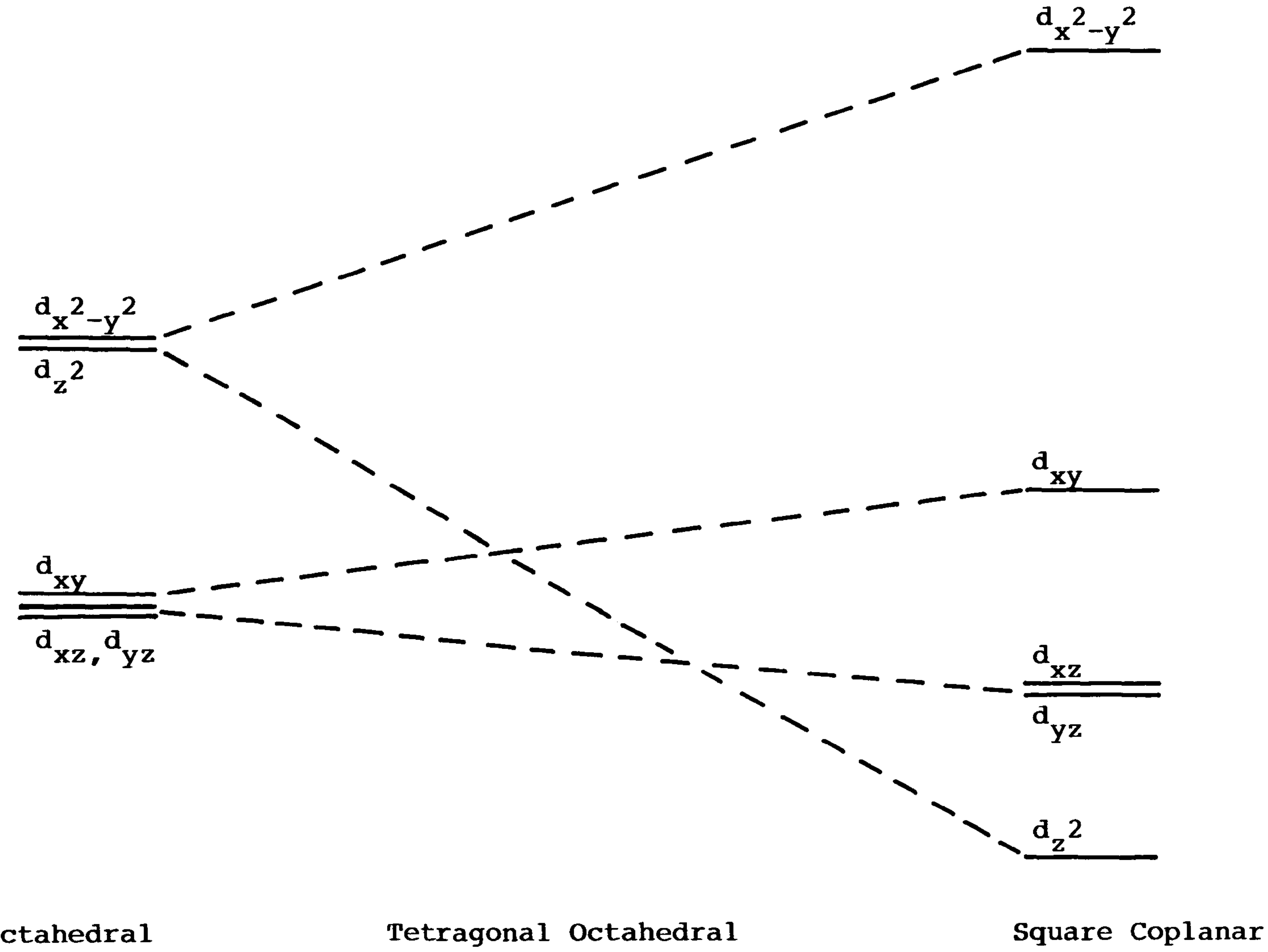


Having established the nature of the ground and excited electronic states of the copper(II) ion in a variety of environments, it is now possible to understand its spectroscopic properties.

Transitions can be envisaged between the ground and excited states of the metal ion. Thus, for a copper(II) ion in an O_h environment one transition ($^2T_{2g} \leftarrow {}^2E_g$) is possible and hence one absorption band should be observed. On tetragonal distortion, geometries of D_{4h} are formed. Three transitions from the $^2B_{1g}$ ground state are possible:

$$^2B_{2g} \leftarrow {}^2B_{1g}, \quad {}^2E_g \leftarrow {}^2B_{1g}, \quad {}^2A_{1g} \leftarrow {}^2B_{1g}$$

FIGURE 1.3 Changes in the electronic energy levels of a copper(II) ion in an octahedral crystal field subjected to increasing tetragonal distortion



with the relative energy of each transition varying as the distortion changes. The d_z2, d_{xy}, d_{xz} orbitals are, however, close in energy throughout the tetragonal distortion and so it follows that the three transitions are of very similar energy. Experimental spectra for complexes with the copper(II) ion in tetragonal octahedral or square coplanar environments all show one broad absorption in the visible region which is considered to be due to the overlapping of the absorption bands due to the three transitions.

For simplicity this analysis has considered the six ligands to be equivalent. The structures determined in this work do not completely satisfy this condition. However, for each structure the ligating atoms are usually similar and at comparable distances from the copper(II) ion. Hence, deviation from this analysis are usually minor. The most common deviation results in C_{2h} symmetry which gives four possible absorptions all close in energy as before. In all cases only one broad band is observed in the visible region. The wavelength of the absorption does vary with changing ligands and coordination number, and so it is possible to qualitatively distinguish between the various complexes.

The paramagnetic properties of the copper(II) ion may now be explained by considering the ground state of the ion.

The magnetic properties of any individual ion or atom will result from some combination of the magnetic moment due to the spinning of the electron on its own axis, the spin moment, and the magnetic moment induced by the electron orbiting the nucleus, the orbital moment. If ions or atoms are sufficiently close then interactions may occur between electrons on adjacent atoms, affecting the magnetic properties.

In magnetically dilute copper(II) complexes, with O_h or D_{4h} symmetries, the effective magnetic moment is given by the spin only value (μ_s) as the ground state ^2E_g or $^2B_{1g}$ does not permit any orbital contribution

$\mu_s = g\sqrt{S(S+1)}$ S = spin = $\frac{1}{2}$

g = gyromagnetic ratio = 2.00

μ_s = 1.73 Bohr magnetons

Experimental values show good agreement with the μ_s value.

In non-magnetically dilute copper(II) complexes the individual copper(II) ions are relatively close {e.g. $[Cu(CH_3CO_2)_2H_2O]_2$ r(Cu-Cu) = 2.64 Å} and spin-spin interactions can occur. These interactions give rise to a molecular spin singlet (S = 0) and triplet (S = 1). If the ground state is the singlet then the interaction is said to be antiferromagnetic, whilst if the triplet is the ground state then the interaction is said to be ferromagnetic. Since the energy gap between the states (J) is relatively small, complexes may be classified by following their magnetic susceptibilities (χ_m) as a function of temperature (T). If $\chi_m.T$ increases on cooling (corresponding to increased population of the triplet ground state) the interaction is ferromagnetic, whilst if χ_m.T decreases on cooling (corresponding to increased population of the singlet ground state) the interaction is antiferromagnetic.

Complexes in which magnetic interactions occur between copper(II) ions have been recently reviewed in detail by Kahn,[31] they are, however, beyond the scope of this thesis and have not been examined.

1.6 **Physical Methods of Structural Analysis**

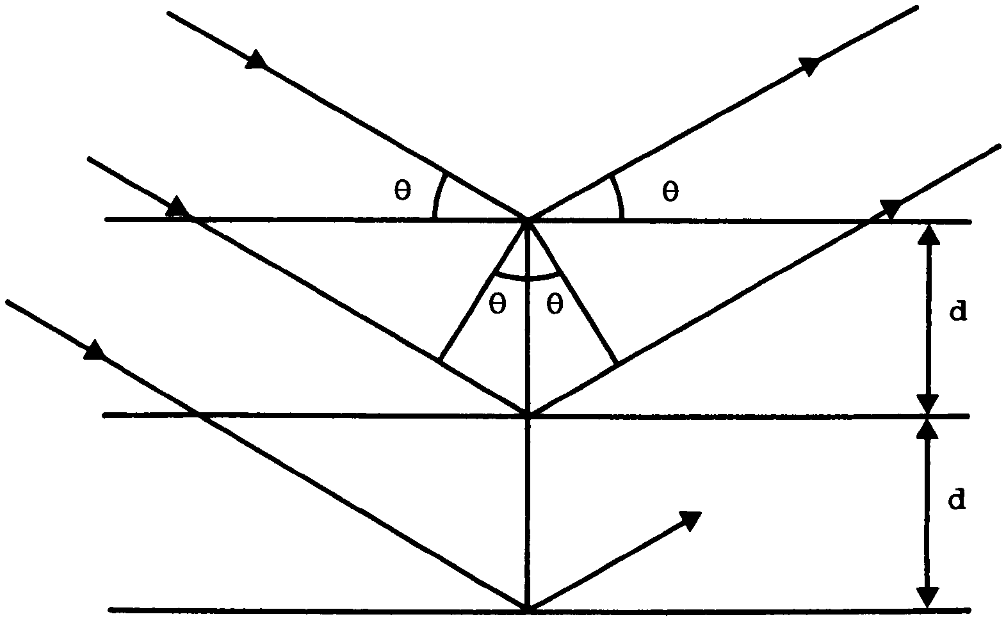
1.6.1 X-ray crystallography

Of all the methods available for structural analysis, one of the most powerful techniques is X-ray crystallography. The technique is limited to the solid crystalline state, although in practice it is possible to use the results to facilitate interpretation of reaction kinetics and mechanisms occurring in other phases.

In the crystalline state, molecules are arranged in a regular three-dimensional array or lattice which may possess a variety of symmetry elements. The lattice nature of the crystal enables it to diffract electromagnetic radiation of a suitable wavelength (X-radiation), according to Bragg's Law, which is illustrated in Figure 1.4. Reinforcement of diffracted rays will occur only when the difference in path length of the rays scattered from different underlying lattice planes (2d sinΘ) is an integral number of wavelengths($n\lambda$).

Thus, $n\lambda = 2d \sin\Theta$.

FIGURE 1.4 Geometrical derivation of the Bragg equation for the reflection of X-rays from a crystal, considered to be an array of parallel equidistant layers of scattering material



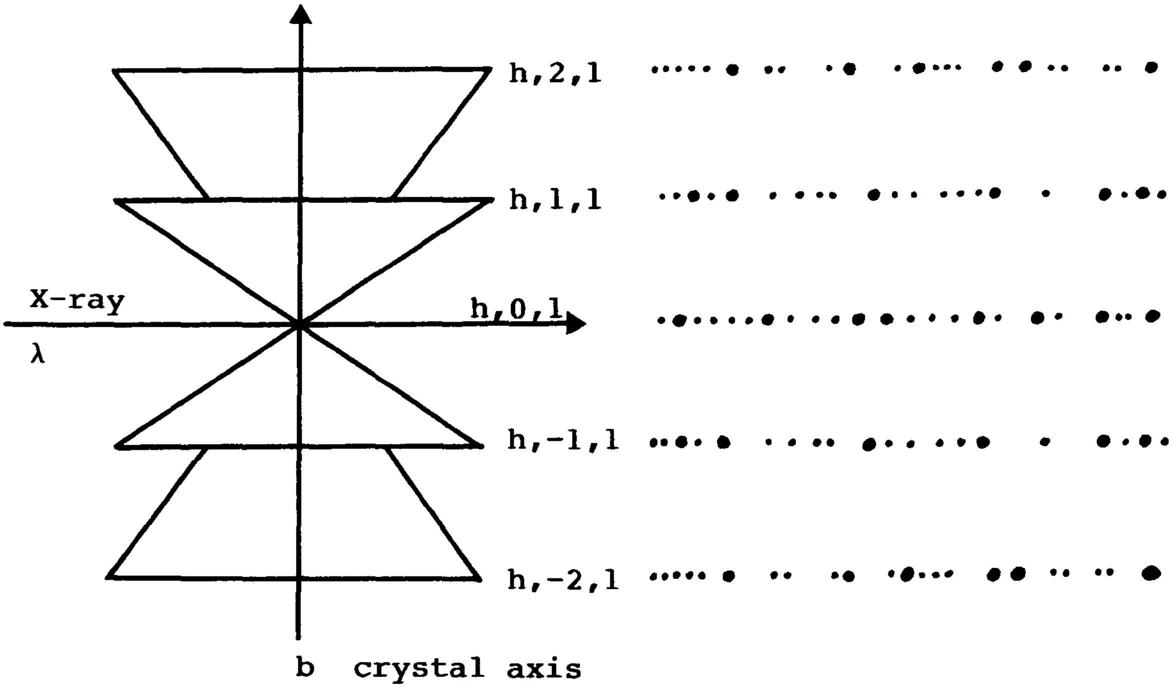
The basic repeating unit of the crystal lattice is the unit cell, which is defined by three vectors, $\underline{a},\underline{b},\underline{c}$, having magnitudes a,b,c, and relative directions defined by the angles α,β,γ. A lattice plane capable of diffracting X-rays must intersect with the unit cell axes ($\underline{a},\underline{b},\underline{c}$) at the points $\underline{a}/h$, $\underline{b}/k$, $\underline{c}/l$, where h,k,l are known as the Miller indices and are necessarily integral quantities. The resulting plane is defined by the notation h,k,l and X-rays reflected from a series of these planes are indexed by the same values. On the basis of the a,b,c,α,β,γ values and the symmetry elements contained in the unit cell, the cell can be classified into one of seven crystal systems, fourteen Bravais lattices and two hundred and thirty space groups.

Determination of the space group of a crystal involves the recognition of its symmetry elements in the diffraction pattern when irradiated by a monochromatic beam of X-rays. The main techniques used for preliminary determination of a,b,c,α,β,γ and space group in this work were oscillation and Weissenberg methods.

For an oscillation photograph the crystal is mounted such that a direct axis is perpendicular to the incident X-ray beam. The crystal is then oscillated by *ca*. ±10° about this axis and the diffracted X-rays are recorded on a cylindrical film coaxial with the oscillation axis. This photograph (Figure 1.5) is a series of parallel lines of spots, called layer lines, resulting from a series of lattice planes in which one Miller index remains constant. From the distance beween the two layer lines it is possible to determine the magnitude of the axis about which the crystal is oscillating. Also is is possible to determine whether the crystal axis is perpendicular to a mirror symmetry element in the lattice.

The next stage in the determination is to obtain photographs using the Weissenberg method. In this method a single layer line is selected by a slotted screen which stops all other diffracted beams from reaching the film. As the crystal is rotated through *ca*. 180° the film is moved past the slot and reflections which occur at different times are recorded at different points on the film. Weissenberg photographs of the zero and first

FIGURE 1.5 The oscillation photograph



layer lines are recorded. From these photographs it is possible to measure the magnitude of the remaining axes and the angles between them and so determine the crystal class. The presence of any symmetry elements and the systematic absence of certain reflections can now help in the choice of space group.

To further narrow down this choice, a knowledge of the number of formula units per unit cell (Z) is useful. This may be calculated from the equation,

$$D = \frac{MZ}{LU}$$

where, D = density of the material

M = relative molecular mass of the material

Z = number of formula units per unit cell

L = Avagadro's number

U = volume of unit cell

U can be calculated from the unit cell dimensions and angles but D must be measured by an independent method.

The density of the crystalline material can be determined by a flotation method. The crystals are suspended in a mixture of two miscible liquids in which the material is insoluble. The proportions of the two liquids are adjusted until the crystals possess neutral bouyancy and the density of the liquid mixture is measured by weighing a known volume. This density is the same as the density of the crystalline material and hence the number of formula units per unit cell can be calculated.

Hexane-bromoform mixtures were used in all the density determinations in this thesis.

The unit cell dimensions obtained from the oscillation and Weissenberg photographs were redetermined and refined by a least squares procedure using ca. 20 strong reflections accurately measured on a Hilger and Watts Y290 four circle diffractometer unless otherwise stated. After refinement of the cell dimensions, one unique set of intensity data was collected on the diffractometer using graphite monochromated MoK_α radiation, normally in the range $0° \leq \theta \leq 25°$. Three standard reflections were monitored every hundred reflections measured and in all cases these remained constant indicating that the crystals were stable.

The intensities were corrected for Lorentz and polarisation effects but not for absorption as there were minimal numbers of heavy atoms in the compounds and crystal sizes were small. Reflections were considered to be observed if their intensities (I) were greater than three times their standard deviations (σ_I), [where σ_I = (total background count + integrated count)$^{\frac{1}{2}}$].

Due to the wavelength of X-rays, it is not physically possible to resynthesize the image of the crystal lattice. Instead, the process can be done mathematically by the Fourier transform method. This is possible because the electron density in the crystal lattice, which is in real space, is the Fourier transform of the diffraction pattern in reciprocal space. The equation that relates the electron density [$\rho(x,y,z)$] to the intensity of the diffracted X-rays [$I(h,k,l)$], is of the form:

$$\rho(x,y,z) = \frac{1}{U} \Sigma\Sigma\Sigma F(h,k,l)\exp[-2\pi i(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c})]$$

where, the structure factor, $F(h,k,l) \propto \sqrt{I(h,k,l)}$. The term $I(h,k,l)$ is a vector quantity having both magnitude and phase of which only the former can be determined experimentally.

All but two of the crystal structures in this thesis contain copper atoms which are significantly heavier than other atoms in the complexes and, as such, constitute a high proportion of the total electron density. By locating the positions of the copper atoms in the structure, an approximation to the phases of the reflection data can be determined. This method of locating the heavy atoms is a modification of the Fourier transform called a Patterson synthesis.

$$P(u,v,w) = \frac{1}{U}\ \Sigma\Sigma\Sigma\ |F(h,k,l)|^2 \exp[-2\pi i(\frac{hu}{a} + \frac{kv}{b} + \frac{lw}{c})]$$

The quantity $|F(h,k,l)|^2$ is phaseless and hence the distribution in Patterson space can be determined directly from the intensity data. Maxima in the quantity P(u,v,w) represent interatomic vectors and their intensities are proportional to the products of the atomic numbers of the two atoms concerned. Those between two heavy atoms, i.e. Cu...Cu, will be prominent and hence the positions of the heavy atoms in the unit cell can be determined.

After location of the heavy atoms, the lighter atoms can be located by a difference Fourier map phased on the positions of the heavy atoms.
i.e.:

$$\rho_{obs}-\rho_{calc} = \frac{1}{U}\ \Sigma\Sigma\Sigma(F_{obs}-F_{calc})\exp[-2\pi i(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c})]$$

In structures where no heavy atoms are present, it is necessary to use direct methods to determine the location of the atoms. Direct methods depend on the application of mathematical relationships to determine the phases of the structure factors. Any atoms not located by direct methods can be found using a difference Fourier map in a similar manner to that defined above.

In both heavy atom and direct methods refinement of the structure is effected by minimising the function:

$$\sum W(|F_{obs}| - |F_{calc}|)^2$$

where, W is a weighing factor. The criterion used for judging the agreement between the observations and the proposed structure is the so-called R value, where,

$$R = \frac{\Sigma \left| |F_{obs}| - |F_{calc}| \right|}{\Sigma |F_{obs}|}$$

The MULTAN 80 series of programs[32] were used for direct methods, whilst all other crystallographic calculations were performed using the CRYSTALS suite of programs.[33]

Standard texts on practical X-ray crystallography which have been found to be most useful are Stout and Jensen[33a] and Buger.[33b]

1.6.2 Vibrational Spectroscopy

Infrared spectra (4000-400 cm^{-1}) were obtained for solid samples in nujol and halocarbon mulls and in potassium bromide discs using a Perkin Elmer 598 grating spectrometer. Spectra of solution samples contained in a cell with sodium chloride windows were obtained using a Perkin Elmer 683 grating spectrometer controlled by a 3600 data station.

Where possible, group theory has been used to examine the spectra and assignments have been made to try to elucidate structural features. Although unequivocal assignments of the bands is difficult, the infrared spectra can be used for identification of the complexes.

1.6.3 Ultraviolet-Visible Spectroscopy

A Perkin Elmer Lambda 5 UV-visible spectrometer with thermostatted cell holders has been used to follow the visible absorption spectrum of the reaction in alcohol solution of copper(II) salts with 1-cyanoguanidine. Characteristic absorption bands have been observed and the kinetics and mechanism of this reaction have been investigated.

Diffuse reflectance UV-visible spectra have been measured for several copper(II) complexes using the above spectrometer. Unlike the solution data, these results are used in a qualitative rather than quantitative manner.

CHAPTER TWO

COPPER(II) COMPLEXES OF 1-CYANOGUANIDINE

2.1 Introduction

Although several transition and alkali metal complexes of 1-cyanoguanidine*(cnge) have been reported, structural and spectroscopic data are limited. The most extensively investigated complexes are those of the cadmium(II) cation.[34]

Structure determinations of cadmium(II)-cnge complexes have shown cnge to act as either a monodentate ligand, in $[Cd(cnge)_2I_2]$,[35] or a bridging bidentate ligand, in $[Cd(cnge)Cl_2]$[36] and $[Cd(cnge)(H_2O)_2(SO_4)]_2$,[34] and that there are changes in the molecular geometry and electronic structure of the ligand on coordination. These changes are manifest in the vibrational spectrum of free and coordinated cnge.

There is a paucity of data available in the literature on copper(II)-cnge complexes, possibly owing to the facile solvolysis of the nitrile group in the presence of copper(II) cations. After an early report of the synthesis of $Cu(cnge)_2SO_4.4H_2O$,[37] fifty years elapsed before $Cu(cnge)_2SO_4.5H_2O$ was prepared as an intermediate during a study of the copper(II) catalysed addition of alcohols to cnge.[25] Dehydration of this latter material at 50°C under vacuum resulted in the corresponding dihydrate. Subsequently, $Cu(cnge)_2(NO_3)_2.2H_2O$ was obtained as a by-product of the attempted solvolysis of

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* Chemical Abstracts Registry Number [461-58-5].

cnge by isopropanol or phenyl-2-ethanol in the presence of $Cu(NO_3)_2.3H_2O$.[38] Other than chemical analytical and electronic absorption spectroscopic data, very few physicochemical characteristics have been reported for these materials.

Structural information has since been published for $[Cu(cnge)_2Cl_2(H_2O)_2]$,[39] which was crystallised from aqueous solution, and for $[Cu(cnge)(aebg)]SO_4.H_2O$ (aebg = 1-(2-aminoethylbiguanide),[40] which was serendipitously obtained from the mother liquor remaining from the preparation of ethylene-bis(biguanide) copper(II) sulphate. In both complexes the cnge ligand is effectively monodentate despite the location of the N(2) atom of the cnge molecule in the latter complex in one of the axial positions above the square planar copper(II) coordination sphere. This contact is quite remote, r(Cu ...N) = 3.14 Å (cf. the van der Waals radii[41] of Cu (1.43 Å) and N (1.55 Å) and cannot be considered a strong bonding interaction as in $[Cd(cnge)Cl_2]$[36] or $[Cd(cnge)(H_2O)_2SO_4]_2$[34] since the lone pair on N(2) is not directed at the copper atom but is involved in the intermolecular hydrogen bonding interactions.

Subsequently, the preparation of the anhydrous compounds, $Cu(cnge)_4X_2$ (X = Cl, Br, ClO_4) and $Cu(cnge)_2X_2$ (X = Cl, Br, NO_3, NCS) in ethanol has been claimed.[28] Analytical, conductance, magnetic susceptibility and electronic absorption spectroscopic data are quoted for these compounds. This report is surprising in view of the facile solvolysis of the nitrile group of the cnge molecule.

Most recently the electroreduction of an aqueous solution of $Cu(cnge)_2SO_4.5H_2O$ has been reported, together with the infrared spectrum of the complex.[42]

In this work the possibiliy of correlating the infrared spectrum and the mode of coordination of cnge to the copper(II) ion, has been investigated. Several copper(II)-cnge complexes have been prepared and their infrared spectra recorded. Also the crystal and molecular structure of bis(1-cyanoguanidine)-di-μ-aquocopper(II) dinitrate dihydrate $\{[Cu(cnge)_2(H_2O)_2]-(NO_3)_2.2H_2O\}$ has been determined.

Ideally, any attempted correlation of spectroscopic and structural properties of coordinated cnge should be based on the three complexes for which structural data are now available, $[Cu(cnge)_2(H_2O)_2](NO_3)_2.2H_2O$, $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $[Cu(cnge)(aebg)]SO_4.H_2O$. Unfortunately, despite repeated attempts, it was not possible to repeat the serendipitous preparation of $[Cu(cnge)(aebg)]SO_4.H_2O$; furthermore, attempts to synthesize the compound by first producing the aebg ligand proved to be unsuccessful. Consequently, for this thesis it was only possible to base the correlation on the former two complexes.

2.2 Experimental

Copper(II)-(1-cyanoguanidine) salts were prepared by the reaction of the requisite molar ratio of cnge and the appropriate copper(II) salt. The copper(II) salt and the cnge were each dissolved in the minimum of hot deionised water. A typical synthesis used 20mmol of the copper(II) salt and 40mmol of cnge. The solutions were mixed and a trace of acid, appropriate to the copper(II) salt, added to prevent precipitation of the basic copper(II) salt. The resulting solution was cooled in ice to facilitate precipitation. The precipitate was filtered off, washed with a little ice-cold deionised water and dried over silica gel for 12 hrs.

This method produced hydrated complexes: lower hydrates and anhydrous complexes were produced by dehydration in an oven with high vacuum facilities as required (see Section 2.4).

Anhydrous copper(II)-cnge chloride and bromide complexes were also prepared by using dry acetone instead of deionised water as a solvent. However, the low solubilities of the copper(II) salts and cnge in acetone necessitated a different method of synthesis.

The anhydrous copper(II) salt (10mmol; 1.34g $CuCl_2$:2.22g $CuBr_2$) and cnge (20mmol; 1.68g) were powdered together in a mortar and pestle. The mixture was added to acetone, previously dried by distillation from a P_2O_5/acetone mixture, and refluxed for 1 hour. The suspended solids were filtered off, washed with dry acetone and dried under a vacuum.

Deuterated hydrated complexes were obtained by repeated solution of the samples in D_2O, under a nitrogen blanket, followed by removal of the excess water under vacuum.

2.3 **The Crystal and Molecular Structure of Bis(1-Cyanoguanidine)Diaquocopper(II)Dinitrate Dihydrate**

2.3.1 Structure solution and crystal data

Needle-like crystals of the title compound were obtained by slow evaporation of an aqueous solution at room temperature. A suitable crystal (0.6 x 0.1 x 0.1 mm) was mounted at the end of a glass fibre with 'Araldite' adhesive.

Cell parameters, space group and X-ray diffraction data, were obtained as described in Section 1.6.1. Of the 1392 intensities collected, 705 were deemed to be observed.

Taking into account the molecular formula allied with the crystal symmetry, suggested that the copper atom must be situated in a special position (0,0,0) of the $P\bar{1}$ space group and that pairs of cnge molecules, nitrate anions and water molecules must be located in centrosymmetrically related positions. Consequently, following the data reduction stage, the positions of the carbon, nitrogen and oxygen atoms were determined by a difference Fourier synthesis. Full matrix least squares refinement with anisotropic temperature factors for all these atoms convered at R = 0.077. Attempts to locate

TABLE 2.1 Analytical Data for Copper(II)-cnge Complexes

Complex	Experimental/Theoretical %		
	C	H	N
$[Cu(cnge)_2(H_2O)_2](NO_3)_2 2H_2O$	11.02/11.23	3.71/3.74	32.25/32.74
$Cu(cnge)_2(NO_3)_2 2H_2O^a$	12.09/12.26	3.07/3.07	32.26/32.76
$Cu(cnge)_2(NO_3)_2{}^a$	13.47/13.50	2.29/2.25	38.92/39.38
$Cu(cnge)_2(SO_4)5H_2O$	11.35/11.50	4.21/4.31	26.48/26.83
$Cu(cnge)_2(SO_4)2H_2O^a$	13.24/13.20	3.16/3.30	30.58/30.81
$Cu(cnge)_2(SO_4)^a$	14.37/14.65	2.60/2.44	33.60/32.20
$[Cu(cnge)_2Cl_2(H_2O)_2]$	14.04/14.18	3.71/3.55	33.39/33.09
$Cu(cnge)_2Cl_2{}^a$	15.59/15.87	2.60/2.64	36.78/37.02
$Cu(cnge)_2Cl_2{}^b$	15.91/15.87	2.61/2.64	36.90/37.02
$Cu(cnge)_2Br_2 2H_2O$	11.39/11.23	2.72/2.81	26.51/26.20
$Cu(cnge)_2Br_2 0.5H_2O^a$	12.02/11.99	2.11/2.25	28.07/27.97
$Cu(cnge)_2Br_2{}^a$	12.04/12.27	2.27/2.04	28.33/28.62
$Cu(cnge)_2Br_2{}^b$	12.34/12.27	2.15/2.04	28.85/28.62

a:- Products of dehydration.

b:- Products of anhydrous reaction.

the positions of the hydrogen atoms by subsequent difference Fourier syntheses were unsuccessful. The positions of the cnge hydrogen atoms were defined using a hydrogen placing routine by analogy with the structures of the free molecule [r(C-H) = 1.00 Å, U(ISO) = 0.05 $Å^2$]; those of the water hydrogen atoms were not determined. Further refinement of the structure with fixed hydrogen atoms converged at R = 0.075. Final positional parameters and thermal parameters are given in Tables 2.2 and 2.3 respectively. Observed and calculated structure factors are included in Appendix B.

Crystal Data

$C_4H_{16}N_{10}O_{10}Cu$, M = 427.8, triclinic, space group $P\bar{1}$, a = 3.508(2), b = 10.201(3), c = 11.927(3) Å, α = 102.45(3), β = 101.58(3), γ = 101.60(3)°, U = 394.67 $Å^3$, D_m = 1.82 $g.cm^{-3}$, D_c = 1.80 $g.cm^{-3}$ for Z = 1, F(000) = 219, $\mu(MoK_\alpha)$ = 15.18 cm^{-1}.

2.3.2 Intermolecular contacts and the coordination of the copper(II) ion

Views of the structure of the complex perpendicular to (120) and to (001) are shown in Figures 2.1 and 2.2 respectively. Figure 2.1 also gives the atom numbering scheme. It comprises a series of planes parallel to (120) which contain $[Cu(cnge)_2(H_2O)_2]^{2+}$ cationic fragments and the nitrate anions, both of which are effectively planar, together with the free water

TABLE 2.2 Final Positional Parameters (x 10^3)

Atom	x/a	y/b	z/c
Cu(1)	0	0	0
C(1)	146(3)	61(1)	271(1)
C(2)	343(3)	189(1)	466(1)
N(1)	129(3)	35(1)	170(1)
N(2)	140(3)	75(1)	381(1)
N(3)	546(3)	303(1)	446(1)
N(4)	343(4)	188(1)	576(1)
O(1)	476(2)	146(1)	11(1)
O(2)	578(4)	709(1)	150(1)
N(5)	941(4)	443(1)	217(1)
O(3)	761(3)	328(1)	226(1)
O(4)	1041(4)	544(1)	308(1)
O(5)	1001(4)	457(1)	123(1)
H(1)	553	306	363
H(2)	694	387	513
H(3)	491	271	642
H(4)	193	102	592

TABLE 2.3 Final Thermal Parameters (x 10^3/Å^2)

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cu(1)	37(2)	20(1)	12(1)	4.0(9)	16(1)	0(1)
C(1)	34(7)	12(6)	26(6)	1(5)	2(5)	-9(5)
C(2)	14(6)	38(7)	23(6)	3(5)	-3(5)	3(5)
N(1)	41(7)	31(6)	14(5)	-2(4)	11(4)	2(5)
N(2)	37(6)	29(5)	19(5)	4(4)	8(4)	-2(4)
N(3)	41(7)	36(6)	28(5)	4(5)	10(5)	1(5)
N(4)	73(8)	27(6)	19(5)	-6(4)	17(5)	-9(5)
O(1)	32(5)	27(4)	30(4)	4(4)	6(4)	-3(4)
O(2)	109(9)	44(6)	35(5)	14(4)	23(6)	6(6)
N(5)	54(7)	26(6)	32(6)	1(5)	15(5)	-2(5)
O(3)	74(7)	32(5)	39(5)	5(4)	23(5)	-13(5)
O(4)	110(10)	47(7)	41(6)	-7(5)	15(6)	-14(7)
O(5)	101(9)	47(6)	35(5)	10(5)	22(6)	-4(6)

In the form: $[\exp -2\pi^2(U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)l^2c^{*2}+2U(12)hka^*b^*+2U(13)hla^*c^*+2U(23)klb^*c^*)]$

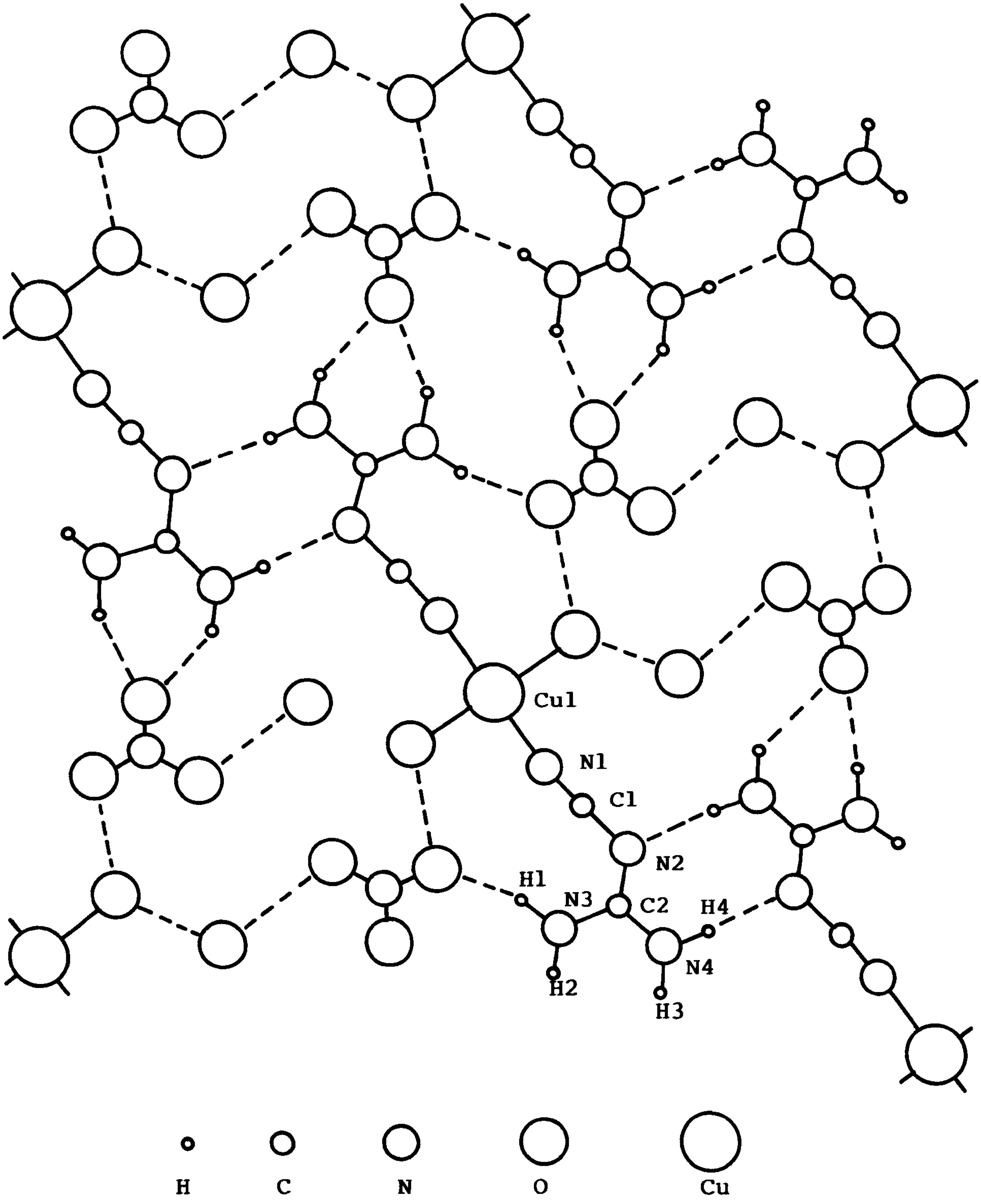


FIGURE 2.1 View of the structure of $[Cu(cnge)_2(H_2O)_2](NO_3)_2.2H_2O$ perpendicular to the (120) plane

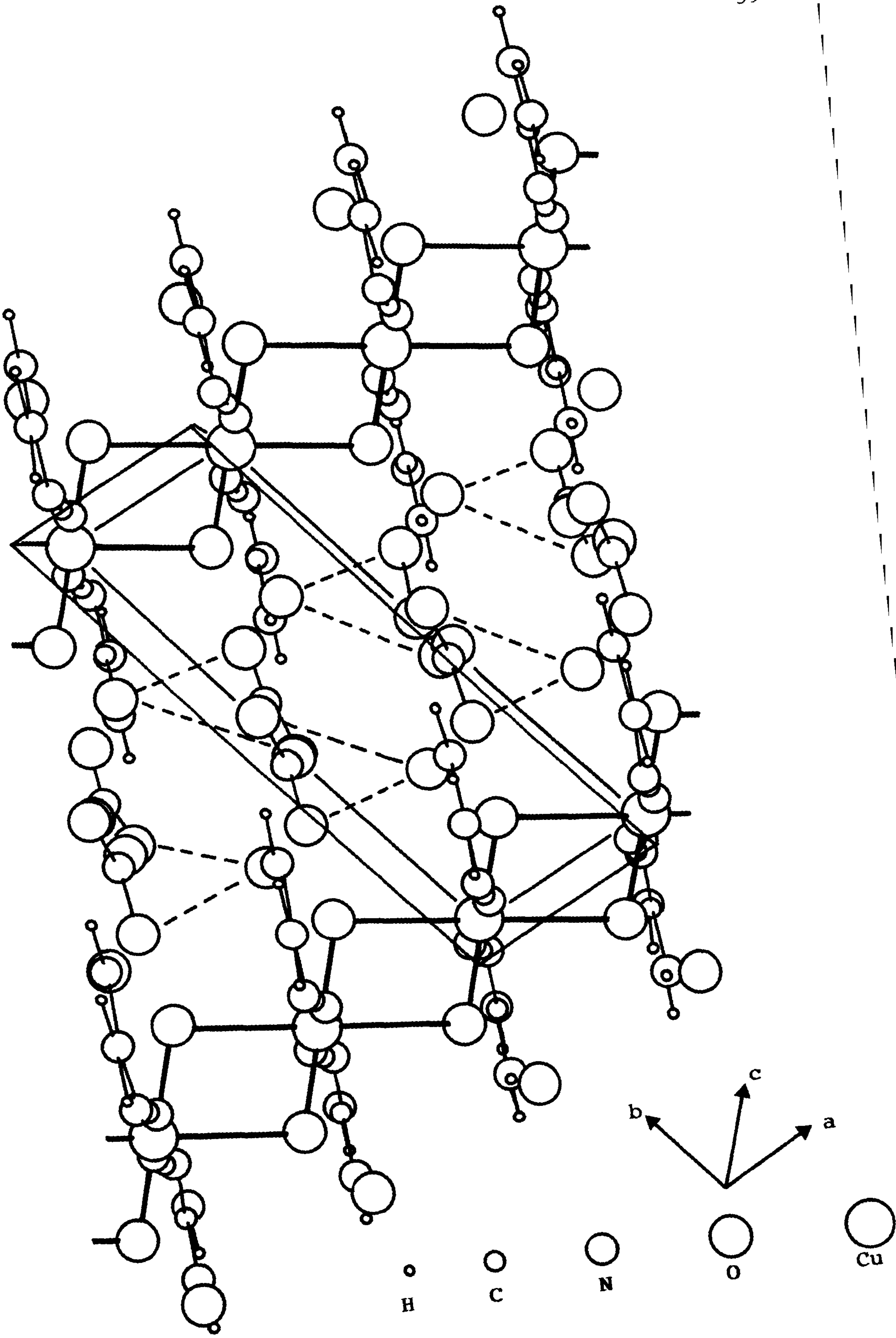


FIGURE 2.2 View of the structure of $[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ perpendicular to the (001) plane

molecules. Within the planes, the molecular units are held together by both electrostatic and hydrogen bonding interactions (Figure 2.1). The planes are linked by Cu-O bridging contacts supported by weak hydrogen bonding between the free water molecule and a nitrate anion (Figure 2.2). Full details of all intra- and inter-planar contacts under 3.30 Å are collated in Table 2.4.

The copper(II) ion is coordinated by the nitrile nitrogens of two centrosymmetrically related cnge molecules, [r(Cu(1)-N(1)) = 1.92 Å] and the oxygen atoms of two centrosymmetrically related water molecules, [r(Cu(1)-O(1)) = 1.96 Å], which form a square planar CuN_2O_2 unit (Figure 2.1). Axial positions above and below this square plane are occupied by the oxygen atoms of two more remote symmetry related water molecules located in two adjacent planes, [r(Cu(1)-O(1)') = 2.60 Å] (Figure 2.2). Assuming the ligating donor atoms to be equivalent then R_S is given by the average of r(Cu(1)-N(1)) and r(Cu(1)-O(1)) (1.94 Å), and R_L is given by r(Cu(1)-O(1)') (2.60 Å). Hence, the tetragonality (T) is 0.75 (Section 1.5.2). This value defines the coordination stereochemistry to be a tetragonally elongated octahedron.

The copper(II) ion's coordination geometry (Table 2.5) is similar to that in $[Cu(cnge)_2Cl_2(H_2O)_2]$.[39] The only difference is the replacement of the axial oxygen by chlorine atoms [r(Cu-Cl) = 2.87 Å, the CuN_2O_2 unit being

TABLE 2.4 Intermolecular Contacts of less than 3.30 Å; Hydrogen Bond and Electrostatic Interactions

Interaction X-H...X'	Symmetry Properties of X'	r(X...X') Å	r(X...H) Å	r(h...X') Å	XHX' °
N(1)...O(3)	x,y,z	3.19	-	-	-
N(3)-H(1)...O(3)	x,y,z	2.92	1.00	1.95	161
N(3)-H(2)...O(4)	2-x,1-y,1-z	2.92	1.00	2.04	145
N(4)-H(3)...O(4)	2-x,1-y,1-z	2.98	1.00	2.11	143
N(4)-H(4)...N(2)	-x,-y,1-z	3.07	1.00	2.07	177
N(4)...O(2)	1-x,1-y,1-z	3.15	-	-	-
O(1)-H...O(2)*	1-x,1-y,-z	2.67	-	-	-
O(1)-H...O(3)*	x,y,z	2.68	-	-	-
O(1)...O(5)	x,y,z	3.17	-	-	-
O(2)...O(4)	x,y,z	3.20	-	-	-
O(2)-H...O(5)#	1+x,y,z	2.84	-	-	-
O(2)...O(5)	x,y,z	3.21	-	-	-

* These contacts are designated hydrogen bond interactions not only because of the short interatomic distances, but also because of appropriate geometries for sp^3 hybridised O(1) (contacts to Cu(1), Cu(1)', O(2) and O(3)) and for sp^2 hybridised O(3) (contacts to N(5), N(3) and O(1)).

The geometry around O(2) is somewhat more complex but one acceptor (contact to O(1)) and one donor interaction (contact to O(5)) can be designated assuming sp^3 hybridisation.

almost identical [r(Cu-N) = 1.92 Å, r(Cu-O) = 2.00 Å].

TABLE 2.5 Coordination of the Copper(II) Ion

Bond distance/Å		Bond angle/°	
Cu(1)-O(1)	1.964(8)	O(1)Cu(1)N(1)	90.7(4)
Cu(1)-N(1)	1.922(9)	O(1)Cu(1)O(1)'	99.6(3)
Cu(1)-O(1)'	2.597(8)	N(1)Cu(1)O(1)'	89.6(4)

Symmetry properties of O(1)'; -1+x,y,z

2.3.3 Molecular geometry of the 1-cyanoguanidine ligand

The cnge ligand is effectively planar, the maximum deviation of the skeletal carbon and nitrogen atoms from the best plane being 0.06 Å (Table 2.6).

TABLE 2.6 Planarity of the cnge ligand

Atom	Deviation from plane/Å	Atom	Deviation from plane/Å
N(1)	+0.042	C(2)	-0.010
C(1)	-0.010	N(3)	-0.013
N(2)	-0.056	N(4)	+0.049

Equation of
best plane: $3.2163x - 5.6568y + 0.4515z = 0.254$

The molecular geometry of the cnge ligand is almost identical to that in $[Cu(cnge)_2Cl_2(H_2O)_2]$,[39] however, it differs considerably from that in [Cu(cnge)(aebg)]-$SO_4.H_2O$.[40] Bond distances and angles for the cnge ligand in these three complexes are collected together with those for free cnge in Table 2.7. It is clear that the C(1)N(2)C(2) bond angle is larger and the C(2)-N(2) bond distance shorter in the dinitrate and dichloro complexes than in the sulphate complex. The differing geometries may be due to the weak interaction in the latter complex between the copper atom and the axially located imino nitrogen atoms, r(Cu(1)...N(2)) = 3.14 Å. A similar situation pertains in the cadmium(II)-cnge complexes for which monodentate and bidentate coordination clearly occurs. Thus, the monodentate cnge molecule in $[Cd(cnge)_2I_2]$[35] has a larger C(1)N(2)C(2) bond angle (120°) and a shorter C(2)-N(2) bond distance (1.31 Å) than the bidentate bridging cnge molecules in $[Cd(cnge)(H_2O)_2(SO_4)]_2$[34] [C(1)N(2)C(2) = 118.8°, r(C(2)-N(2)) = 1.34 Å] and in $[Cd(cnge)Cl_2]$[36] [C(1)N(2)C(2) = 116.4°: r(C(2)-N(2)) = 1.363 Å].

The molecular geometry of the nitrate anion is unremarkable, data are given in Table 2.8.

TABLE 2.7 Molecular Geometries of 1-Cyanoguanidine in the Free Molecule and in a number of Copper(II)-(Cyanoguanidine) Complexes

Bond Distances /Å	cnge[7]	$[Cu(cnge)_2(H_2O)_2](NO_3)_2.2H_2O$	$[Cu(cnge)_2Cl_2(H_2O)_2]$[39]	$[Cu(cnge)(aebg)]SO_4.H_2O$[40]
C(1)-N(1)	1.1694(3)	1.16(2)	1.16(1)	1.17(1)
C(1)-N(2)	1.3054(4)	1.29(2)	1.29(1)	1.28(1)
C(2)-N(2)	1.3414(3)	1.33(2)	1.33(1)	1.39(1)
C(2)-N(3)	1.3391(3)	1.34(2)	1.34(1)	1.33(1)
C(2)-N(4)	1.3327(3)	1.31(2)	1.32(1)	1.33(1)

Bond Angles /°	cnge[7]	$[Cu(cnge)_2(H_2O)_2](NO_3)_2.2H_2O$	$[Cu(cnge)_2Cl_2(H_2O)_2]$[39]	$[Cu(cnge)(aebg)]SO_4.H_2O$[40]
N(1)C(1)N(2)	175.10(2)	173.0(1.1)	170.6(9)	172.6(6)
C(1)N(2)C(2)	118.38(2)	122.8(1.0)	123.1(7)	118.6(6)
N(2)C(2)N(3)	123.75(2)	123.3(1.1)	123.8(4)	124.4(5)
N(2)C(2)N(4)	117.50(2)	117.7(1.1)	117.4(7)	116.6(5)
N(3)C(2)N(4)	118.73(2)	118.9(1.1)	118.8(7)	118.9(6)

TABLE 2.8 Molecular Geometry and Planarity of the Nitrate Anion

Bond Distance/Å		Bond Angle/°	
N(5)-O(3)	1.25(2)	O(3) N(5) O(4)	117(1)
N(5)-O(4)	1.26(2)	O(4) N(5) O(5)	121(1)
N(5)-O(5)	1.22(2)	O(5) N(5) O(3)	121(1)

Atom	Deviation from Plane/Å	Atom	Deviation from Plane/Å
N(5)	+0.014	O(4)	-0.005
O(3)	-0.005	O(5)	-0.005

Equation of
best plane: $3.2403x - 4.7700y + 1.5408z = 1.257$

2.4 Thermal behaviour of hydrated copper(II)-(1-cyanoguanidine) complexes

The hydrated copper(II)-cnge complexes, $[Cu(cnge)_2Cl_2(H_2O)_2]$, $Cu(cnge)_2Br_2.2H_2O$, $Cu(cnge)_2(SO_4).5H_2O$ and $[Cu(cnge)_2(H_2O)_2](NO_3)_2.2H_2O$ crystallised from aqueous solutions containing cnge and the appropriate copper(II) salt. Varying either the reaction conditions or the molar ratios of the reactants had no effect on the identity of the product.

The thermal behaviour of the hydrates was studied by both dynamic and isothermal methods. Thermogravimetric analyses (tga) were carried out using a Stanton Redcroft TG750 instrument (~10mg sample; 2°C min^{-1} heating rate). The dehydrations were effected on ~1g samples in an isothermal oven ($\pm$1°C) with high vacuum (0.1 Pa) facilities when required.

Tga curves for the four hydrates and for $Cu(cnge)_2SO_4.2H_2O$ are shown in Figure 2.3. Those for the halides (curves B and C) and sulphates (curves D and E) show that with the exception of bromide, which appears to form a hemihydrate intermediate at 45°C, they all dehydrate directly to the anhydrous material commencing at ~60°C. All three anhydrous complexes are fairly stable, further decomposition, which commenced at 160°C (for the sulphate), 175°C (chloride) or 190°C (bromide), being complete at about 600°C. The tga curve for the nitrate (curve A, Figure 2.3) shows the formation of a dihydrate commencing at 45°C, followed by a gradual decomposiiton process at 80°C. A plateau corresponding to the anhydrous material was not observed, however, the decomposition culminating in an explosive reaction at 162°C.

Careful isothermal dehydration experiments at ambient pressures confirmed the tga results yielding samples of $Cu(cnge)_2Cl_2$, $Cu(cnge)_2Br_2$, $Cu(cnge)_2Br_2.0.5H_2O$, $Cu(cnge)_2(SO_4)$ and $Cu(cnge)_2(NO_3)_2.2H_2O$ (Table 2.9). All attempts to produce the anhydrous nitrate by this route failed. Low temperature (50°C) thermal decomposition under vacuum (0.1 Pa) led to

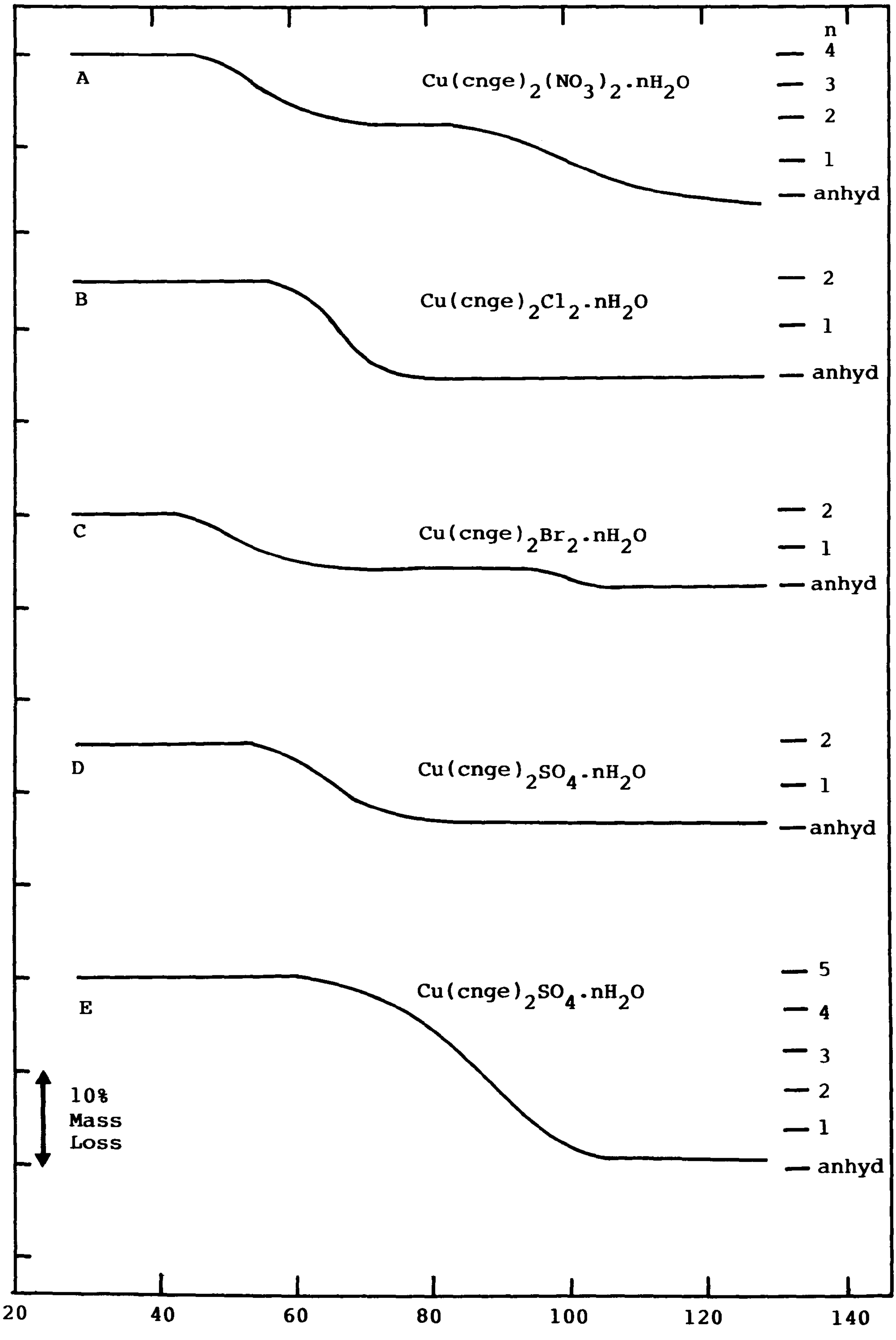


FIGURE 2.3 Tga curves for hydrated copper(II)-1-cyanoguanidine complexes

$Cu(cnge)_2X_2$ (X = Cl, Br), $Cu(cnge)_2(NO_3)_2$ and $Cu(cnge)_2(SO_4)2H_2O$ (Table 2.9)

The facile loss of two water molecules from the nitrate is consistent with the removal of the two water molecules of crystallisation, the two water molecules in the cation coordination sphere being retained. It is assumed that the similar loss of three of the five water molecules in $Cu(cnge)_2(SO_4).5H_2O$ indicates that again only two are directly coordinated to the cation.

TABLE 2.9 Thermal Behaviour of Hydrated Copper(II)-(1-Cyanoguanidine) Complexes; Isothermal Experiments

Hydrate	Product	Experimental Weight Loss /%	Calculated Weight Loss /%	Temp. /°C
$[Cu(cnge)_2(H_2O)_2](NO_3)_22H_2O$	$Cu(cnge)_2(H_2O)_2(NO_3)_2$	8.5	8.1	50
$[Cu(cnge)_2(H_2O)_2](NO_3)_22H_2O$	$Cu(cnge)_2(NO_3)_2$	16.1	16.8	50*
$Cu(cnge)_2(SO_4)5H_2O$	$Cu(cnge)_2(SO_4)2H_2O$	13.8	12.9	50*
$Cu(cnge)_2Cl_2 2H_2O$	$Cu(cnge)_2Cl_2$	11.9	10.6	105
$Cu(cnge)_2Br_2 2H_2O$	$Cu(cnge)_2Br_2 0.5H_2O$	6.4	6.4	65
$Cu(cnge)_2Br_2 2H_2O$	$Cu(cnge)_2Br_2$	8.1	8.4	120

* Under vacuum (0.1 Pa)

2.5 Anhydrous Copper(II)-(1-Cyanoguanidine) Derivatives

The anhydrous bis(cnge) derivatives of copper(II) chloride, bromide and nitrate, prepared in this work, differ completely from the description given by Panda et al[28] for their products. A comparison of the data is effected in Table 2.10. Repeated attempts to prepare the anhydrous halides by refluxing the requisite molar ratio of copper(II) halide and 1-cyanoguanidine in ethanol, Panda's route, failed. Depending on the molar ratios of the reactants, either blue (or green) crystals of $[Cu(aOeu)Cl_2]$ $\{$or $Cu(aOeu)Br_2.2H_2O\}$ or pink crystals of $[Cu(aOeu)_2]Cl_2.2H_2O$ $\{$or $Cu(aOeu)_2Br_2\}$ (aOeu = 1-amidino-O-ethylurea), were invariably obtained, presumably as a result of solvolysis of cnge in the presence of the copper(II) salt. These products have been characterised in single crystal X-ray diffraction, infrared and UV-visible spectroscopic studies, the results of which are reported in Chapters Six, Seven and Eight. Since these materials closely resemble, and the anhydrous copper(II)-cnge salts described herein differ from, those prepared by Panda et al, then their results must be considered with extreme caution.

2.6 Vibrational Spectroscopy of Copper(II)-(1-Cyanoguanidine) Complexes

The vibrational spectra for various anhydrous, hydrated and deuterated copper(II)-cnge complexes were recorded (4000-400 cm^{-1}), with the exception of the

TABLE 2.10 Products of the Reaction between cnge and Copper(II) Halides in Refluxing Ethanol

Product	Appearance	UV-visible spectra λ_{max}/nm
Present Results*		
Cu(aOeu)$_2$Cl$_2$.2H$_2$O	pink	515
Cu(aOeu)Cl$_2$	blue	650
Cu(aOeu)$_2$Br$_2$	pink	515
Cu(aOeu)Br$_2$.2H$_2$O	dark green	660
Panda's Results[28]		
Cu(cnge)$_2$Cl$_2$	pink	530
Cu(cnge)$_4$Cl$_2$	blue	675
Cu(cnge)$_2$Br$_2$	pink	525
Cu(cnge)$_4$Br$_2$	blue	665

Anhydrous Bis(cnge) Copper(II) Complexes Produced in this work

Product	Appearance	UV-visible spectra λ_{max}/nm	ν_{as}(C≡N) cm^{-1}	ν_s(C≡N) cm^{-1}
Cu(cnge)$_2$Cl$_2$	bright green	870	2240 2180	1280
Cu(cnge)$_2$Br$_2$	pale brown	865	2245 2200	1280
Cu(cnge)$_2$(NO$_3$)$_2$	bright green	870	2225 2185	1285

*These compounds are described in Chapters Six, Seven and Eight.

copper(II) nitrate derivatives, in both nujol and halocarbon mulls using KBr windows as well as in KBr discs. Spectra of the nitrates were recorded solely in mulls using AgCl windows owing to the susceptibility of KBr to oxidative attack. The spectra are compared with those for cnge and D_4-cnge in Tables 2.11 and 2.12. Bands attributable to the anions have been omitted.

The vibrational spectrum of cnge (point group C_s) has been discussed by Jones and Orville-Thomas.[9] There are 24 fundamental vibrational modes (15A' and 9A") all of which should be infrared active. Jones and Orville-Thomas assigned frequencies to five of the six (3A' and 3A") fundamental vibrations associated with each of the NH_2 fragments and to nine of the 12 (9A' and 3A") skeletal vibrational modes. These assignments are used as a basis in this work. However, it must be remembered that for a molecule of this complexity the descriptions of the vibrations can only be approximate owing to the extensive mixing of the internal coordinates.

The present spectrum of cnge is in agreement with that reported by Jones et al.[9] However, advances in spectrophotometric accuracy have led to slight changes in the absorption frequencies.

In all the complexes studied, the spectra of coordinated cnge are similar, they do, however, differ significantly from the spectrum of free cnge.

The spectra of the two complexes for which structural data are available $[Cu(cnge)_2Cl_2(H_2O)_2]$[39] and

TABLE 2.11

TABLE 2.11 Infrared Spectroscopic Data/cm^{-1} for cnge and Various Copper(II) cnge Salts

cnge[18]	cnge	$Cu(cnge)_2Cl_2$	$Cu(cnge)_2Br_2$	$Cu(cnge)_2(SO_4)$
			3540 mw,br	
3422 3370 3324 s,br	3422 3370 3331 s,br	3420 3340 s,br	3390 3320 s,br	3340 vs,br
3175 3134 s,br	3187 3154 s,br	3210 3160 s,br	3210 3160 s,br	3200 vs,vbr
2203 s	2208 s	2240 2180 vs	2240 vs	2235 2180 vs
2159 s	2164 s		2200 ms	
1657 1633 s,br	1662 1643 1635 s,br	1690 vs 1650 vs	1670 1640 s	1650 vs,vbr
1567 s,br	1574 s 1570 s	1565 vs	1555 vs	1550 vs,vbr
1500 ms	1506 ms	1520 ms	1515 s	
1252 ms	1255 ms	1280 m	1280 m	1280 m,br
1085 w,br	1088 w,br	1110 mw	1110 w	*
928 ms	930 ms	935 m	935 w	
721 w	721 w	720 vw	720 vw	
668 m	668 m	685 m	680 vw	*
550 ms,br	560 ms,br	535 m,br	540 m,br	550 m,br
525 517 508 m	530 517 509 m	515 m		
470 ms,br	473 ms,br	460 m,br	460 m,vbr	500 m,br

*Masked by anion vibrations

$Cu(cnge)_2(NO_3)_2$	$[Cu(cnge)_2Cl_2(H_2O)_2]$	$Cu(cnge)_2Br_2.2H_2O$	Assignment
		3540 ms,br	ν_a[N-H] and ν_s[N-H]
3430 sh			
	3427 m		
3330 vs,br			
	3355 3323 s,br	3400 3320 s,br	
3190 vs,br	3200 s,br	3200 s,br	
2225 2185 s	2256 2205 s	2240 vs 2200 ms	ν_a[N(1)C(1)N(2)]
1660 vs,vbr	1660 vs,br	1680 1650 s	δ[NH_2]
1540 s,br	1565 1537 s,br	1550 1520 s	ν_a[N(3)C(2)N(4)] ν_a[N(2)C(2)N(3)]
1295 m,br	1300 m	1275 ms	ν_s[N(1)C(1)N(2)]
1100 w,br	1100 m	1110 m	δ[NH_2]
935 w,br	921 m	935 mw	ν_s[N(2)C(2)N(3)]
*	710 mw		γ[N(3)C(2)N(4)]
665 w	665 m	690 w	δ[N(3)C(2)N(4)]
565 w,br	560 m,br	540 m,br	γ[NH_2]
510 w,br	530 m 515 m	510 w	γ[N(1)C(1)N(2)] δ[N(3)C(1)N(4)]
480 w,br	430 w,br	450 m,br	γ[NH_2]

TABLE 2.11 (contd.)

$Cu(cnge)_2$-$SO_4 \cdot 2H_2O$	$Cu(cnge)_2$-$(NO_3)_2 \cdot 2H_2O$	$Cu(cnge)_2$-$SO_4 \cdot 5H_2O$	$[Cu(cnge)_2(H_2O)]$ $(NO_3)_2 \cdot 2H_2O$	Assignment
			3580 m,br	ν_a[N-H] and ν_s[N-H]
3360 vs,vbr	3400 3350 vs,br	3400 vs,vbr	3420 3320 s,br	
3200 s,br	3240 vs,vbr	3220 vs,vbr	3220 3160 s,br	
2240 2200 vs	2240 2200 s,br	2250 2210 s	2240 2200 s	ν_a[N(1)C(1)N(2)]
1660 vs,vbr	1650 s,br	1680 vs,br	1660 s,br	δ[NH_2]
1560 vs,vbr	1550 s,br	1580 vs,vbr	1570 s,br	ν_a[N(3)C(2)N(4)]
1530 sh	1530 sh		1530 m	ν_a[N(2)C(2)N(3)]
1280 ms,br	1275 m	1300 m	1295 m	ν_s[N(1)C(1)N(2)]
*	1120 w,br	*	1100 w,br	δ[NH_2]
930 mw	950 m	930 m	925 w	ν_s[N(2)C(2)N(3)]
	*		*	γ[N(3)C(2)N(4)]
*	690 mw	*	670 mw	δ[N(3)C(2)N(4)]
550 m,br	565 m,br	550 m,br	550 w,br	γ[NH_2]
	540 m			γ[N(1)C(1)N(2)]
			525 m,br	δ[N(3)C(1)N(4)]
500 m,br	500 m,br		500 w,br	γ[NH_2]

*Masked by anion vibrations

TABLE 2.12 Infrared Spectroscopic Data for D_4-cnge and Copper(II)-(D_4-cnge) Salts

D_4-cnge	$Cu(D_4\text{-cnge})_2Cl_2 \cdot 2D_2O$	$Cu(D_4\text{-cnge})_2Br_2 \cdot 2D_2O$	Assignment
2580 2540 s	2570 s,br	2550 s,br	ν_a[N-D] and ν_s[N-D]
2415 2345 s,br	2410 s,sh 2380 s,br	2380 s,br	
2170 vs,br	2230 vs,br	2235 vs,br	ν_a[N(1)C(1)N(2)]
1185 1155 w	1195 1165 w	1195 1160 w	δ[ND_2]
1570 1540 vs,br	1595 1520 vs,br	1590 1510 vs,br	ν_a[N(3)C(2)N(4)]
1255 ms	1280 s	1280 ms	ν_s[N(1)C(1)N(2)]
835 w	845 w,br	835 vw,br	δ[ND_2]
920 m	925 m	920 m	ν_s[N(2)C(2)N(3)]
715 s	715 m	715 m	γ[N(3)C(2)N(4)]
635 mw	660 mw	660 mw	δ[N(3)C(2)N(4)]
410 m,br	400 m,br	400 m,br	γ[ND_2]
565 m	565 mw	555 mw	γ[N(1)C(1)N(2)]
480 m	485 mw	490 mw	δ[N(3)C(2)N(4)]
360 m,br	360 m,br	345 m,br	γ[ND_2]

$[Cu(cnge)_2(H_2O)_2](NO_3)_2.2H_2O$ are very similar in accord with the near identical geometries of the cnge molecules. Bands diagnostic of cnge coordination to copper(II) are apparent for these two compounds, and, indeed, for all the complexes studied; they have been attributed to the asymmetric and symmetric stretches of the nitrile group. Both bands move to higher frequency on coordination; whereas the band designated $\nu_a[N(1)C(1)N(2)]$, which appears as a sharp doublet, moves from 2208/2164 cm^{-1} (for cnge) to at least 2235/2180 cm^{-1} (for $Cu(cnge)_2SO_4$), $\nu_s[N(1)C(1)N(2)]$ moves from 1255 cm^{-1} (for cnge) to at least 1275 cm^{-1} (for $[Cu(cnge)_2Cl_2(H_2O)_2]$ or $Cu(cnge)_2(NO_3)_2.2H_2O$). This increase in frequency is typical of unidentate coordinated nitrilesand has been attributed to a more effective σ-donor than π-acceptor interaction.[43]

The N(1)C(1)N(2) fragment of free cnge should give rise to only two infrared active stretching vibrations - the asymmetric, ν_a(NCN), and symmetric, ν_s(NCN), stretches. Jones et al[9] assigned these vibrations to the 1255 cm^{-1} band [ν_s(NCN)] and to the doublet band at 2208/2164 cm^{-1} [ν_a(NCN)]. They attributed the doublet structure of the latter band to the splitting of a fundamental vibration by the crystal field, a correlation interaction. They claimed that the infrared spectrum of a pyridine solution of cnge exhibited only a single band in the 2300-2000 cm^{-1} region at 2182 cm^{-1}. Repeating this spectrum in this work, a doublet was observed at

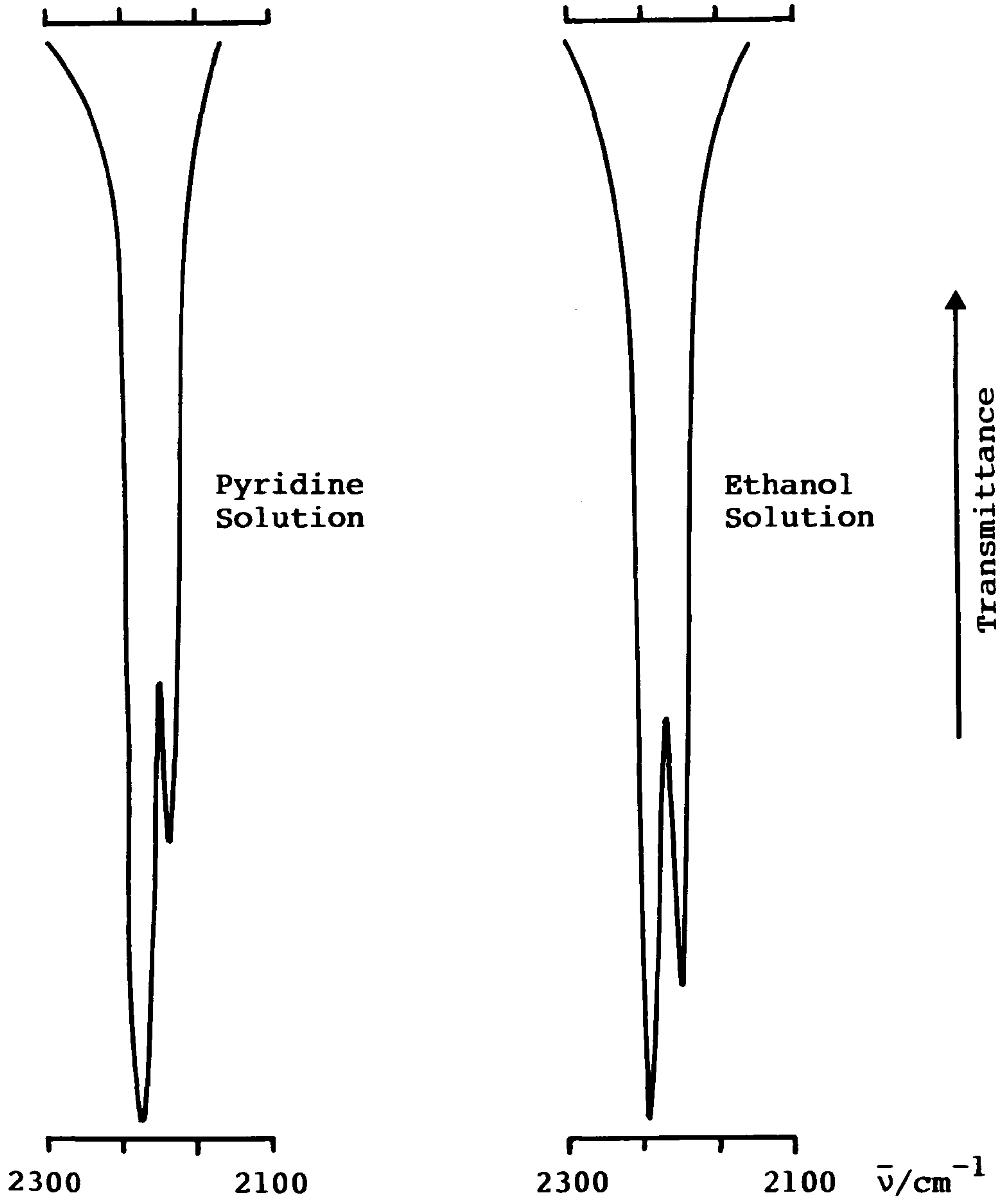
2184/2150 cm^{-1} (Figure 2.4). Indeed, an ethanol solution of cnge also gave a doublet at 2200/2157 cm^{-1}, so ruling out a correlation interaction as a possible explanation of this phenomenon.

Careful examination of the infrared spectra of coordinated cnge and of deuterated free and coordinated cnge in the 2300-2000 cm^{-1} region, does help in the explanation of the curious 'ν_a(NCN)' doublet.

For this analysis $[Cu(cnge)_2Cl_2(H_2O)_2]$, $Cu(cnge)_2Br_2.2H_2O$ and their deuterated analogues have been chosen as typical examples since there are no consistent differences between the spectra of the anhydrous and hydrated complexes, and the spectra of the halides exhibit much better resolution than those of the oxy-salts, presumably owing to reduced hydrogen bonding. A comparison of the 2300-2000 cm^{-1} region of the infrared spectra of cnge, $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $Cu(cnge)_2Br_2.2H_2O$ is effected in Figure 2.5.

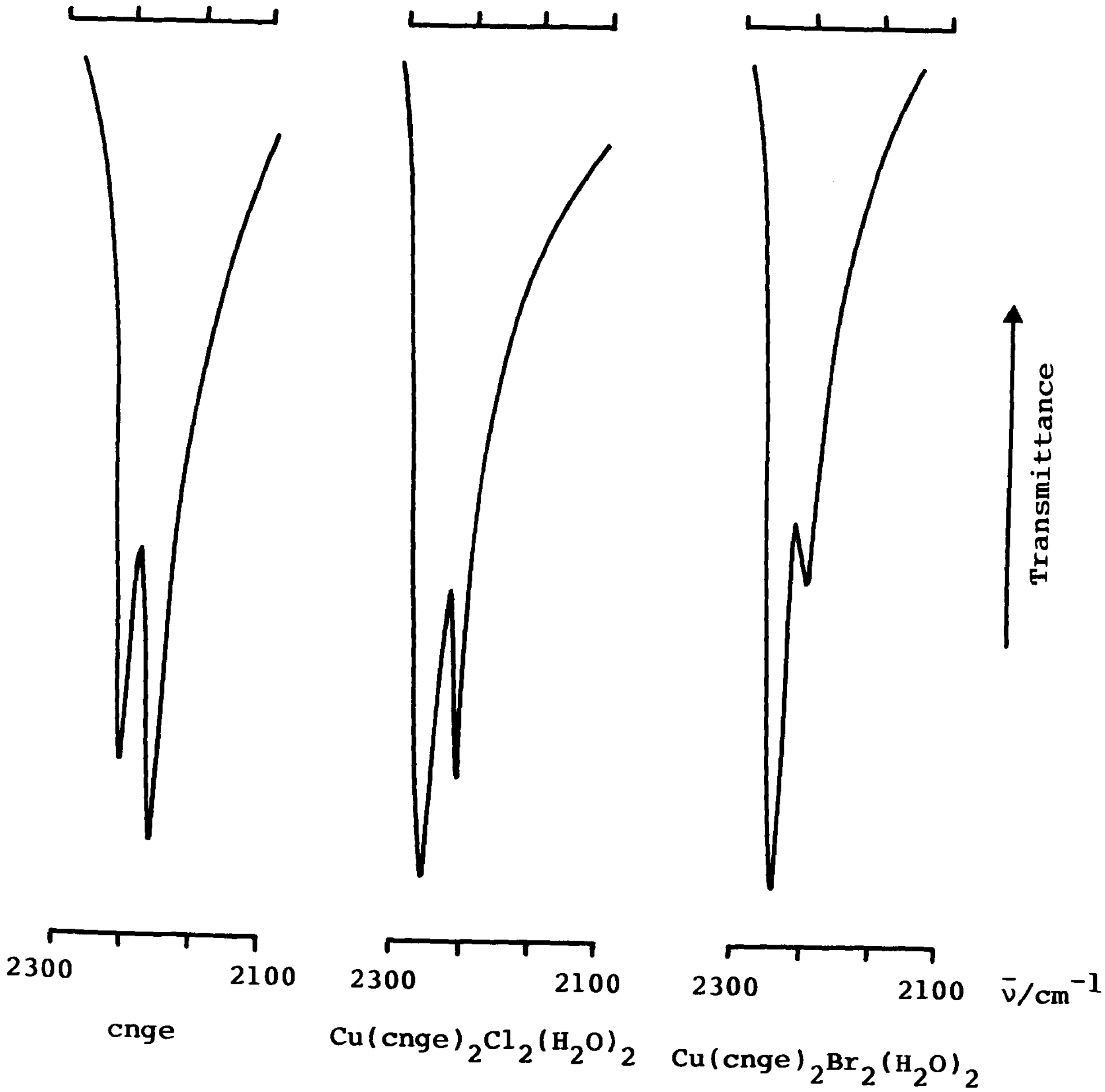
For free cnge the lower frequency band, 2164 cm^{-1}, is of slightly greater intensity than its higher frequency partner, 2208 cm^{-1}, whereas for $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $Cu(cnge)_2Br_2.2H_2O$ the reverse is observed: bands at 2255 and 2240 cm^{-1} being greater in intensity than those at 2205 and 2200 cm^{-1} respectively. This could imply that upon coordination of cnge it is the band at 2164 cm^{-1} which shifts to 2255 or 2240 cm^{-1}, whilst the band at 2208 cm^{-1} shifts but marginally. Assuming this interpretation the band at 2208 cm^{-1} of

FIGURE 2.4 IR spectra of 1-cyanoguanidine in pyridine and ethanol solutions



FOOTNOTE Compared to the solid state spectrum of cnge the frequencies of the doublet have been shifted and the relative intensities of the individual bands reversed. The effect of a solvent on infrared frequency and intensity has been investigated for nitriles with only limited success leaving the phenomenon relatively unexplained.[44]

FIGURE 2.5 IR spectra of cnge, $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $[Cu(cnge)_2Br_2(H_2O)_2]$



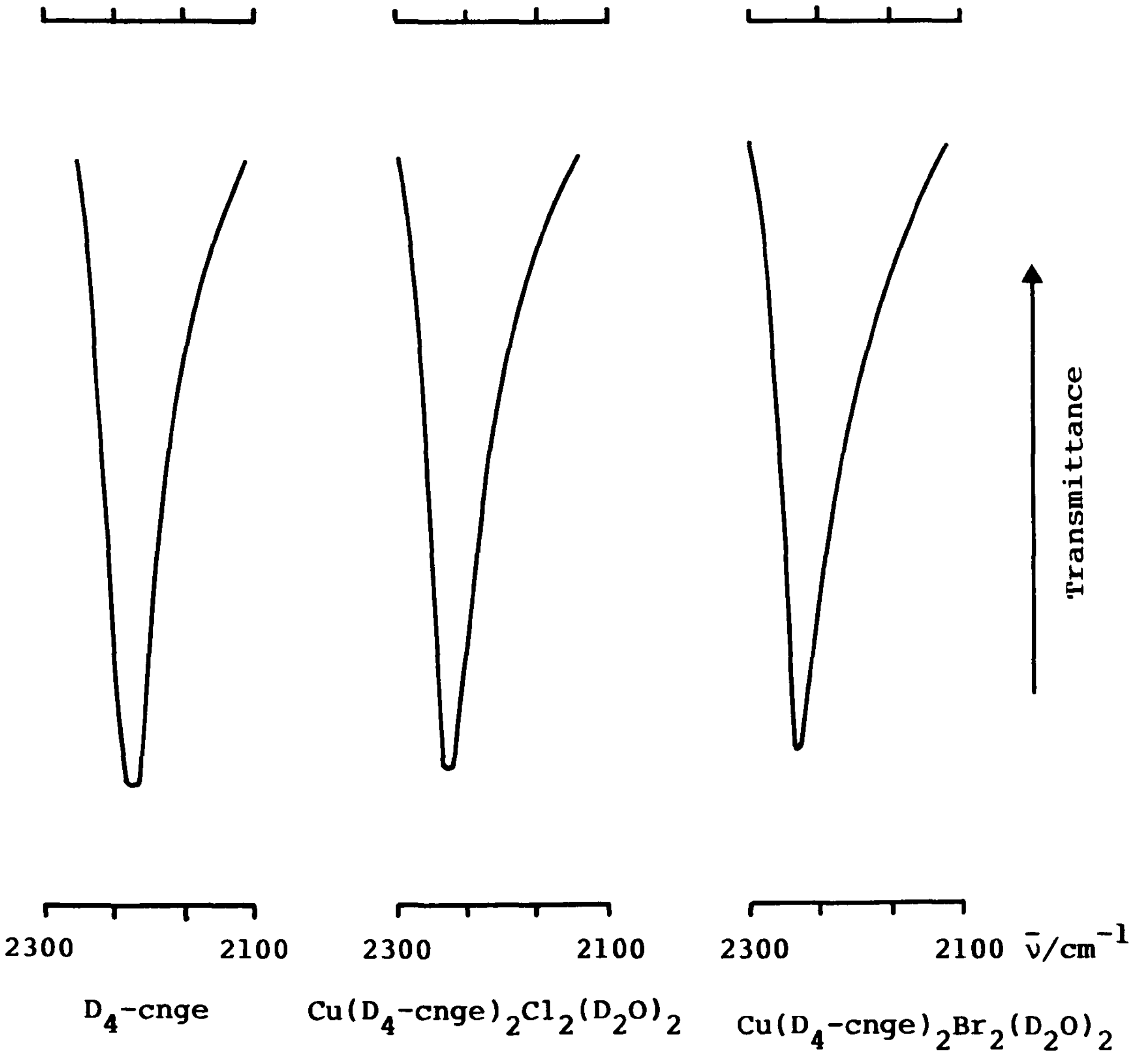
cnge and those at 2205 and 2200 cm^{-1} of the complexes are probably incorrectly assigned to a nitrile stretching vibration.

To try to clarify the situation, cnge, $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $Cu(cnge)_2Br_2.2H_2O$ were deuterated. Bands in cnge and in the two copper(II) complexes that were assigned to $\nu(NH)$, $\delta(NH_2)$, and $\gamma(NH_2)$ clearly shifted to lower frequencies and with the exception of the band designated $\nu_a(NCN)$, there were only minor changes in the frequencies of the bands assigned to the C-N skeletal vibrations (Table 2.12). Figure 2.6 compares the 2300-2000 cm^{-1} region of the spectra of D_4-cnge, $[Cu(D_4\text{-cnge})_2Cl_2(D_2O)_2]$ and $Cu(D_4\text{-cnge})_2Br_2.2D_2O$. For cnge deuteration modifies the doublet to give a single broad band centred at 2170 cm^{-1}.

Coordinated cnge also exhibits a similar modification of the doublet on deuteration. The absorption occurs as a single broad band centred at 2230 cm^{-1} for both $[Cu(D_4\text{-cnge})_2Cl_2(D_2O)_2]$and $Cu(D_4\text{-cnge})_2\text{-}Br_2.2D_2O$. These results further indicate that it is the 2164 cm^{-1} band of cnge which shifts to higher frequency (to 2255 and 2240 cm^{-1}) whilst the 2208 cm^{-1} band only shifts marginally (to 2205 and 2200 cm^{-1}) implying that only the 2164 cm^{-1} absorption should be attributed to the asymmetric nitrile stretch of free cnge.

The loss of the 2208 cm^{-1} band on deuteration suggests that it involves an N-H vibration and that an alternative explanation involving Fermi resonance may account for the doublet structure.

FIGURE 2.6 IR spectra of D_4-cnge, $[Cu(D_4\text{-cnge})_2Cl_2(D_2O)_2]$ and $[Cu(D_4\text{-cnge})Br_2(D_2O)_2]$



Fermi resonance occurs when two different vibrations (or combinations of vibrations) of the same symmetry species have nearly the same energy, that is, they are accidentally degenerate. It results in a shift of one vibration towards lower energy and the other towards higher energy.[45] Thus, the doublet may be due to the interaction of the nitrile vibration with an overtone or combination band involving an N-H vibration. For free cnge the mean of the observed doublet (2208/2164 cm^{-1}) is 2186 cm^{-1}. Possible combinations of vibrations which have frequencies close to this mean are the first overtone of the 1088 cm^{-1} band [assigned $\delta(NH_2)$] and the combination of the 1662 cm^{-1} [assigned $\delta(NH_2)$] and 530 cm^{-1} (undefined assignment) bands giving values of 2176 and 2192 cm^{-1} respectively.

2.7 Conclusions

The studies of transition metal-cnge complexes all show that infrared spectroscopy is sometimes effective in assessing the coordination of cnge.

On coordination of cnge to cadmium(II) only minor changes are noted in the infrared spectra. Differentiation between mono- and bidentate coordination is not possible since neither the absorption bands, nor the structural parameters vary consistently. Some of the absorption bands $\{\nu_s[N(1)C(1)N(2)]$, $\nu_s[N(2)C(2)N(3)]$, $\delta[N(3)C(2)N(4)]\}$ do, however, tend to mirror trends in structural parameters.[34]

The similarity of the spectra of all the copper(II) complexes studied, which exhibit significant changes relative to free cnge, implies that coordination is exclusively monodentate.

It is difficult to rationalise the differing behaviour of cnge in the presence of cadmium(II) (Cd^{2+}) and copper(II) (Cu^{2+}) cations. Hubberstey et al determined that cnge also acts as a bidentate ligand in the presence of potassium (I) ions (K^+).[46] The similarity in the coordination properties of cnge towards Cd^{2+} and K^+, both of which have fully occupied electronic configurations, suggests that the bonding interactions may be predominantly electrostatic in nature. In a recent structural and theoretical study of cnge[7] the net atomic charges on N(1) and N(2) have been shown to be similar and much greater than those on the other atoms of cnge (Figure 2.7).

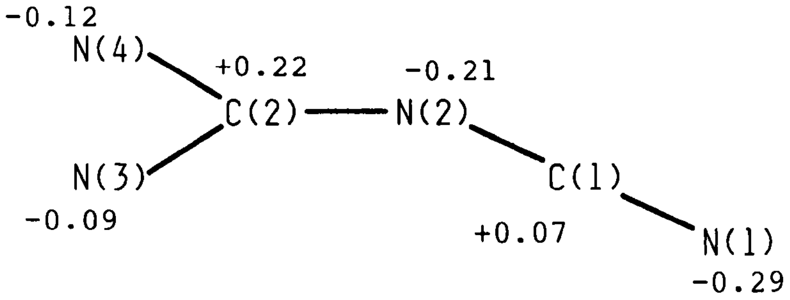
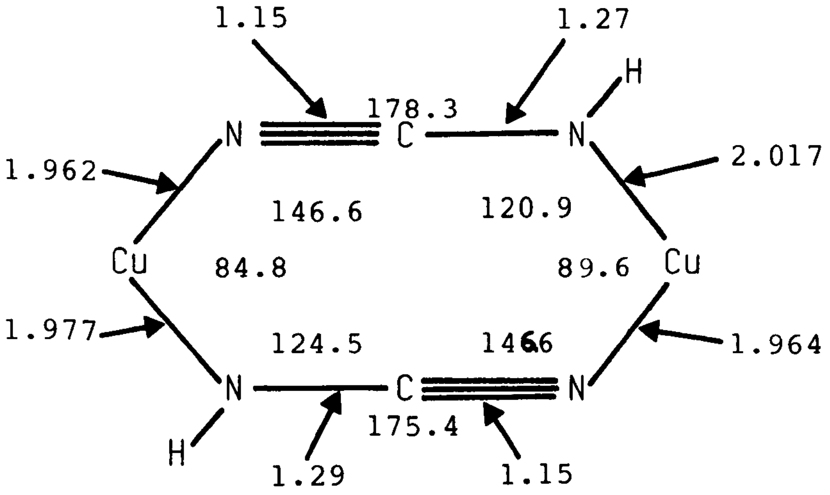


FIGURE 2.7 Net Atomic Charges /e for cnge

Electrostatic interactions would favour equally N(1) and N(2) as ligating atoms giving the possibility of both mono- and bidentate behaviour.

For Cu^{2+}, which has a d^9 configuration and coordinates cnge equatorially, the bonding may involve a more covalent interaction utilising the single occupied $d_{x^2-y^2}$ orbital of Cu^{2+}. Monodentate bonding via N(1) alone is probably preferred to give a strong σ-donor interaction.

Although no copper(II)-cnge complexes with bidentate cnge are known, a structure has been reported in which two copper(II) ions are bridged by two hydrocyanamido(-1) ligands[47] (Figure 2.8). These ligands are of similar geometry to the N(1) C(1) N(2) fragment of cnge.



<u>FIGURE 2.8</u> Geometry of bridging hydrocyanamido(-1) ligands in $[Cu(C_9H_{21}N_3)_2(\mu HNCN)_2](ClO_4)_2.H_2O$ (Bond distances/Å, bond angles/°).

The nitrile nitrogen is, however, not directly end-on bonded and the ligand is anionic, the negative charge obviously influencing the coordinating properties. This structure does imply that under appropriate conditions bridging bidentate cnge ligands may be possible with copper(II) ions.

Confirmation of this interpretation of the coordinating properties of cnge is obviously dependent on the synthesis and structural characterisation of cnge complexes of a wider range of metals, with both filled and partially filled electronic configurations.

CHAPTER THREE

COPPER(II) COMPLEXES OF 1-CARBAMOYLGUANIDINE

3.1 Introduction

As an extension to the study of the coordination properties of 1-cyanoguanidine described in Chapter Two, a similar investigation of the chemistry of its hydrolysis product, variously referred to in the literature as 1-carbamoylguanidine, ureidoguanidine, dicyandiamidine, guanylurea, guanylcarbamate, aminoiminourea, aminoiminomethylurea*, was undertaken. (The choice of nomenclature, 1-carbamoylguanidine, is based on the structure determinations described in this Chapter.) The diversity of nomenclature undoubtedly arises from the fact that three tautomeric forms (3.1-3.3) can be envisaged for this material for which no definite structural analysis has been published. All previous structural analyses, which tend to favour form 3.2, have been based on spectroscopic (ir, UV-visible) and chemical analytical data.[3,48,49,50]

1-Carbamoylguanidine (clge) has been reported to bond to transition metals.[48] The early literature on transition metal-clge complexes is, however, extremely difficult to follow owing to the indiscriminate application of pseudonyms to neutral clge as well as its cationic, $[\text{clgeH}]^+$, and anionic , $[\text{clge}]^-$, derivatives.

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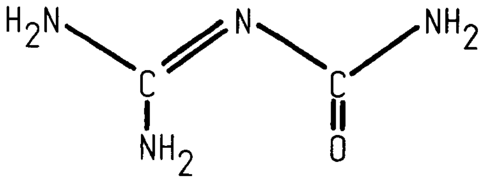
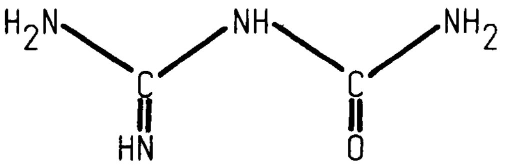
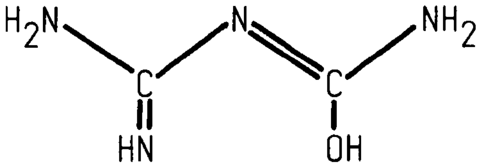
* Chemical Abstracts Registry Number [141-83-3].



3.1



3.2

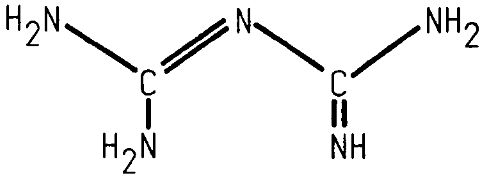


3.3

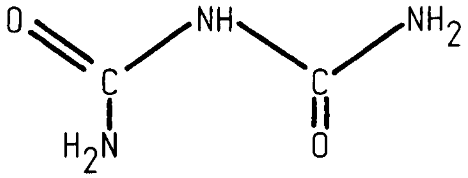
The majority of papers refer to complexes containing either $[clgeH]^+$ or $[clge]^-$ moieties and there appears to be only two original reports of the preparation of copper(II) complexes containing the neutral molecule, clge. They are both superficial; characterisation of the products being based almost exclusively on chemical analytical data; Dubsky and Strnad[51] claim the preparation of $Cu(clge)_2SO_4$ and $Cu(clge)_2(NO_3)_2$, whereas Ray and Bandopadhyay[52] claim the preparation of $Cu(clge)_2SO_4$, $1.5H_2O$ and $Cu(clge)_2Cl_2$.

These complexes are, however, quite significant owing to their similarity to corresponding complexes of biguanide (bg; 3.4) and biuret (bu; 3.5).

Structural studies of $[Cu(bg)_2]Cl_2.2H_2O$[21] and of $[Cu(bu)_2Cl_2]$[22] have shown that bg chelates copper(II) via

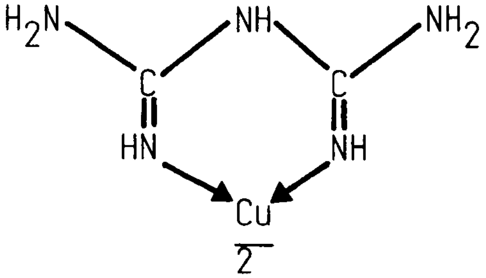


3.4

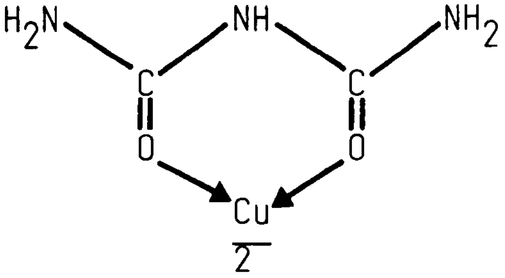


3.5

two imine groups (3.6) whereas bu chelates copper(II) through its two carbonyl groups (3.7).



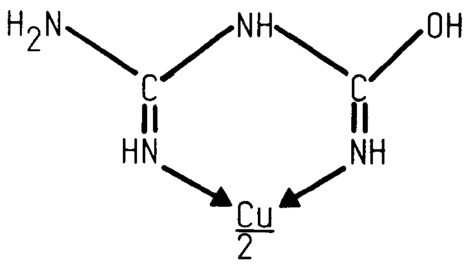
3.6



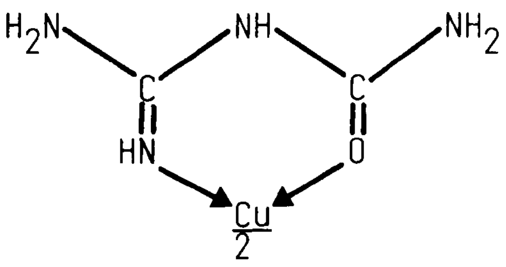
3.7

Since clge contains fragments of bg and bu, a number of coordination modes can be envisaged, the most probable being those involving either two imine groups (3.8) or one imine and one carbonyl group (3.9) as donor centres.

In an early attempt to ascertain how clge bonds to transition metals, Syamal[53] repeated Ray's work[52] and undertook a spectroscopic (i.r. and UV-visible) study of his products which he designated on the basis of chemical analytical data, as $Cu(clge)_2SO_4.1.5H_2O$ and $Cu(clge)_2Cl_2.1H_2O$. He concluded that the carbonyl group of clge,

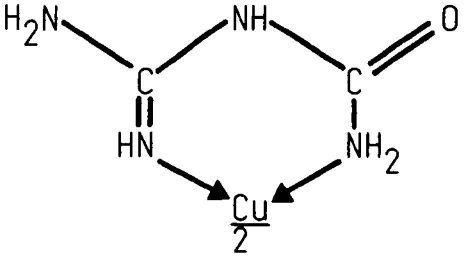


3.8



3.9

although retained on coordination to copper(II), is not bonded to the metal ion and that both donor atoms are nitrogen atoms. This conclusion is not consistent with either of the coordination modes (3.8, 3.9) derived by analogy with copper(II) complexes of bg and bu, but is best described by a Lewis structure (3.10) which involves coordination through an amine group.



3.10

Since no definitive evidence is available for uncoordinated clge or any transition metal-clge complexes, the crystal and molecular structures of the 1:1 ethanol adduct of 1-carbamoylguanidine (clge.EtOH) and of bis(1-carbamoylguanidine)dinitrato copper(II)

$[Cu(clge)_2(NO_3)_2]$ have been determined. Furthermore, the vibrational spectra of these compounds, their deuterated analogues and the analogous complexes $Cu(clge)_2X_2$ (X = Cl, Br) have also been recorded with a view to using them as an effective diagnostic tool in assessing the mode of coordination of the ligand.

3.2 **Experimental**

3.2.1 Clge.EtOH and clge

1-Carbamoylguanidine was prepared by a modified version of the capricious synthesis reported by Piskala.[54]

An aqueous solution of 1-carbamoylguanidinium hydrochloride (5g in 50 cm^3) (see Section 4.2 for preparation) was treated with Dowex-1 ion exchange resin (100g, previously soaked in sodium hydroxide (10M) for seven days, then washed in deionised water) by allowing the mixture to stand for two days. The resin was filtered off and washed with water. The combined filtrates were evaporated under vacuum at temperatures not exceeding 35°C and crystallised from ethanol. Colourless crystals of the adduct were stored in a stoppered bottle to prevent loss of ethanol. The unsolvated product was obtained, in powder form, by drying the adduct under vacuum over concentrated sulphuric acid and potassium hydroxide. Yield 2.1g (58%), mpt 103-104°C.

Analytical data for these and all subsequent products are collated in Table 3.1.

3.2.2 $[Cu(clge)_2(NO_3)_2]$

Bis(1-carbamoylguanidine)dinitrato copper(II) was prepared via two routes:- (a) the hydrolysis of bis(1-cyanoguanidine)di-μ-aquocopper(II) dinitrate dihydrate and (b) the reaction of clge with copper(II) nitrate trihydrate in aqueous solution. The former route produced small amounts of a crystalline sample whilst the latter gave an almost 100% yield of the product in powder form.

Route (a)

An aqueous solution of bis(1-cyanoguanidine)di-μ-aquocopper(II) dinitrate dihydrate [2.1g (5 mmol) in 10 cm^3] was allowed to stand in an open conical flask (100 cm^3) at room temperature. After 7 days a few dark blue crystals had grown from the solution. They were collected, washed with deionised water, and dried over silica gel. Further quantities of the product were produced on leaving the solution to stand for several more days.

Route (b)

An excess of an aqueous solution of copper(II) nitrate trihydrate [2.4g (10 mmol) in 10 cm^3] was added to an aqueous solution of clge [2.04g (20 mmol) in 5 cm^3]. The blue precipitate which formed immediately was collected, washed with deionised water, and dried over silica gel. Yield 3.80g (97%).

3.2.3 $Cu(clge)_2Cl_2$ and $Cu(clge)_2Br_2$

Attempted preparations of copper(II)-clge chloride and bromide complexes by a method analogous to Route (b) for $[Cu(clge)_2(NO_3)_2]$ were unsuccessful, due to the instability of the complexes in aqueous solutions. However, ethanol proved to be a suitable alternative to water and $Cu(clge)_2Cl_2$ and $Cu(clge)_2Br_2$ complexes were synthesised in powder form using the following method.

The addition of an ethanolic solution of $CuCl_2.2H_2O$ [0.17g (1 mmol) in 10 cm^3] or $CuBr_2$ [0.22g (1 mmol) in 10 cm^3] to an ethanolic solution of clge [0.20g (2 mmol) in 20 cm^3] yielded blue precipitates which, after collection, washing with cold ethanol, and air drying, were analysed for $Cu(clge)_2Cl_2.H_2O$ or $Cu(clge)Br_2$. Isothermal dehydration of $Cu(clge)_2Cl_2.H_2O$ at 110°C for 2 hours gave $Cu(clge)_2Cl_2$. Yields:- 0.31g (97%) $Cu(clge)_2Cl_2$, 0.36g (84%) $Cu(clge)_2Br_2$.

3.2.4 D_6-clge and $Cu(D_6\text{-clge})_2(NO_3)_2$

Deuterated clge was obtained by repeated solution of clge in D_2O followed by removal of excess water under vacuum.

$[Cu(clge)_2(NO_3)_2]$ could not be deuterated directly because the material was insoluble in most common deuterated solvents with labile deuterium atoms (e.g. D_2O or C_2H_5OD).

$Cu(D_6\text{-clge})_2(NO_3)_2$ was prepared by the addition of a D_2O solution of copper(II) nitrate trihydrate

TABLE 3.1 Analytical Data for clge and Copper(II)-clge Complexes

Compound	Experimental/Theoretical %		
	C	H	N
clge.EtOH*	32.24/32.43	7.60/8.11	41.81/37.84
clge	23.15/23.53	5.88/5.88	54.90/54.94
$[Cu(clge)_2(NO_3)_2]^a$	12.06/12.26	3.18/3.06	36.03/35.76
$[Cu(clge)_2(NO_3)_2]^b$	12.13/12.26	3.25/3.06	35.93/35.76
$Cu(clge)_2Cl_2.H_2O$	13.56/13.47	3.71/3.96	31.43/31.42
$Cu(clge)_2Cl_2$	14.10/14.18	3.66/3.57	32.78/33.09
$Cu(clge)_2Br_2$	11.33/11.24	2.88/2.81	26.02/26.21

* The poor analytical data is undoubtendly due to ethanol loss during analytical handling.

a Product from Route (a)

b Product from Route (b)

(previously deuterated by the same method as clge) [0.25g (1 mmol) in 2 cm^3] to a D_2O solution of D_6-clge [0.2g (2 mmol) in 2 cm^3] under a dry nitrogen blanket. The blue precipitate which formed immediately was collected, washed with D_2O and dried under vacuum. Yield .37g (92%).

3.3 Crystal and Molecular Structures of the 1:1 Ethanol Adduct of 1-Carbamoylguanidine and of Bis(1-carbamoylguanidine)dinitratocopper(II)

3.3.1 Structure solution and crystal data for clge.EtOH

The ethanol adduct was chosen for structural analysis since clge formed initially in aqueous solution could not be crystallised as the free molecule from any solvent.

A suitable colourless crystal (0.4 x 0.2 x 0.2 mm) of the adduct was obtained by allowing a warm saturated ethanol solution of clge to cool slowly to room temperature. The crystal was mounted in a sealed Lindemann tube to prevent loss of ethanol.

Cell parameters, space group and X-ray diffraction data were obtained as described in Section 1.6.1. Of the 830 intensities collected, 715 were deemed to be observed.

The carbon, nitrogen and oxygen atoms of the two molecules were located by direct methods using the 'MULTAN 80' suite of programs.[32] Full matrix least squares refinement with anisotropic temperature factors for all these atoms converged at $R = 0.075$. The top six peaks (electron densities 0.41 to 0.34 e/$Å^3$) of a subsequent difference Fourier synthesis gave the positions of all the hydrogen atoms of the clge molecule. The eighth distinct peak (density 0.23 e/Å^3) gave the position of the hydroxyl hydrogen atom. The thermal lability of the ethyl group prevented accurate location of its hydrogen atoms which had to be positioned using a hydrogen placing routine [r(C-H) = 0.95 Å, U(ISO) = 0.05 Å^2]. Further refinement of the structure included the clge and alcoholic hydrogen atoms with isotropic thermal parameters; it converged at R = 0.046. The ethyl hydrogen atoms were included in the structure factor calculations without refinement. Final positional parameters and thermal parameters are given in Tables 3.2 and 3.3. Observed and calculated structure factors are included in Appendix B.

Crystal Data

$C_4H_{12}N_4O_2$, M = 148.2, orthorhombic, space group $P2_12_12_1$, a = 7.509(3), b = 8.896(3), c = 11.565(3) Å, U = 772.5 Å^3, D_m = 1.25, D_c = 1.27 g cm^{-3} for Z = 4, F(000) = 320, $\mu(MoK_\alpha)$ = 1.1 cm^{-1}.

3.3.2 Structure solution and crystal data for $[Cu(clge)_2(NO_3)_2]$

Deep blue crystals of $[Cu(clge)_2(NO_3)_2]$ were obtained by slow hydrolysis of bis(1-cyanoguanidine)di-µ-aquo-copper(II)dinitrate dihydrate as described in Section 3.2.2a. Several crystal were mounted in

TABLE 3.2 Final Positional Parameters (x10^3) for clge.EtOH

Atom	x/a	y/b	z/c
O(1)	319.1(3)	135.6(2)	388.4(2)
C(1)	173.4(4)	198.5(3)	409.1(2)
C(2)	2.2(4)	64.0(3)	275.6(3)
N(1)	165.3(4)	307.8(3)	490.9(2)
N(2)	16.3(3)	174.9(3)	354.4(2)
N(3)	-155.2(4)	51.6(4)	222.1(3)
N(4)	127.4(4)	-34.3(3)	247.8(3)
O(2)	545.9(4)	267.3(4)	224.2(3)
C(3)	455.2(8)	281.5(6)	117.3(4)
C(4)	465(1)	151.9(8)	44.8(6)
H(1)	258(7)	327(5)	533(5)
H(2)	53(9)	339(6)	521(5)
H(4)	-232(6)	127(5)	231(4)
H(5)	157(6)	-5(5)	164(4)
H(6)	103(6)	-105(5)	206(4)
H(7)	242(7)	-26(5)	282(4)
H(8)	476(9)	233(7)	275(5)
H(9)	513	368	73
H(10)	328	307	131
H(11)	399	171	-30
H(12)	591	126	27
H(13)	406	65	85

TABLE 3.3 Thermal Parameters (x10^3)/Å^2 for clge.EtOH

Atom	U(1)	U(22)	U(33)	U(23)	U(13)	U(12)	U(ISO)
O(1)	24(1)	45(1)	48(1)	-11(1)	-1(1)	4(1)	
C(1)	29(1)	28(1)	32(1)	2(1)	0(1)	-2(1)	
C(2)	29(1)	29(1)	36(2)	-2(1)	0(1)	1(1)	
N(1)	29(1)	41(1)	37(1)	-12(1)	-1(1)	0(1)	
N(2)	26(1)	28(1)	36(1)	-4(1)	-1(1)	2(1)	
N(3)	39(2)	45(2)	55(2)	-18(2)	-14(1)	8(1)	
N(4)	35(2)	35(1)	51(2)	-15(1)	-5(1)	4(1)	
O(2)	40(1)	78(2)	51(2)	-3(1)	-2(1)	-3(1)	
C(3)	83(3)	79(2)	67(3)	-7(3)	-26(3)	19(3)	
C(4)	102(4)	117(5)	80(4)	-28(4)	-9(4)	-1(4)	
H(1)							40(10)
H(2)							60(20)
H(4)							20(10)
H(5)							20(10)
H(6)							20(10)
H(7)							20(10)
H(8)							60(20)

In the form: $[\exp-2\pi^2(U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)lc^{*2}+$

$2U(12)hka^*b^*+2U(13)hla^*c^*2U(23)klb^*c^*)]$

Lindemann tubes for preliminary study. Oscillation and Weissenberg photographs revealed cell parameters, space group and the fact that the crystals were twinned about the (100) plane. The ratio of the two components varied from crystal to crystal. X-ray diffraction data for the refinement of cell parameters and structure determination were calculated as described in Section 1.6.1 for the major component of the crystal (0.3 x 0.2 x 0.2 mm) which was found to have the maximum component ratio; allowance was made, at a later stage, for the twinning of the crystals. Of the 1301 intensities collected 555 were deemed to be observed.

Consideration of the molecular formula within the context of the crystal symmetry indicated that the copper atom must be situated in one of the two-fold special positions (0.5, 0.5, 0.5) of the $P2_1/n$ space group and that the pairs of clge molecules and nitrate anions must be located in centrosymmetrically related positions. Consequently, subsequent to the data reduction stage, the positions of the carbon, nitrogen and oxygen atoms were determined by a difference Fourier synthesis. The identities of the skeletal atoms of the chelating ligand were confirmed by equating their atomic scattering factors to that of carbon and then determining their isotropic temperature factors. Those atoms with factors between 0.0296 and 0.0318, between 0.0105 and 0.0235, and equal to -0.0067 were designated carbon, nitrogen and oxygen, respectively. Full matrix least squares refinement with anisotropic temperature factors for all these atoms converged at R = 0.070. A subsequent difference Fourier synthesis indicated the presence of electron density (varying from 0.50 to 0.29 e/Å^3) consistent with the ligand adopting coordination mode 3.9. The positions of the corresponding hydrogen atoms were then defined [r(N-H) = 0.95 Å; U(ISO) = 0.03 Å^2] using a hydrogen placing routine. Further refinement of the structure with fixed hydrogen atoms converged at R = 0.066. Final positional parameters and thermal parameters are given in Tables 3.4 and 3.5 respectively. Observed and calculated structure factors are included in Appendix B.

Crystal Data

$C_4H_{12}N_{10}O_8Cu$, M = 391.8, monoclinic, space group $P2_1/n$, a = 9.146(3), b = 6.654(3), c = 11.183(3) Å, β = 98.56(3)°, μ = 672.9 Å^3, D_m = 1.89, D_c = 1.93 g.cm^{-3} for Z = 2, F(000) = 398, μ(MoK_α) = 17.60 cm^{-1}.

3.3.3 Molecular geometries of uncoordinated and coordinated 1-carbamoylguanidine

Whereas the clge molecules are held by hydrogen bond interactions in the structure of the ethanol adduct, they act as bidentate ligands in the structure of the complex. Two centrosymmetrically related clge molecules chelate the copper(II) ion to form a $[Cu(clge)_2]^{2+}$ moiety. The molecular geometries of the clge molecule in the adduct and in the $[Cu(clge)_2]^{2+}$ moiety are shown in

TABLE 3.4 Final Positional Parameters ($\times 10^3$) for $[Cu(clge)_2(NO_3)_2]$

Atom	x/a	y/b	z/c
Cu(1)	500	500	500
C(1)	245(1)	338(2)	598(1)
C(2)	215(1)	358(2)	377(1)
N(1)	171(1)	293(2)	686(1)
N(2)	164(1)	321(2)	486(1)
N(3)	115(1)	333(2)	280(1)
N(4)	350(1)	420(2)	371(1)
N(5)	298(1)	339(2)	11(1)
O(1)	376(1)	402(1)	617(1)
O(2)	369(1)	348(2)	112(1)
O(3)	361(1)	295(2)	-75(1)
O(4)	163(1)	372(2)	12(1)
H(1)	219	306	767
H(2)	74	244	669
H(3)	63	284	482
H(4)	19	288	289
H(5)	140	360	203
H(6)	378	426	293

TABLE 3. 5 Final Thermal Parameters ($\times 10^3$)/Å^2 for $[Cu(clge)_2(NO_3)_2]$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cu(1)	27(1)	54(2)	28(1)	-1(2)	1.0(8)	-4(2)
C(1)	29(7)	28(8)	24(6)	-10(6)	7(5)	-4(6)
C(2)	22(6)	21(8)	37(7)	1(6)	0(5)	3(5)
N(1)	32(6)	63(9)	23(5)	-6(5)	0(4)	-14(6)
N(2)	15(5)	39(7)	29(5)	0(5)	8(4)	-9(5)
N(3)	24(6)	62(9)	31(6)	-8(6)	3(4)	-12(5)
N(4)	21(5)	41(7)	30(5)	-13(5)	6(4)	-9(4)
N(5)	29(6)	35(8)	38(6)	14(6)	14(5)	6(5)
O(1)	15(4)	50(6)	22(4)	3(4)	0(3)	-7(4)
O(2)	49(6)	100(10)	27(5)	-8(6)	3(4)	15(7)
O(3)	29(5)	80(9)	27(5)	0(5)	7(4)	12(5)
O(4)	19(5)	74(9)	80(7)	3(7)	18(5)	5(6)

In the form: $[\exp -2\pi^2(U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)l^2c^{*2}+2U(12)hka^*b^*+2U(13)hla^*c^*+2U(23)klb^*c^*)]$

Figures 3.1 and 3.2 respectively; bond lengths and angles are compared in Table 3.6.

It is clear that the geometry of coordinated clge differs from that of free clge. Uncoordinated clge adopts tautomeric form 3.1 such that an intramolecular hydrogen bond occurs between O(1) and N(4). Proton transfer from N(4) to N(2) during the coordination process results in tautomeric form 3.2, which can readily chelate the copper(II) ion giving rise to coordination form 3.9.

Both clge molecules are close to planarity, the maximum deviation of the skeletal atoms from the best planes (Table 3.7) being 0.098 Å for free clge and 0.028 Å for coordinated clge, inferring sp^2 hybridisation of the skeletal atoms and the presence of a delocalised π-system over the entire C-N-O skeleton. This inference is supported by the intermediate length C-O and C-N bonds [typical bond lengths:[55] r(C-O) = 1.43, r(C=O) = 1.22, r(C-N) = 1.47, r(C=N) = 1.27 Å] and the O-C-N, N-C-N and C-N-C bond angles which are close to 120°.

The tautomeric change on coordination, generation of a C-NH-C bridge at the expense of a C=N-C bridge, has several ramifications. The bridging C-N bonds lengthen at the expense of the terminal C-N bonds, the C-N-C bond angle increases and the molecule is flattened. Pertinent structural features of free and coordinated clge are compared in Table 3.8, together with the corresponding data for bg and bu.

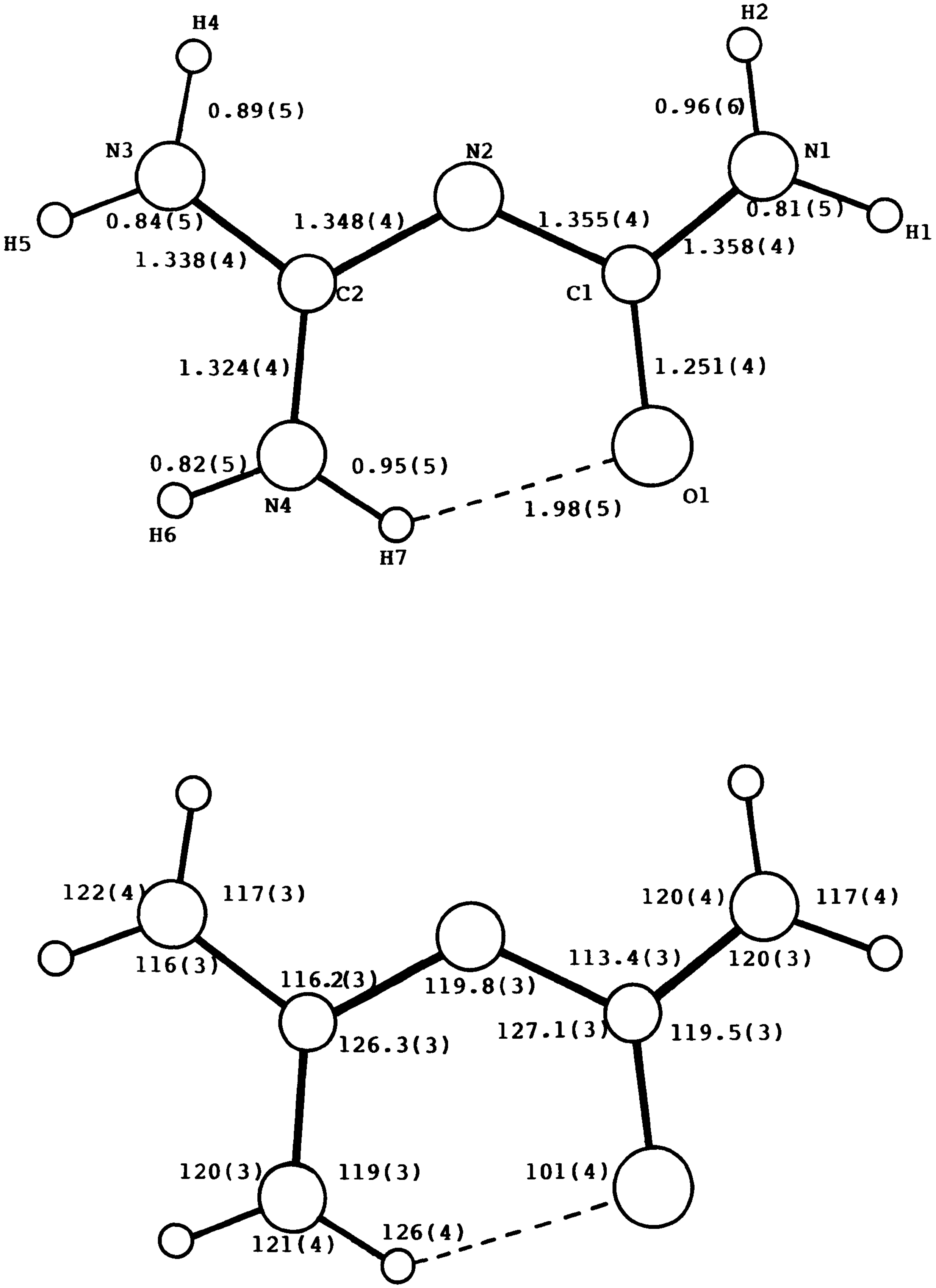


FIGURE 3.1 Molecular geometry of 1-carbamoylguanidine (bond lengths/Å and bond angles/°)

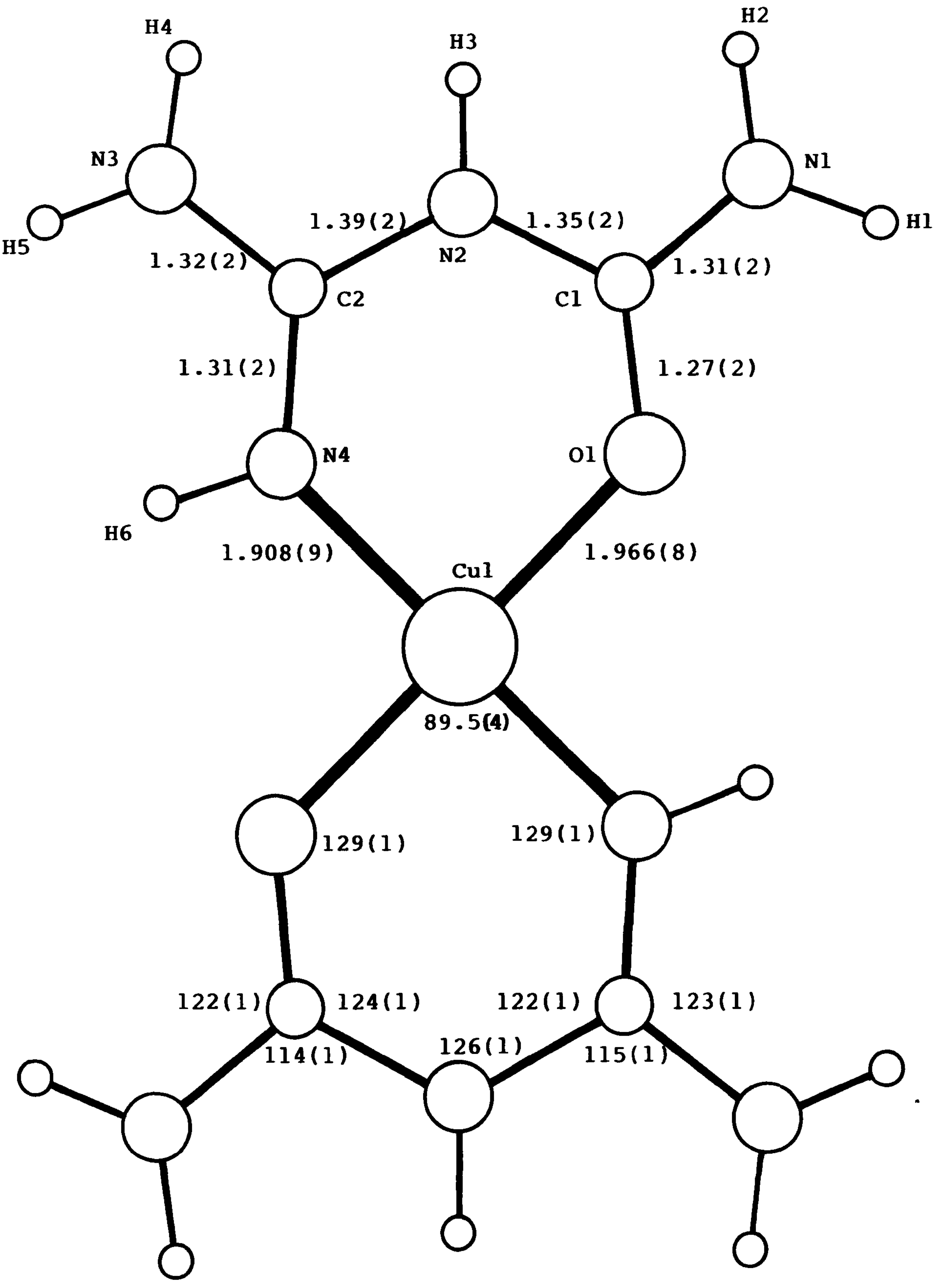


FIGURE 3.2 Molecular geometry of $[Cu(clge)_2]^{2+}$ cationic fragment (bond lengths/Å and bond angles/°)

TABLE 3.6 Molecular Geometries of Uncoordinated and Coordinated 1-Carbamoylguanidine

Bond Distances/Å	clge.EtOH	$[Cu(clge)_2(NO_3)_2]$
C(1)-O(1)	1.251(4)	1.27(2)
C(1)-N(1)	1.358(4)	1.31(2)
C(1)-N(2)	1.355(4)	1.35(2)
C(2)-N(2)	1.348(4)	1.39(2)
C(2)-N(3)	1.338(4)	1.32(2)
C(2)-N(4)	1.324(4)	1.31(2)

Bond Angles/°	clge.EtOH	$[Cu(clge)_2(NO_3)_2]$
O(1)C(1)N(1)	119.5(3)	122(1)
O(1)C(1)N(2)	127.1(3)	124(1)
N(1)C(1)N(2)	113.4(3)	114(1)
C(1)N(2)C(2)	119.8(3)	126(1)
N(2)C(2)N(3)	116.2(3)	115(1)
N(2)C(2)N(4)	126.3(3)	122(1)
N(3)C(2)N(4)	117.4(3)	123(1)

TABLE 3.7 Planarities of Free and of Coordinated 1-Carbamoylguanidine and of the $[Cu(clge)_2]^{2+}$ Fragment

clge in clge.EtOH

Atom	Deviation from Plane/Å	Atom	Deviation from Plane/Å
O(1)	-0.098	N(2)	-0.008
C(1)	-0.001	N(3)	-0.055
C(2)	+0.006	N(4)	+0.095
N(1)	+0.062		

Equation of best plane: $-1.9704x - 5.76071y + 8.27349z = 1.901$

Clge in $[Cu(clge)_2(NO_3)_2]$

Atom	Deviation from Plane/Å	Atom	Deviation from Plane/Å
O(1)	+0.028	N(2)	+0.003
C(1)	-0.018	N(3)	+0.020
C(2)	-0.014	N(4)	-0.016
N(1)	-0.005		

Equation of best plane: $-2.8725x + 6.3119y + 0.9582z = 2.018$

$[Cu(clge)_2]^{2+}$ in $[Cu(clge)_2(NO_3)_2]$

Atom	Deviation from Plane/Å	Atom	Deviation from Plane/Å
Cu(1)	+0.072	N(1)	+0.017
O(1)	-0.028	N(2)	+0.018
C(1)	-0.026	N(3)	+0.042
C(2)	-0.022	N(4)	-0.074

Equation of best plane: $-3.1976x + 6.2292y + 0.9938z = 1.940$

The coordination mode of clge is intermediate between that of bg and that of bu; bg coordinates via two imine groups (3.6), clge via one imine and one carbonyl group (3.9), and bu via two carbonyl groups (3.7). On coordination to copper(II), clge undergoes an analogous tautomeric change to that experienced by bg, proton transfer from a terminal amine group to the central nitrogen atom generating a C-NH-C bridge at the expense of a C-N=C bridge. No tautomeric change occurs in bu on coordination, both free and coordinated bu having a C-NH-C bridge.

It is clear from the data in Table 3.8 that the effect of protonation at N(2), caused by coordination, is extremely marked and consistent within this group of molecules.

It is significant that in none of these complexes does the ligand coordinate the transition metal through an amine group, a coordination mode generally accepted by early workers in this field.[48,52,53] Since the ligand is planar, an extensive delocalised π-system must extend over the whole molecule, resulting in sp^2 hybridisation of the amino groups. Consequently, the groups do not have lone pairs of electrons which can be directed towards a transition metal and hence coordination through amine residues is not possible; the only functional groups which act as coordinating centres in these ligands are imine and carbonyl fragments.

TABLE 3.8 Significant Features of the Molecular Geometries of Free and Coordinated clge, bg and bu.

	Dihedral angle/°*	Average $r(\text{C-N}_{\text{bridge}})$/Å	Average $r(\text{C-N}_{\text{terminal}})$/Å #	C-N-C angle/°
clge (free)	7.5	1.352(4)	1.348(4)	119.8(3)
clge (coord)	1.7	1.370(20)	1.315(20)	126.0(1.0)
bg (free)[13]	12.5	1.356(2)	1.358(2)	119.9(1)
bg (coord)[21]	-	1.374(8)	1.349(8)	127.3(5)**
bu (free)[17]	6.3	1.385(3)	1.325(3)	128.5(2)
bu (coord)[22]	6.4	1.371(6)	1.321(6)	126.8

* This is the angle between the normals to the planes which best represent the two halves of the molecule.

\# This average does not include those contacts, formally defined as double bonds, between carbon and terminal imine groups.

** Average of two determinations.

3.3.4 Intermolecular contacts in clge.EtOH

A projection of the structure of the adduct onto the (100) plane is shown in Figure 3.3. The structure is composed of mutually perpendicular ribbons of clge molecules, running parallel to the x axis, with ethanol molecules located above and attached to the carbonyl oxygen by a fairly strong hydrogen bond, r(O(1)...O(2)) =

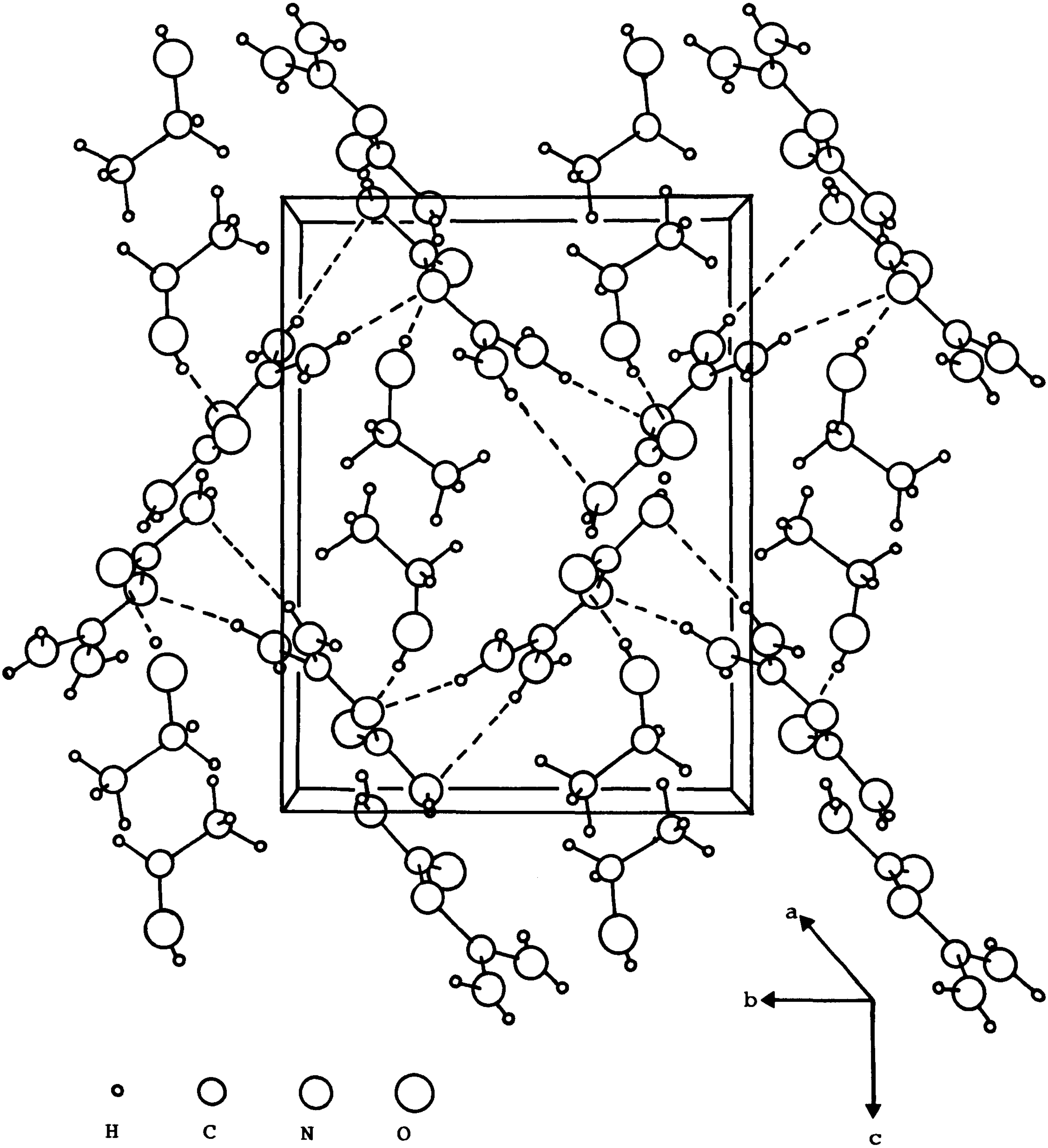


FIGURE 3.3 Projection of the structure of clge.EtOH onto the (100) plane

2.806 Å. The ribbon-like structure is more clearly seen in Figure 3.4 which shows a projection of the structure perpendicular to the plane of the clge molecule. Hydrogen bonds (Table 3.9) maintain the inter- and intra-ribbon contacts and strengthen the rigidity of the ethanol oxygen atom. The inter- and intra-ribbon hydrogen bonds are depicted in Figures 3.3 and 3.4. Details of the molecular geometry of the ethanol molecule are given in Table 3.10. With the exception of the short C-C bond distance which results from the thermal libration of the ethyl moiety, this data is unremarkable.

TABLE 3.9 Intermolecular Contacts of Less than 3.30 Å in clge.EtOH; Hydrogen Bond and Electrostatic Interactions

Interaction X-H...X'	Symmetry Properties of X'	r(X...X') Å	r(X-H) Å	r(H...X') Å	XHX' °
N(1)-H(1)...N(2)	$\frac{1}{2}+x,\frac{1}{2}-y,1\frac{1}{2}-z$	3.189	0.87	2.23	168
N(1)-H(2)...O(1)	$-\frac{1}{2}+x,\frac{1}{2}-y,1\frac{1}{2}-z$	2.994	0.96	2.06	166
N(3)-H(4)...O(2)	-1+x,y,z	2.953	0.89	2.08	165
N(3)-H(5)...N(1)	$-x,-\frac{1}{2}+y,\frac{1}{2}-z$	3.283	0.84	2.45	174
N(4)-H(6)...N(2)	$-x,-\frac{1}{2}+y,\frac{1}{2}-z$	3.042	0.82	2.26	160
N(4)-H(7)...O(2)*	$1-x,-\frac{1}{2}-y,\frac{1}{2}-z$	3.039	0.95	2.44	121
O(2)-H(8)...O(1)	x,y,z	2.806	0.84	1.97	175

* For this interaction the angle at H(7) is very low owing to the N(4)-H(7)...O(1) intramolecular hydrogen bond interaction, r(N(4)-H(7)) = 0.95, r(H(7)...O(1)) = 1.98, r(N(4)...O(1)) = 2.646 Å and N(4)H(7)O(1) = 126°.

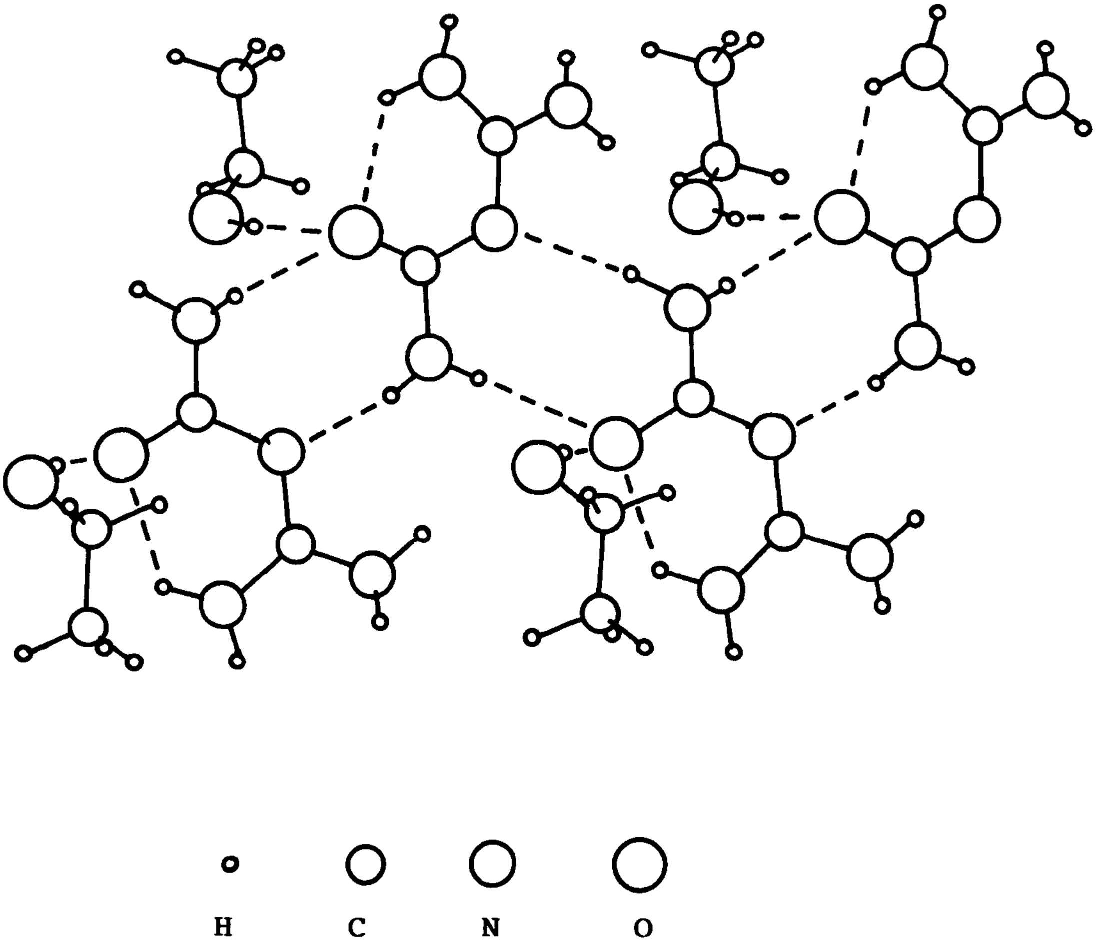


FIGURE 3.4 Projection of the structure of clge.EtOH perpendicular to the plane of the clge molecule

Table 3.10 Geometry of the Ethanol Molecule in clge.EtOH

Bond Distances/Å		Bond Angles/°	
C(3)-O(2)	1.417(6)	O(2)C(3)C(4)	114.5(5)
C(3)-C(4)	1.428(8)	H(8)O(2)C(3)	110(4)
O(2)-H(8)	0.84(6)		

3.3.5 Intermolecular Contacts and the Coordination of the Copper(II) Ion in $[Cu(clge)_2(NO_3)_2]$

Views of the structure of the complex perpendicular to (001) and (120) are shown in Figures 3.5 and 3.6 respectively. It consists of ribbons of coplanar $[Cu(clge)_2]^{2+}$ cationic fragments and nitrate anions linked through the anions to give two sets of planes parallel to (120) and $(\bar{1}20)$. The intra- and inter-ribbon contacts involve both electrostatic and hydrogen bonding interactions. All intermolecular contacts of less than 3.30 Å are summarised in Table 3.11; the principal hydrogen bonding interactions are also shown in Figure 3.6.

The copper(II) ion is coordinated by two centrosymmetrically related clge molecules which form an effectively planar $[Cu(clge)_2]^{2+}$ cationic fragment, the maximum deviation of the constituent atoms being 0.074 Å (Table 3.7). The Cu(1)-O(1) and Cu(1)-N(4) bond distances, 1.966 Å and 1.908 Å respectively, are

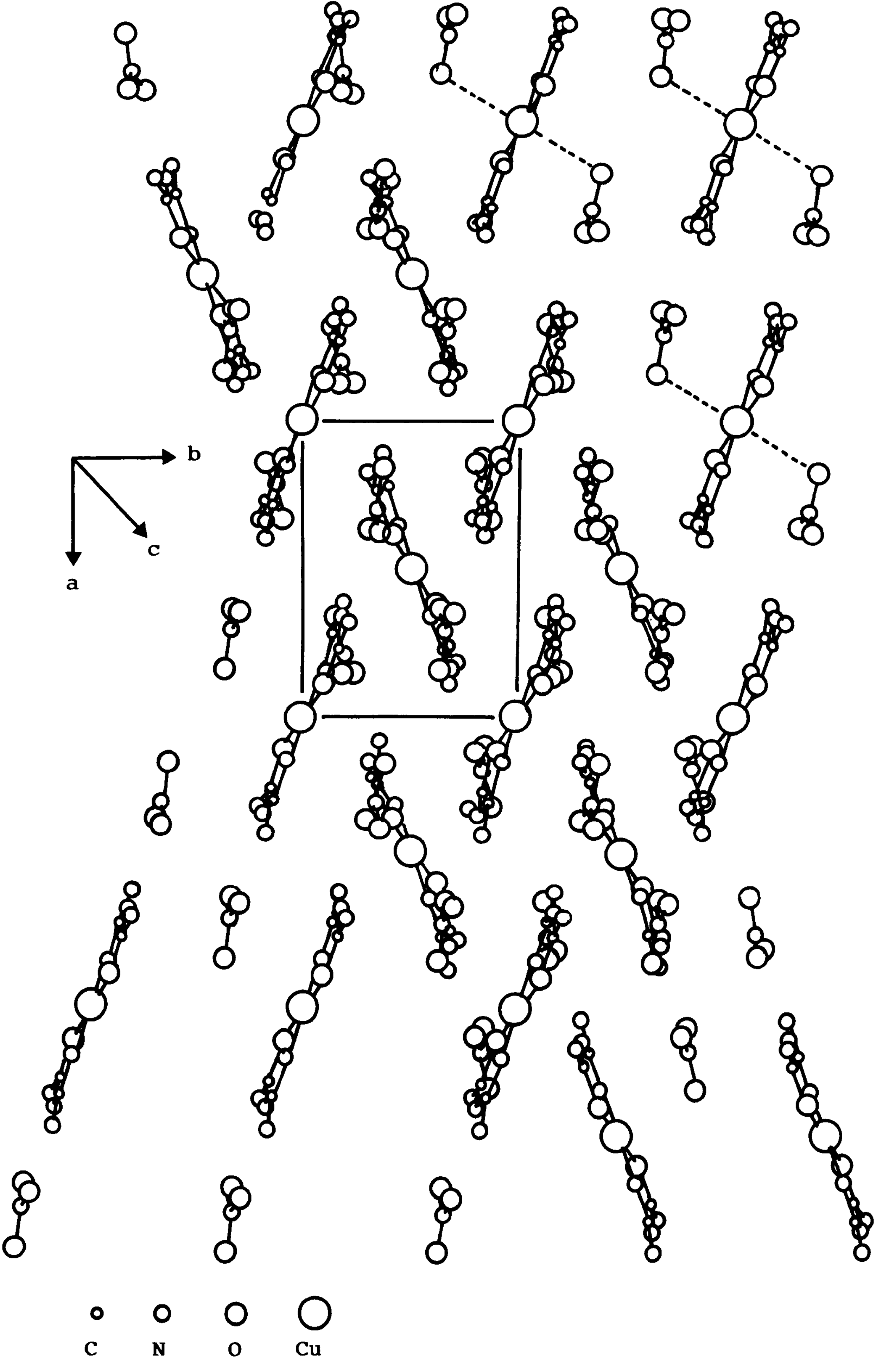


FIGURE 3.5 View of the structure of [Cu(clge)$_2$(NO$_3$)$_2$] perpendicular to the (001) plane

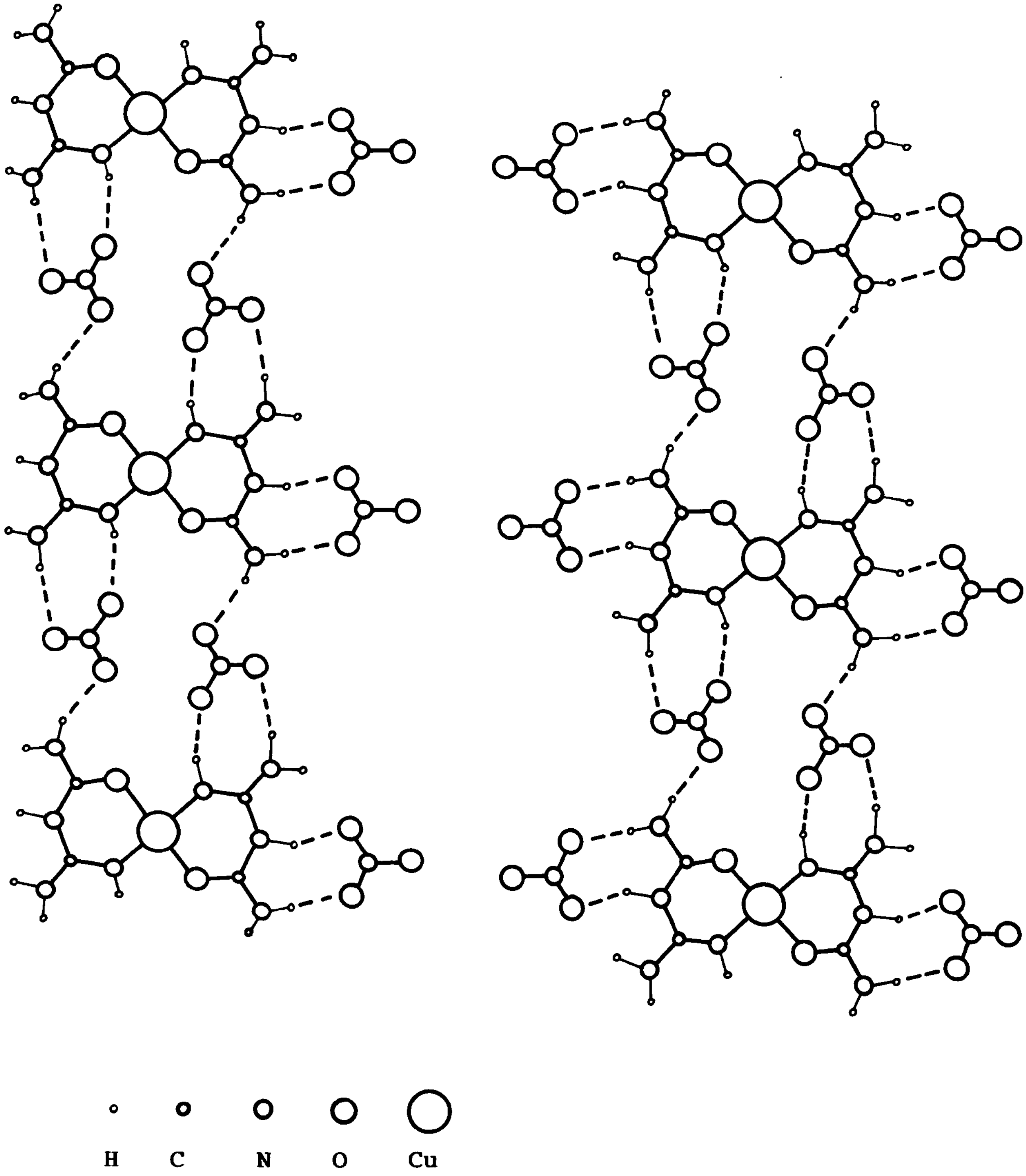


FIGURE 3.6 View of the structure of [Cu(clge)$_2$(NO$_3$)$_2$] perpendicular to the (120) plane

TABLE 3.11 Intermolecular Contacts of Less than 3.30 Å in $[Cu(clge)_2(NO_3)_2]$: Hydrogen Bond and Electrostatic Interactions

Interaction X-H...X'	Symmetry Properties of X'	r(X...X') Å	r(X...H) Å	r(H...X') Å	XHX' °
N(1)-H(1)...O(3)	x,y,1+z	2.96	0.95	2.03	166
N(1)-H(2)...O(2)	$-\frac{1}{2}$+x,$\frac{1}{2}$-y,$\frac{1}{2}$+z	2.92	0.94	1.98	173
N(2)-H(3)...O(3)	$-\frac{1}{2}$+x,$\frac{1}{2}$-y,$\frac{1}{2}$+z	2.86	0.95	1.94	163
N(3)...O(1)*	$-\frac{1}{2}$+x,$\frac{1}{2}$-y,$-\frac{1}{2}$+z	3.06	-	-	-
N(3)...O(3)*	$-\frac{1}{2}$+x,$\frac{1}{2}$-y,$\frac{1}{2}$+z	3.14	-	-	-
N(3)...O(2)*	x,y,z	3.20	-	-	-
N(3)...O(4)*	x,y,z	3.26	-	-	-
N(3)...N(4)*	$\frac{1}{2}$-x,$-\frac{1}{2}$+y,$\frac{1}{2}$-z	3.27	-	-	-
N(4)-H(6)...O(2)	x,y,z	2.97	0.95	2.08	156

* The strengths of the intermolecular contacts involving N(3) are much weaker than those involving N(1), N(2) and N(4) inferring much weaker hydrogen bonding interactions. Indeed, unequivocal designation of the hydrogen bonds about N(3) is not possible, only H(5) lying along an intermolecular contact [N(3)H(5)O(4) = 168°]. Although H(4) is located near the contact to O(3) [N(3)H(4)O(3) = 146°], it is difficult to consider this a true hydrogen bonding interaction, since O(1) also acts as a hydrogen bond acceptor from N(1) and N(2), the three angles at O(3) summing to exactly 360° inferring sp^2 hybridisation of the oxygen atom. The only other contact which H(4) is remotely near is that to O(1), [N(3)H(4)O(1) = 118°] but the angle is too small for it to be a significant hydrogen bonding contact.

comparable to the Cu-O and Cu-N bond distances found for coordinated bu [r(C-O) = 1.935 Å][22] and coordinated bg [average r(Cu-N) = 1.946 Å].[21]

A weak bonding interaction also occurs between the copper atom and the nitrate anions in adjacent planes, theO(4) atoms of centrosymmetrically related nitrate anions being located in the axial positions of the square planar CuO_2N_2 chromophore. This contact is almost at the limit of the copper atom's sphere of influence, the Cu(1)...O(4) interatomic distance (2.98 Å) being marginally less than the sum (2.95 Å) of the van der Waal's radii of copper (1.43 Å) and oxygen (1.52 Å).[41] Assuming the copper(II) ions coordination sphere to consist of six equivalent donor atoms then the tetragonality (T) can be calculated. A value for R_S of 1.937 Å is obtained by averaging r(Cu(1)-O(1)) and r(Cu(1)-N(4)) and R_L is taken as r(Cu(1)-O(4)) = 2.890 Å. Hence T is calculated to be 0.67 which defines the copper(II) ion's stereochemistry to be at the limit of a tetragonally elongated octahedron, just outside the range for square coplanar stereochemistry (Section 1.5.2). This is in agreement with the stereochemistry predicted from the van der Waal data noted above. Full details of the copper(II) ion's coordination geometry are given in Table 3.12.

The molecular geometry of the nitrate anion (Table 3.13) is consistent with D_{3h} symmetry. The infrared spectrum of the complex, which is compared with those of

TABLE 3.12 Coordination Geometry of the Copper(II) Ion in $[Cu(clge)_2(NO_3)_2]$

Bond Distances/Å		Bond Angles/°	
Cu(1)-O(1)	1.966(8)	O(1)Cu(1)N(4)	81.5(4)
Cu(1)-N(4)	1.908(10)	O(1)Cu(1)O(4)	86.1(4)
Cu(1)-O(4)	2.890(11)	N(4)Cu(1)O(4)	85.9(4)

TABLE 3.13 Geometry and Planarity of the Nitrate Anion in $[Cu(clge)_2(NO_3)_2]$

Bond Distances/Å		Bond Angles/°	
N(5)-O(2)	1.22(2)	O(2)N(5)O(3)	119(1)
N(5)-O(3)	1.23(2)	O(2)N(5)O(4)	119(1)
N(5)-O(4)	1.23(2)	O(3)N(5)O(4)	120(1)

Atom	Deviation from Plane/Å	Atom	Deviation from plane/Å
N(5)	+0.005	O(3)	-0.002
O(2)	-0.002	O(4)	-0.002

Equation of best plane: $1.8042x + 6.4539y - 1.9050z = 2.698$

$Cu(clge)_2X_2$ (X = Cl, Br) in Figure 3.7 (1800-600 cm^{-1}) does not, however, entirely support this conclusion. It contains bands which can be attributed to the B_2 (1390 cm^{-1}; probably superimposed on a vibrational mode of the coordinated clge ligand) and A_1 (1330 and 1050 cm^{-1}) stretching vibrations and to the A_2 (620 cm^{-1}), A_1 (760 cm^{-1}) and B_2 (720 cm^{-1}) deformation vibrations of a unidentate C_{2v} nitrate anion.[56] These observations are also consistent with a very weak copper(II)-nitrate interaction which reduces the local symmetry of the anion from D_{3h} to C_{2v}.

3.4 Spectroscopic properties

Assignment of the vibrational spectra of species as complex as clge can only be approximate owing to extensive mixing of the internal coordinates of the planar skeleton exacerbated by the delocalised π-system. Accepting this, a limited qualitative vibrational analysis has been attempted for uncoordinated clge. This assignment has then been used as a basis for interpretation of the spectrum of the coordinated ligand.

Uncoordinated clge has C_s symmetry and should have 33 (23A' and 10A") vibrational modes all of which are infrared active. The in-plane vibrations consist of six N-H [designated as three ν_s(N-H) and three ν_a(N-H)] plus six skeletal [three ν(C-$N_{terminal}$), two ν(C-$N_{bridging}$) and one ν(C-O)] stretching vibrations and six NH_2 [three scissors and three rocking] plus five skeletal [two at

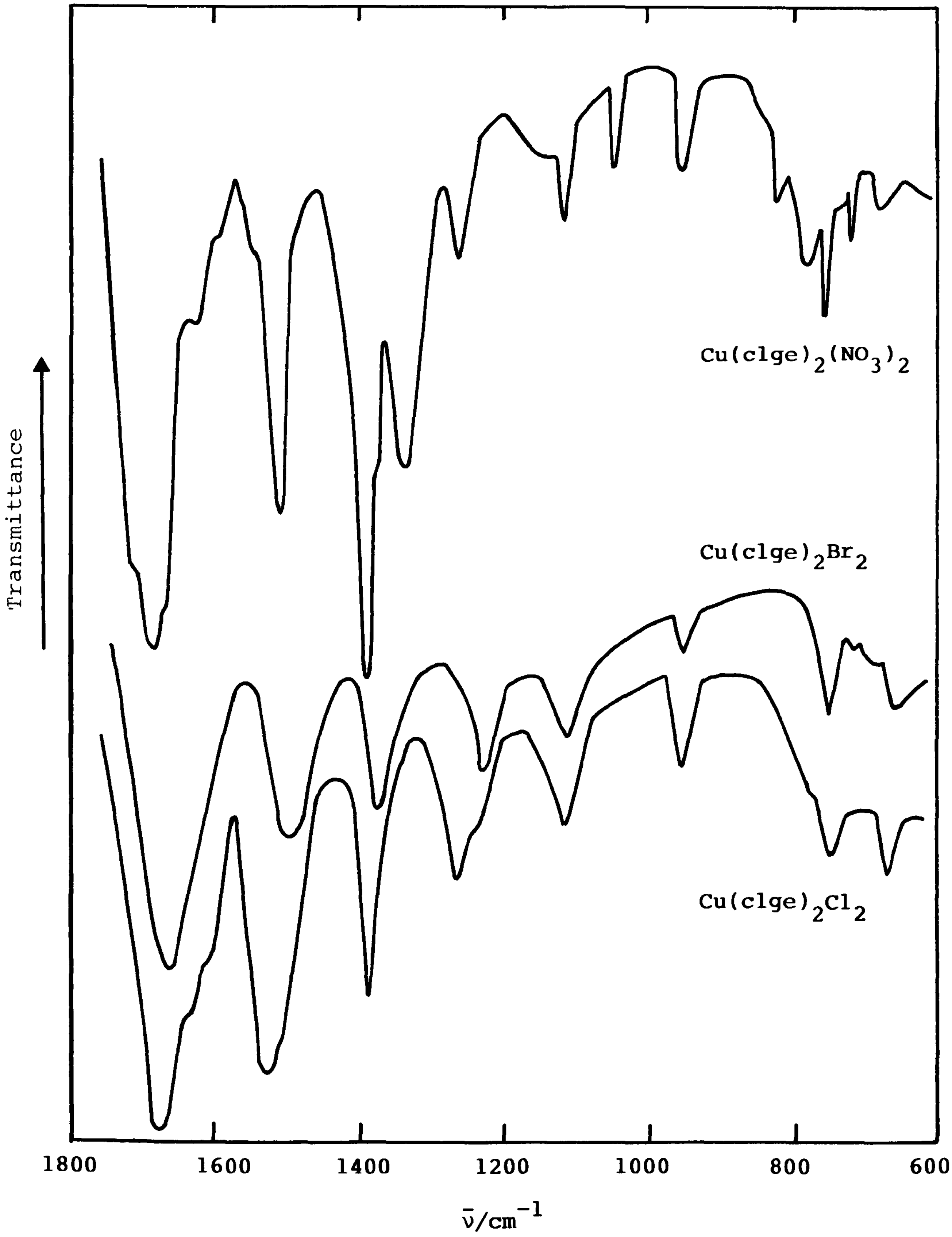


FIGURE 3.7 IR spectra of $Cu(clge)_2X_2$ ($X = NO_3$, Br, Cl)

C(1), one at N(2) and two at C(2)] deformation vibrations. The ten out-of-plane deformations can be split into six N-H [three wagging and three twisting] and, by difference, four skeletal deformation vibrations.

Infrared spectra for clge.EtOH, clge, D_6-clge, Cu(clge)$_2$X$_2$ (X = NO_3, Cl, Br) and Cu(D_6-clge)$_2$(NO_3)$_2$ were measured in nujol and halocarbon mulls and in KBr discs on a Perkin Elmer 598 spectrometer (4000-400 cm^{-1}). They are collated in Table 3.14. For uncoordinated clge the ν(N-H) and δ(NH_2) vibrations were assigned by comparison of the spectra of the protonated and deuterated samples using, as a basis, the analysis proposed by Jones et al for cnge[9] and guanidine.[57] Assignment of the skeletal vibrations is restricted to those stretches, ν(C-N), ν(C-O), which give bands in the limited wavenumber range 1750-1350 cm^{-1}. Also observed in this region are bands due to δ(NH_2) scissors deformation. All of these vibrations have A' symmetry and are extensively mixed.

The spectra of clge.EtOH, clge and D_6-clge in the region (1800-1250 cm^{-1}) are compared with that of cnge in Figure 3.8. The deuteration experiments indicate that the bands due primarily to the δ(NH_2) scissors deformations occur in the 1680-1630 cm^{-1} range; the other bands must be attributable to the skeletal stretches. The spectra of clge.EtOH and of clge are very similar and contain an isolated band at ~1410 cm^{-1} which is absent from the spectrum of cnge. The spectra also differ from that of cnge in the complex structure in the range

TABLE 3.14

TABLE 3.14 Infrared Spectroscopic Data/cm^{-1} for clge,clge.EtOH,

clge	clge.EtOH	$[Cu(clge)_2(NO_3)_2]$	$Cu(clge)_2Cl_2$
3450 3430 3380 3340 s,br	3440sh 3400 3350 s,br	3480 3380 s,br	3420 3330 s,br
3220 3150 s,br	3230 3160 s,br	3220 s,br	3190 s,br
1675 1640 s,br	1650 s,br	1710 sh	1700 sh
		1685 s	1680 s
		1645 m	1630 s
1600 1540 s,br	1600 1550 s,br		
		1510 s	1520 s
1420 s,br	1405 s,br	1385 m	1380 s
		1390 s	
		1330 m	
		1260 mw	1265 m
1175 w	1170 w		1230 m
1100 ms	1105 1095 mw	1115 mw	1110 m
1040 vw	1045 m	1050 w	
920 w	925 mw	950 w	950 m
805 mw	820 mw	820 mw	
		790 mw	750 m
		760 m	
710 mw	725 m	720 mw	
		670 w	670 mw
560 m,br	570 m,br	580 mw	600 m,vbr
		515 w	
460 m,br	450 m,br	480 mw	495 m
		410 mw	420 m,br

Key

a $Cu(clge)_2X_2$ (X = NO_3, Cl, Br) and $Cu(D_6\text{-}clge)_2(NO_3)_2$ only.

b clge, clge.EtOH and D_6-clge only.

c $[Cu(clge)_2(NO_3)_2]$ and $Cu(D_6\text{-}clge)_2(NO_3)_2$ only.

d $Cu(D_6\text{-}clge)_2(NO_3)_2$ and D_6-clge only.

s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

$[Cu(clge)_2(NO_3)_2]$, $Cu(clge)Cl_2$, $Cu(clge)_2Br_2$, D_6-clge and $Cu(D_6\text{-}clge)_2(NO_3)_2$

$Cu(clge)_2Br_2$	D_6-clge	$Cu(D_6\text{-}clge)_2(NO_3)_2$	Assignment
	2600 2560] m,br	2600 2545] m	ν_a[N-H] and
3300 s,vbr			ν_s[N-H] or
3160 s,br	2450 2290] s,br	2480 2430] m 2380 s	ν_a[N-D]^d and ν_s[N-D]^d
1655 s,br	1240 1215] w	1200 w 1610 s 1635 s	$\delta[NH_2]$ or $\delta[ND_2]^d$ ν[O(1)C(1)N(1)]^a
	1580 1540	1460 s	ν[O(1)C(1)N(1)]^b
1490 s,br	1520] s,br		ν[N(3)C(2)N(4)]
1370 m,br	1420 s,br	1385 s	ν[N(2)C(2)N(3)]
		1400 1335] s 1265m	$\nu[NO_3]^c$
1220 m	1185 w		
	1130 m		
1110 mw	960 m		
			$\delta[NH_2]$ or $\delta[ND_2]^d$
	1055 vw	1045 mw	$\nu[NO_3]^c$
		1015 m	
950 w	890 w	945 m	
	815sh 795] m	820 mw	$\nu[NO_3]^c$
755 m			
	740 mw	760 ms	$\nu[NO_3]^c$
	720 w	720 mw	
		690 w	
650 m,br	660 w	620 w	
570 m,br		565 w	
		546 w	$\gamma[NH_2]$ or $\gamma[ND_2]^d$
480 mw		480 m	
		455 mw	
400 w,br		420 mw,br	

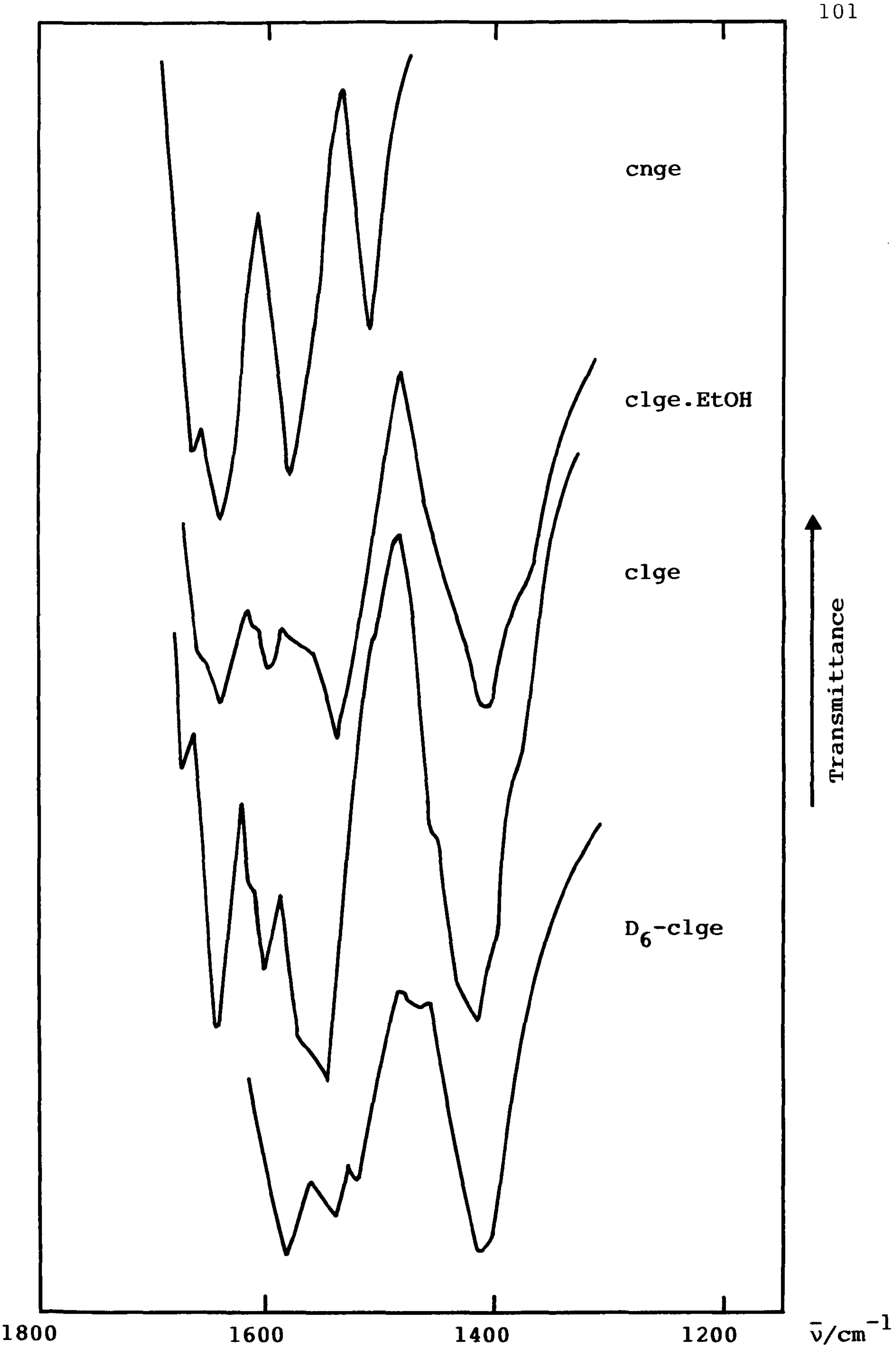


FIGURE 3.8 IR spectra of cnge, clge.EtOH, clge and D_6-clge

1600-1500 cm^{-1} where an extra band occurs. These two bands are additional to those assigned by Jones et al to the stretching vibrations (at 1580 and 1510 cm^{-1}) of the guanidine residue of the cnge molecule;[9] they are attributed primarily to the carbamoyl function. The absence of bands in the spectrum of D_6-clge at wavenumbers greater than 1580 cm^{-1} suggests that the carbonyl band is moved to lower wavenumbers not only by mixing with other skeletal stretches, but also by intramolecular hydrogen bond formation to the adjacent amine group (Figure 3.1).

The spectra of the complexes $Cu(clge)_2X_2$ ($X = NO_3$, Cl, Br) are compared in Figure 3.7 in the region 1800-600 cm^{-1}. After subtraction of the bands attributable to the vibration of the nitrate anion they are very similar suggesting the presence of the planar centrosymmetric $[Cu(clge)_2]^{2+}$ moiety in all three complexes. This is confirmed by the similarity of their diffuse reflectance UV-visible spectra which exhibit very broad absorption bands with λ_{max} values between 695 and 705 nm.

The spectra of uncoordinated and coordinated clge are compared in Figure 3.9 in the 1800-1200 cm^{-1} region. Although different, it is clear that spectroscopic methods cannot be used on their own to determine the exact mode of coordination as evidenced by Syamals incorrect interpretation of the tautomeric form and coordination mode (3.10) adopted by the clge molecule.[53] Unfortunately, the extensive mixing of internal

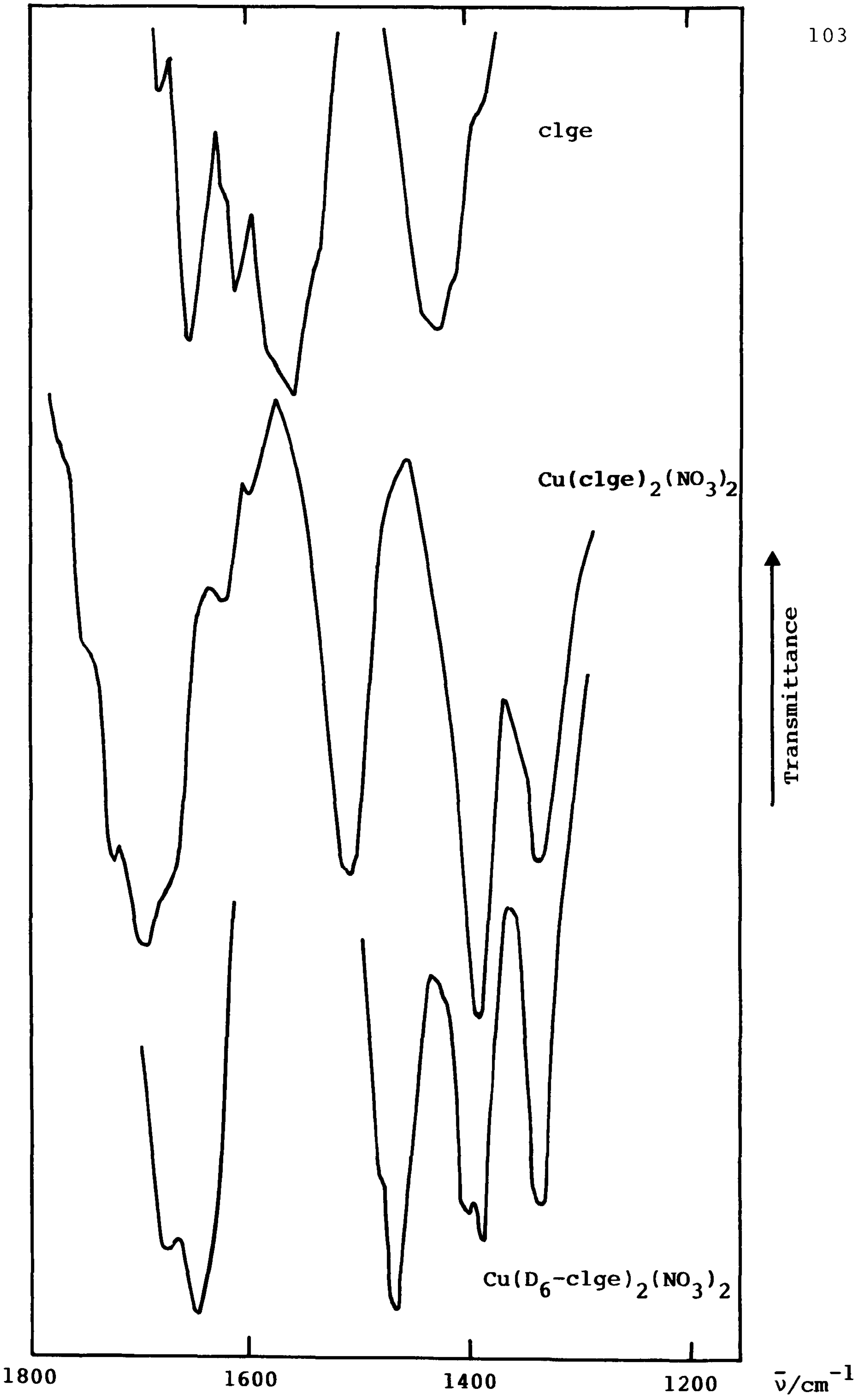


FIGURE 3.9 IR spectra of clge, [Cu(clge)$_2$(NO$_3$)$_2$] and [Cu(D$_6$-clge)$_2$(NO$_3$)$_2$]

coordinates which occurs in molecules of this type means that changes in the vibrational frequencies do not necessarily reflect changes in one particular functional group. Indeed, in the 1800-1300 cm^{-1} range of the spectra of $[Cu(clge)_2(NO_3)_2]$ (Figure 3.9) which should contain bands due to ν(C-N), ν(C-O) and $\delta(NH_2)$ vibrations, all of which have A' symmetry, we were unable to separate the $\delta(NH_2)$ vibration from the others, even following deuteration experiments. The sole observable effect of deuteration was to reduce the frequency at which the two higher energy bands absorb (Figure 3.9).

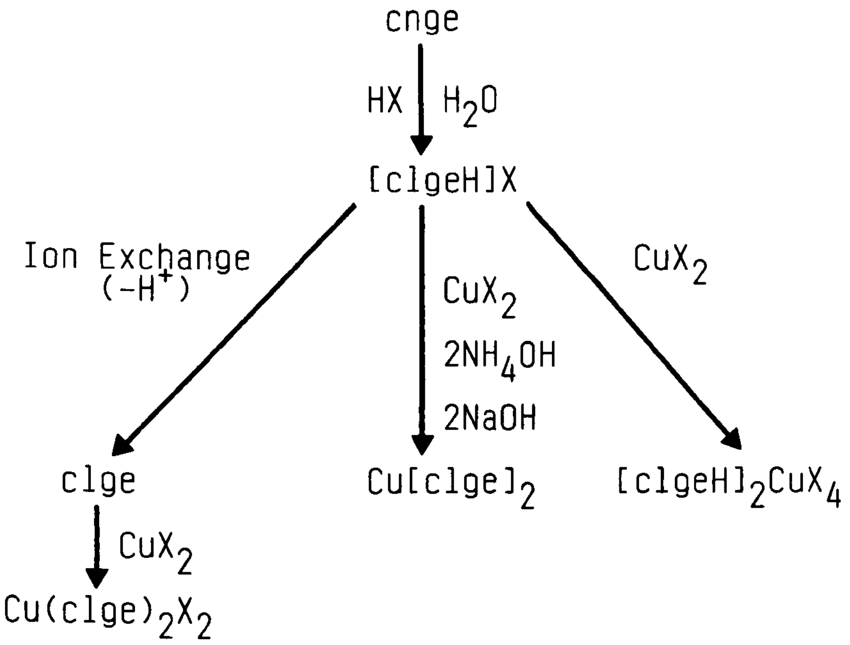
Clearly, unambiguous assignment of the vibrational spectra of clge and its derivatives is impossible without further isotopic enrichment experiments and a full normal coordinate analysis. It is probable, however, that the ν(C-O) stretching vibration of the carbonyl fragment of coordinated clge is a major component of the band at 1700 cm^{-1}. Compared with the free molecule for which the maximum frequency for this band is 1600 cm^{-1} (the bands at 1675 and 1645 cm^{-1} have been assigned to $\delta(NH_2)$ vibrations), this absorption has moved to higher frequency (Figure 3.9). Although carbonyl stretching frequencies are generally expected to decrease on coordination through the oxygen atoms,[43] in this case the increase can be rationalised by the loss of the intramolecular hydrogen bond present in free clge. Previously, the vibrational spectroscopy of these materials has been little studied. The only spectrum in the literature is that reported by Babykutty et al[49] for 'guanylurea'. Comparison with out data indicates that their spectrum is not that of clge, as inferred by their nomenclature, but is that of a $[\mathrm{clgeH}]^+$ salt.

CHAPTER FOUR

SALTS AND COPPER(II) COMPLEXES OF THE 1-CARBAMOYLGUANIDINIUM CATION

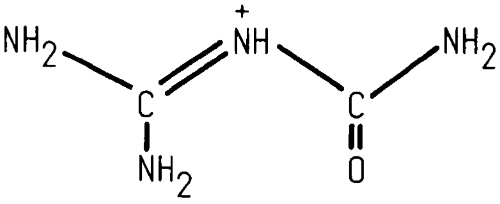
4.1 Introduction

The primary precursors to all 1-carbamoylguanidine (clge) compounds, are the 1-carbamoylguanidinium salts ([clgeH]X) produced by the acid hydrolysis of 1-cyanoguanidine (cnge).

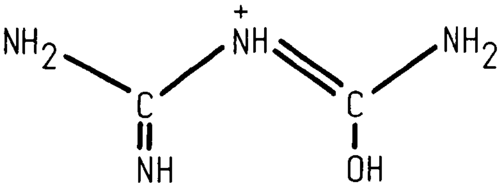


The chemistry of the cationic species $[clgeH]^+$ will be discussed in this chapter. Chapter Three described the synthesis of neutral clge compounds, whilst Chapter Five will describe the production of anionic $[clge]^-$ compounds.

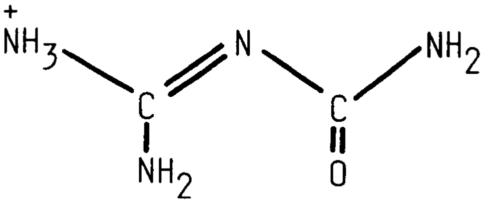
The salts ([clgeH]X) are frequently mentioned in the literature on clge derivatives,[48] but little is known of their electronic structure which might be described by any of the numerous forms (4.1-4.8) shown below.



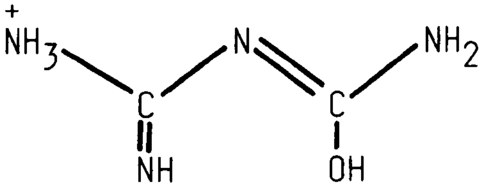
4.1



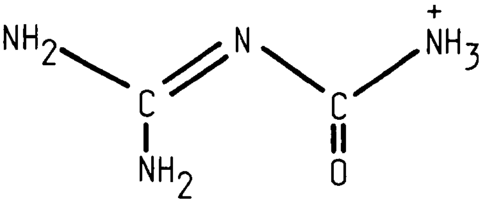
4.2



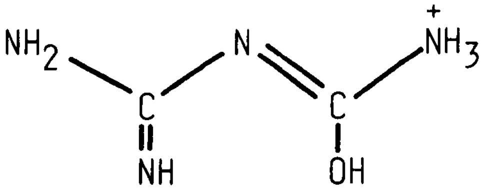
4.3



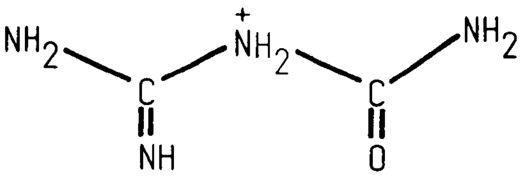
4.4



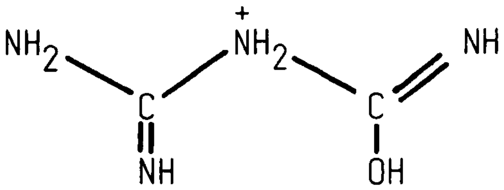
4.5



4.6



4.7



4.8

Forms 4.1 and 4.2 retain a completely sp^2 hydridised skeleton, similar to that found in neutral clge, whilst forms 4.3-4.8 all contain one sp^3 hybridised skeletal atom. This would result in a less extensive delocalised π-system in the latter sextet than in the former pair of tautomers, and hence 4.1 and 4.2 are the most probable description of the electronic structure of $[clgeH]^+$.

There has been little mention of complexes containing $[clgeH]^+$ and transition metal ions. Evidence for the formation of such complexes containing copper(II) ions is based on the early report by Dubsky and Strnad[51] which was reviewed by Ray.[48] Dubsky and Strnad[51] reported that the reaction of copper(II) chloride, [clgeH]Cl and hydrochloric acid in aqueous solutions, produced products which, by elemental analysis, had a copper(II):chloride:$[clgeH]^+$ ratio of 1:4:2 and were green to blue in colour. Corresponding compounds could be produced using bromide analogues of the starting materials. No data is available on the structure of these compounds, particularly as to whether $[clgeH]^+$ acts as a ligand or a cation.

To investigate the nature of the $[clgeH]^+$ cation, a number of salts and copper(II) complexes have been synthesised and characterised. The crystal and molecular structures of 1-carbamoylguanidinium perchlorate ($[clgeH]ClO_4$) and di(1-carbamoylguanidinium)diaquotetrachlorocuprate(II)$\{[clgeH]_2[CuCl_4(H_2O)_2]\}$ have been determined and the infrared spectra of all the salts and complexes have been recorded.

4.2 Experimental

4.2.1 1-Carbamoylguanidinium salts

A number of $[clgeH]^+$ salts were synthesised by the acid hydrolysis of cnge in aqueous solution.

(a) $[clgeH]ClO_4$

Perchloric acid (6 cm^3; 70%) was slowly added to cnge (5g) dissolved in the minimum of boiling deionised water. The solution was further boiled to reduce its volume by half before cooling in ice. The fine white precipitate so formed was recrystallised from water and dried over silica gel. Yield 8.9g (74%); m.p. ca. 176°C. Analytical data for this and all subsequent products are collated in Table 4.1.

(b) [clgeH]Cl and $[D_7\text{-}clgeH]Cl$

As for (a) with the substitution of hydrochloric acid (10 cm^3; 36%) for perchloric acid. Yield 7.1g (86%); m.p. 173-175°C. $[D_7\text{-}clgeH]Cl$ was produced by successive solvation in D_2O and then removal of the excess water under vacuum.

(c) $[clgeH]NO_3$

As for (a) with the substitution of nitric acid (5 cm^3; 70%) for perchloric acid. Yield 8.2g (83%); m.p. ca. 220°C.

(d) $[\text{clgeH}]H_2PO_4$

As for (a) with the substitution of orthophosphoric acid (5 cm^3; 85%) for perchloric acid. Yield 7.3g (61%); m.p. 184-185°C.

(e) $[\text{clgeH}]_2SO_4.2H_2O$

As for (a) with the substitution of sulphuric acid (10 cm^3; 47%) for perchloric acid. Yield 8.2g (82%); m.p. ca. 190°C.

(f) $[\text{clgeH}]HSO_4$

As for (a) with the substitution of sulphuric acid (5 cm^3; 95%) for perchloric acid. The product was not recrystallised but simply washed with ice-cold deionised water. Yield 4.3g (36%); m.p. 150-151 °C.

This material was also obtained by adding sulphuric acid (30 cm^3, 30%) to $[\text{clgeH}]_2SO_4.2H_2O$ (5g) dissolved in the minimum of hot deionised water. After boiling for 10 minutes the solution was cooled in ice. The crystals so formed were washed with ice-cold deionised water. Yield 4.6g (78%); m.p. 150-151°C.

(g) $[\text{clgeH}]_2(C_2O_4)$

As for (a) with the substitution of oxalic acid (3.75g), dissolved in the minimum of hot deionised water, for perchloric acid. Yield 7.4g (85%); m.p. 205-206°C.

(h) [clgeH]Br

$[clgeH]_2SO_4.2H_2O$ (4.13g) was added to barium bromide (4.12g) dissolved in the minimum of hot deionised water. The solution was boiled for 10 minutes before removal of precipitated barium sulphate by filtration. When cooled, the filtrate yielded crystals of the product which were subsequently recrystallised from hot deionised water. Yield 3.0g (78%); m.p. 178-180°C.

(i) [clgeH]I

$[clgeH]_2SO_4.2H_2O$ (4.95g) and ammonium iodide (4.73g) were added to an aqueous solution of barium hydroxide (98.8 cm^3, 0.165M). The solution was boiled until no more ammonia was given off. The precipitated barium sulphate was then filtered off and the solution cooled. The crystals so formed were recovered and dried under vacuum. Yield 0.6g (17%).

4.2.2 1-Carbamoylguanidinium copper(II) complexes

Two complexes were produced by two different routes (i) reaction of $[clgeH]^+$ salts with copper(II) salts, (ii) reaction of copper(II)di(1-carbamoylguanidate)-dihydrate($Cu[clge]_2.2H_2O$) with aqueous acid.

(a) $[clgeH]_2[CuCl_4(H_2O)_2]$

Route (i): Solutions of $CuCl_2.2H_2O$ (10mmol, 1.71g) and [clgeH]Cl (20mmol, 2.77g) in the minimum of hot deionised water, were mixed together and the resulting solution reduced under a vacuum at 45°C until the onset of precipitation. The blue-green precipitate was filtered off and washed with ice-cold deionised water and dried over silica gel. Yield 4.07g (91%).

Route (ii): Cu[clge] $2H_2O$ (see Section 5.2 for preparation) was dissolved in the minimum of dilute hydrochloric acid (2M). The solution was allowed to evaporate at room temperature and the crystals produced were filtered off, washed with ice-cold deionised water and dried over silica gel. Yield ~95%. Analytical data for this and all subsequent copper(II) products are collated in Table 4.1.

Isothermal dehydration of the blue-green $[clgeH]_2[CuCl_4(H_2O)_2]$ complex at 100°C produced the yellow $[clgeH]_2[CuCl_4]$ complex.

(b) $\underline{[clgeH]_2[CuBr_4(H_2O)_2]}$

This complex was synthesised in a similar manner to that used for (a) by either Route (i) or (ii).

For Route (i): $CuBr_2$ (10 mmol, 2.23g) was substituted for $CuCl_2.2H_2O$. Yield 5.44g (87%).

For Route (ii): Dilute hydrobromic acid (2M) was substituted for dilute hydrochloric acid. Yield ~95%.

Isothermal dehydration of $[clgeH]_2[CuBr_4(H_2O)_2]$ at 100°C produced $[clgeH]_2[CuBr]_4$. No colour change was observed, both the hydrated and anhydrous complexes being dark brown-black in colour.

For both (a) and (b), Route (ii) produced better quality of crystals than Route (i) even if the reaction mixture from (i) was allowed to evaporate slowly.

TABLE 4.1 Analytical Data for the Products

	Experimental/Theoretical %		
Product	C	H	N
[clge]ClO_4	11.58/11.86	3.47/3.49	28.23/27.66
[clgeH]Cl	17.06/17.32	5.14/5.05	41.05/40.43
[clgeH]Br	13.03/13.11	3.78/3.83	30.46/30.61
[clgeH]I	9.28/10.44	3.17/3.04	22.52/24.36
[clgeH]NO_3	14.32/14.54	4.22/4.24	42.58/42.42
[clgeH]H_2PO_4	11.82/12.00	4.53/4.50	27.66/28.00
$[clgeH]_2SO_4.2H_2O$	14.03/13.20	5.36/5.32	33.08/33.14
[clgeH]HSO_4	12.32/12.00	4.11/4.00	29.25/28.00
$[clgeH]_2(C_2O_4)$	24.36/24.54	4.82/4.81	38.39/38.13
$[clgeH]_2[CuCl_4(H_2O)_2]$	10.59/10.73	3.97/4.02	25.20/25.03
$[clgeH]_2[CuCl_4]$	11.55/11.66	3.42/3.40	27.34/27.22
$[clgeH]_2[CuBr_4(H_2O)_2]$	7.79/7.68	2.89/2.88	18.02/17.92
$[clgeH]_2[CuBr_4]$	8.05/8.15	2.40/2.38	19.20/19.01

4.3 Crystal and Molecular Structure of 1-Carbamoylguanidinium Perchlorate and Di(1-Carbamoylguanidinium)diaquotetrachlorocuprate(II)

4.3.1 Structure solution and crystal data for 1-Carbamoylguanidinium Perchlorate

The perchlorate salt was chosen for structure determination because of the poor coordinating properties of the anion and the ease of crystallisation.

Colourless crystals were prepared by the slow evaporation of an aqueous solution of the salt. A suitable needle-like crystal (0.5x0.2x0.1mm) was mounted in a Lindemann tube. Oscillation and Weissenberg photographs revealed preliminary cell parameters and space group. X-ray diffraction data for the refinement of cell parameters and structure determination were collected using an Enraf-Nonius CAD 4 four circle diffractometer. One unique set of data was collected in the range $1 \leqq \theta \leqq 66°$ using CuK_α radiation. Of the 1540 observable intensities collected, 1108 were deemed to be observed.

The chlorine atom was located from a Patterson function. The carbon, nitrogen and oxygen atoms were then located by difference Fourier syntheses. Full matrix least squares refinment with anisotropic temperature factors for all these atoms converged at R = 0.057. The top seven distinct peaks (densities 0.80 to 0.46 $e/Å^3$) of a subsequent difference Fourier synthesis gave the positions of all the hydrogen atoms.

No other feature with density greater than 0.25 e/Å^3 was apparent. Further refinement of the structure with fixed hydrogen atoms converged at R = 0.041. Final positional parameters and thermal parameters are given in Tables 4.2 and 4.3 respectively. Observed and calculated structure factors are given in Appendix B.

Crystal Data

$C_2H_7N_4ClO_5$, M = 202.6, monoclinic, space group $P2_1/c$, a = 8.020(3), b = 9.999(3), c = 9.611(3) Å, β = 105.54(3)°, U = 742.6 Å^3, D_m = 1.79, D_c = 1.81 g.cm^{-3} for Z = 4, F(000) = 416, μ(CuK_α) = 47.8 cm^{-1}.

4.3.2 Structure solution and crystal data for di(1-carbamoylguanidinium)diaquotetrachlorocuprate(II)

A suitable crystal (*ca*. 0.1x0.45x0.4mm) was chosen from a crop grown by slow evaporation of a dilute aqueous hydrochloric acid solution of copper(II)bis(1-carbamoylguanidinate) and was mounted in a Lindemann tube. Cell parameters, space group and X-ray diffraction data were obtained as described in Section 1.6.1. Of the 1509 intensities collected, 1244 were deemed to be observed.

Consideration of the molecular formula within the context of the crystal's symmetry indicated that the copper atom must be situated in a special position (0,0,0) of the $P2_1/c$ space group and that pairs of [clgeH]$^+$ cations, chlorine anions and water molecules must be located in centrosymmetrically related positions.

TABLE 4.2 Final Positional Parameters (x10^3) for [clgeH]ClO$_4$

Atom	x/a	y/b	z/c
O(1)	-59.8(2)	277.1(2)	-86.3(2)
C(1)	-124.8(3)	286.0(3)	15.0(3)
C(2)	126.9(3)	390.4(3)	181.7(3)
N(1)	-285.4(3)	249.0(3)	8.9(3)
N(2)	-35.1(3)	337.8(3)	148.5(2)
N(3)	190.3(5)	435.2(3)	314.4(2)
N(4)	214.4(3)	398.2(3)	84.4(2)
Cl(1)	346.19(8)	54.3(7)	216.87(7)
O(2)	457.0(3)	99.7(3)	133.3(3)
O(3)	404.8(3)	-77.9(2)	272.5(3)
O(4)	172.7(2)	42.7(3)	127.1(2)
O(5)	350.8(3)	143.5(3)	332.1(3)
H(1)	-339.1	219.2	-64.5
H(2)	-330.7	264.8	78.1
H(3)	-83.2	321.9	221.8
H(4)	137.6	439.5	382.8
H(5)	291.6	466.2	337.9
H(6)	294.8	426.0	105.9
H(7)	179.7	426.0	105.9

TABLE 4.3 Thermal Parameters (x10^3)/Å^2 for [clgeH]ClO$_4$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
O(1)	43(1)	61(1)	29(1)	-101(9)	163(9)	-10(1)
C(1)	34(1)	41(2)	29(1)	0(1)	12(1)	0(1)
C(2)	31(1)	40(2)	29(1)	2(1)	7(1)	4(1)
N(1)	38(1)	72(2)	46(1)	-16(1)	19(1)	-13(1)
N(2)	33(1)	52(1)	25(1)	-1(1)	133(9)	-2(1)
N(3)	39(2)	69(2)	29(1)	-10(1)	7(1)	-5(1)
N(4)	32(1)	60(2)	35(1)	-4(1)	15(1)	0.6(3)
Cl(1)	28.3(3)	43.9(4)	28.0(3)	2.1(3)	11.3(2)	0.6(3)
O(2)	53(1)	80(2)	65(2)	14(1)	36(1)	-1(1)
O(3)	47(1)	51(1)	63(1)	18(1)	6(1)	7(1)
O(4)	32(1)	79(2)	52(1)	9(1)	22(9)	1(1)
O(5)	80(2)	81(2)	52(1)	-24(1)	24(1)	-2(1)

In the form: $[\exp -2\pi^2(U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)l^2c^{*2}+ 2U(12)hka^*b^*+2U(13)hla^*c^*+2U(23)klb^*c^*)]$

Consequently, subsequent to the data reduction stage, the positions of the chlorine anions, and then the oxygen atoms of the water molecules and the carbon, nitrogen and oxygen atoms of the $[clgeH]^+$ cations, were determined by successive difference Fourier syntheses. Full matrix least squares refinment with anisotropic temperature factors converged at R = 0.052. A difference Fourier synthesis gave the positions of the hydrogen atoms of the $[clgeH]^+$ cation and the water molecule (the electron density varied from 0.77 to 0.37 e/Å^3). Further refinement of the structure including the hydrogens with isotropic temperature factors converged at R = 0.044. Final positional parameters and thermal parameters are given in Tables 4.4 and 4.5 respectively. Observed and calculated structure factors are included in Appendix B.

Crystal Data

$C_4H_{18}N_8O_4Cl_4Cu$, M = 447.3, monoclinic, space group $P2_1/c$, a = 6.522(3), b = 11.218(3), c = 11.790(3) Å, β = 110.66(3)°, U = 807.1 Å^3, D_m = 1.82 g.cm^{-3}, D_c = 1.84 g.cm^{-3} for Z = 2, F(000) = 454, $\mu(MoK_\alpha)$ = 20.88 cm^{-1}.

4.3.3 Molecular geometries of $[clgeH]^+$ in $[clgeH]ClO_4$ and $[clgeH]_2[CuCl_4(H_2O)_2]$

In both the salt and the complex the $[clgeH]^+$ moiety (designated $[clgeH]_s^+$ for $[clgeH]ClO_4$ and $[clgeH]_c^+$ for $[clgeH]_2[CuCl_4(H_2O)_2]$) acts as a cation.

TABLE 4.4 Final positional parameters ($\times 10^3$) for $[\mathrm{clgeH}]_2[\mathrm{CuCl}_4(\mathrm{H}_2\mathrm{O})_2]$

Atom	x/a	y/b	z/c
Cu(1)	0	0	0
Cl(1)	203.6(2)	2.25(8)	204.38(9)
Cl(2)	-303.9(1)	-143.91(8)	52.64(8)
C(1)	783.6(6)	121.8(3)	346.6(3)
C(2)	735.4(6)	-90.9(3)	375.3(3)
N(1)	812.7(6)	196.9(3)	267.5(3)
N(2)	775.6(5)	2.5(2)	313.3(3)
N(3)	729.8(6)	-197.6(3)	326.4(3)
N(4)	708.0(6)	-77.3(3)	478.9(3)
O(1)	765.3(5)	151.3(2)	443.3(3)
O(2)	-190.0(4)	128.1(2)	26.2(2)
H(1)	828(9)	270(6)	290(5)
H(2)	835(8)	169(5)	200(5)
H(3)	789(8)	-17(4)	243(5)
H(4)	737(8)	-200(5)	255(4)
H(5)	710(1)	-259(5)	368(6)
H(6)	682(8)	-134(4)	516(5)
H(7)	710(1)	-6(6)	511(6)
H(8)	-188(9)	196(5)	-4(5)
H(9)	-320(2)	103(9)	-6(9)

TABLE 4.5 Final thermal parameters ($\times 10^3$)/Å^2 for $[\mathrm{clgeH}]_2[\mathrm{CuCl}_4(\mathrm{H}_2\mathrm{O})_2]$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)	U(ISO)
Cu(1)	27.2(4)	21.1(4)	21.8(4)	-0.9(2)	2.3(3)	5.6(2)	
Cl(1)	29.6(6)	31.2(6)	25.0(6)	0.0(3)	1.6(4)	2.1(3)	
Cl(2)	30.6(5)	24.7(5)	33.1(5)	-2.0(4)	9.7(4)	-3.1(4)	
C(1)	26(2)	25(2)	31(2)	-3(1)	9(1)	0(1)	
C(2)	23(2)	24(2)	28(2)	1(1)	5(1)	3(1)	
N(1)	57(2)	22(2)	33(2)	-4(1)	17(2)	-4(2)	
N(2)	36(2)	21(2)	28(2)	-3(1)	12(1)	0(1)	
N(3)	56(2)	20(2)	28(2)	-1(1)	11(2)	-1(1)	
N(4)	44(2)	26(2)	35(2)	2(2)	18(2)	0(1)	
O(1)	58(2)	26(1)	38(2)	-9(1)	25(1)	-5(1)	
O(2)	28(1)	20(1)	31(1)	4(1)	7(1)	2(1)	
H(1)							20(10)
H(2)							20(10)
H(3)							10(10)
H(4)							30(10)
H(5)							20(10)
H(6)							30(10)
H(7)							10(20)
H(8)							20(10)
H(9)							90(40)

In the form: $[\exp -2\pi^2(U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)l^2c^{*2}+ 2U(12)hka^*b^*+2U(13)hla^*c^*+2U((23)klb^*c^*)]$

Significantly $[clgeH]_c^+$ does not ligate the copper(II) ion in the complex. Hence, the molecular geometries of $[clgeH]_s^+$ and $[clgeH]_c^+$ are very similar. The atom numbering scheme is shown in Figure 4.1, and bond distances and angles are compared in Table 4.6.

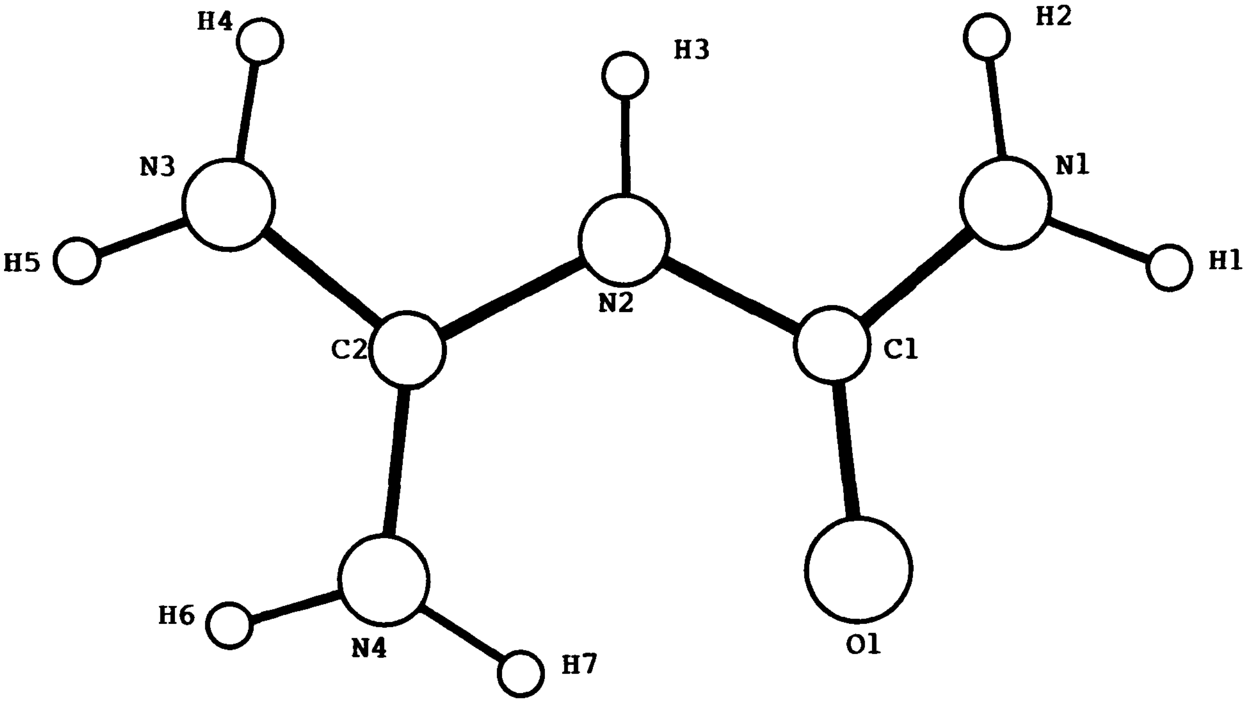
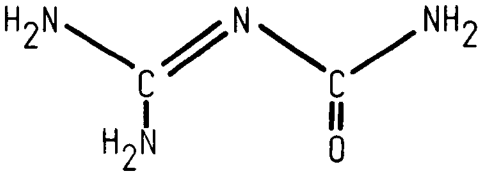


FIGURE 4.1 Numbering scheme for $[clgeH]^+$

Comparison with the structure of uncoordinated clge (form 4.9; Section 3.3.3 for full details) reveals that



4.9

TABLE 4.6 Molecular geometries of the $[clgeH]^+$ cation in $[clgeH]ClO_4$ and $[clgeH]_2[CuCl_4(H_2O)_2]$

Bond Distances/Å	$[clgeH]ClO_4$	$[clgeH]_2[CuCl_4(H_2O)_2]$
C(1)-O(1)	1.224(3)	1.232(5)
C(1)-N(1)	1.326(3)	1.319(5)
C(1)-N(2)	1.392(3)	1.391(5)
C(2)-N(2)	1.358(3)	1.354(5)
C(2)-N(3)	1.319(3)	1.323(5)
C(2)-N(4)	1.314(3)	1.305(5)
N(1)-H(1)	0.78	0.85
N(1)-H(2)	0.85	0.92
N(2)-H(3)	0.90	0.90
N(3)-H(4)	0.87	0.86
N(3)-H(5)	0.84	0.88
N(4)-H(6)	0.82	0.82
N(4)-H(7)	0.68	0.89

Bond Angles/°	$[clgeH]ClO_4$	$[clgeH]_2[CuCl_4(H_2O)_2]$
O(1)C(1)N(1)	124.0(3)	124.6(4)
O(1)C(1)N(2)	122.4(2)	120.9(4)
N(1)C(1)N(2)	113.6(2)	114.5(4)
C(1)N(2)C(2)	125.9(2)	126.0(4)
N(2)C(2)N(3)	117.1(2)	116.5(4)
N(2)C(2)N(4)	121.0(2)	122.1(4)
N(3)C(2)N(4)	121.8(3)	121.4(4)
H(1)N(1)C(1)	116	115
H(2)N(1)C(1)	122	120
H(1)N(1)H(2)	122	124
H(3)N(2)C(1)	116	120
H(3)N(2)C(2)	118	114
H(4)N(3)C(2)	127	117
H(5)N(3)C(2)	119	117
H(4)N(3)H(5)	114	126
H(6)N(4)C(2)	118	122
H(7)N(4)C(2)	117	122
H(6)N(4)H(7)	124	116

protonation occurs at the central bridging nitrogen atom, N(2), giving tautomer 4.1. This permits retention of the intramolecular hydrogen bond and the totally sp^2 hybridised planar skeleton with the associated π-system. The cations have intermediate length C-N and C-O bonds, bond angles close to 120° and are effectively planar (the maximum deviation from the best planes being 0.053 Å for $[clgeH]_s^+$, and 0.033 Å for $[clgeH]_c^+$, Table 4.7).

TABLE 4.7 Planarities of the $[clgeH]^+$ cation in $[clgeH]ClO_4$ and $[clgeH]_2[CuCl_4(H_2O)_2]$

Atom	Deviation from the plane/Å	
	$[clgeH]ClO_4$ *	$[clgeH]_2[CuCl_4(H_2O)_2]$ #
O(1)	0.046	0.036
C(1)	0.012	0.004
C(2)	0.003	-0.006
N(1)	-0.048	-0.027
N(2)	0.025	0.033
N(3)	0.014	-0.002
N(4)	-0.053	-0.018

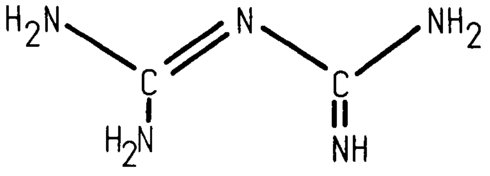
* Equation of best plane:

$$2.39358x - 9.06193y + 2.00330z = -2.873$$

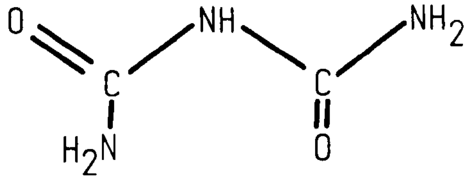
\# Equation of best plane:

$$5.72655x - 1.04191y + 1.52695z = 4.885$$

There are but minor differences between clge and $[clgeH]^+$. On cation formation the bridging C-N bonds lengthen, the terminal C-N bonds shorten, and the C(1)N(2)C(2) bond angle increases. These changes are analogous to those found upon coordination of clge and biguanide (bg; 4.10) when proton transfer occurs from a terminal amine to a bridging nitrogen. It seems apparent



4.10



4.11

that protonation of the central nitrogen decreases the π-character in the central C-N-C system, whilst increasing it in the terminal C-N bonds of coordinated clge, bg and $[clgeH]^+$. As noted in Chapter Three, biuret (bu; 4.11) has a C-NH-C bridge in both free and coordinated forms. Its geometry in these two forms is similar to that of coordinated clge and bg and $[clgeH]^+$ but differs from those of free clge and bg.

Significant features of $[clgeH]_s^+$, $[clgeH]_c^+$ and clge, bg and bu (free and coordinated) are compared in Table 4.8.

Also, it is instructive to compare structural data for the protonated derivatives of bg. They have been reported for both mono- and di- protonated derivatives of

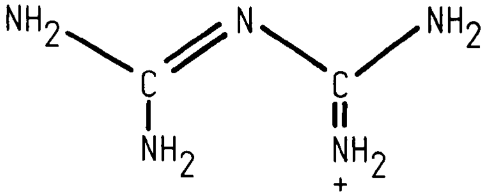
TABLE 4.8 Significant features of the molecular geometries of free and coordinated clge, bg and bu and $[\text{clgeH}]^+$, $[\text{bgH}]^+$ and $[\text{bgH}_2]^{2+}$

	Dihedral angle/°*	C-N-C angle/°	Average $r(\text{C-N}_{\text{bridge}})$ /Å	Average $r(\text{C-N}_{\text{terminal}})$ /Å#
bu (free)[17]	6.3	128.5(2)	1.385(3)	1.325(3)
bu (coord)[22]	6.4	126.8	1.371(6)	1.321(6)
clge (free)	7.5	119.8(3)	1.352(4)	1.340(4)
clge (coord)	1.7	126.0(1.0)	1.370(20)	1.315(20)
bg (free)[13]	12.5	119.9(1)	1.356(2)	1.358(2)
bg (coord)[21]	-	127.3(5)	1.374(8)	1.349(8)
$[\text{clgeH}].\text{ClO}_4$	4.4	125.9(2)	1.375(3)	1.320(3)
$[\text{clgeH}]_2[\text{CuCl}_4(\text{H}_2\text{O})_2]$	3.8	126.0(4)	1.373(5)	1.321(5)
$[\text{bgH}]\text{Cl}$[14]	39.5	122.8(4)	1.330(5)	1.338(5)
$[\text{bgH}]_2\text{CO}_3$[13]	42.1	122.6(2)	1.338(4)	1.331(4)
$[\text{bgH}]_2\text{SO}_4$[13]	46.6	121.2(2)	1.346(4)	1.328(4)
$[\text{bgH}_2]\text{SO}_4$[13]	48.4	126.2(3)	1.378(5)	1.307(5)

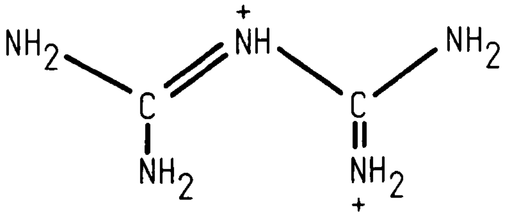
* This is the angle between the normals to the planes which best represent the two halves of the molecule.

\# This average does not include those contacts, formally defined as double bonds, between carbon and terminal imine groups.

bg, viz $[bgH]^+$ and $[bgH_2]^{2+}$, details of which are included in Table 4.8. Protonation occurs first at the imino nitrogen and then at the bridging nitrogen atom to give forms 4.12 and 4.13 respectively. Although free bg, free clge, free bu, and $[clgeH]^+$ are effectively planar, the dihedral angles between the normals to the planes which best represent the two halves of the molecules, do not exceed 12.5°, the out of the plane distortion is extensive for $[bgH]^+$ and $[bgH_2]^{2+}$, with dihedral angles of ca. 40° and 48°, respectively (Table 4.8). Thus, whereas the planarity of the former species is enhanced by the formation of an intramolecular hydrogen bond between an amine donor and either an oxygen or imine acceptor, for the latter species the juxtaposition of amine groups results in steric interactions between hydrogen atoms and hence a loss of planarity.



4.12



4.13

The electronic structures of the molecules, however, do not appear to be influenced by the dihedral angle; they are dependent solely on the adopted tautomeric form. Thus, coordinated clge, bg, free and coordinated bu, $[clgeH]^+$ and $[bgH_2]^{2+}$, all of which have a bridging C-NH-C group, have longer bridging than terminal C-N bonds and a C-N-C bond angle between 125 and 129° (Table 4.8). The other three species, free bg, free clge and $[bgH]^+$, all of which have a bridging C=N-C group, exhibit near equivalence of C-N bond distances and a C-N-C bond angle between 119 and 123° (Table 4.8). Obviously, the out of plane distortion has little effect on the delocalised π-system which exists over the sp^2 hybridised C-N skeleton.

4.3.4 Intermolecular contacts in $[clgeH]ClO_4$ and $[clgeH]_2[CuCl_4(H_2O)_2]$

Views of the structures of the salt and the complex perpendicular to (100) are shown in Figures 4.2 and 4.3 respectively.

Both structures consist of an array of alternating cationic and anionic fragments. Whereas for the salt single cations ($[clgeH]^+$) and anions (ClO_4^-) alternate, in the complex pairs of cations ($[clgeH]^+$) alternate with the dinegative anions ($[CuCl_4(H_2O)_2]^{2-}$). Details of intermolecular contacts for both structures are given in Tables 4.9 and 4.10. An extensive hydrogen-bonded network enhances the electrostatic interactions. For the salt it is obvious that extensive charge delocalisation occurs in both $[clgeH]^+$ and ClO_4^- because of the near equivalence of many interactions (Table 4.9) and the fact that the shortest interaction [r(N(2)-H(3)...O(1)) = 2.85 Å], occurs between adjacent cations. For the complex

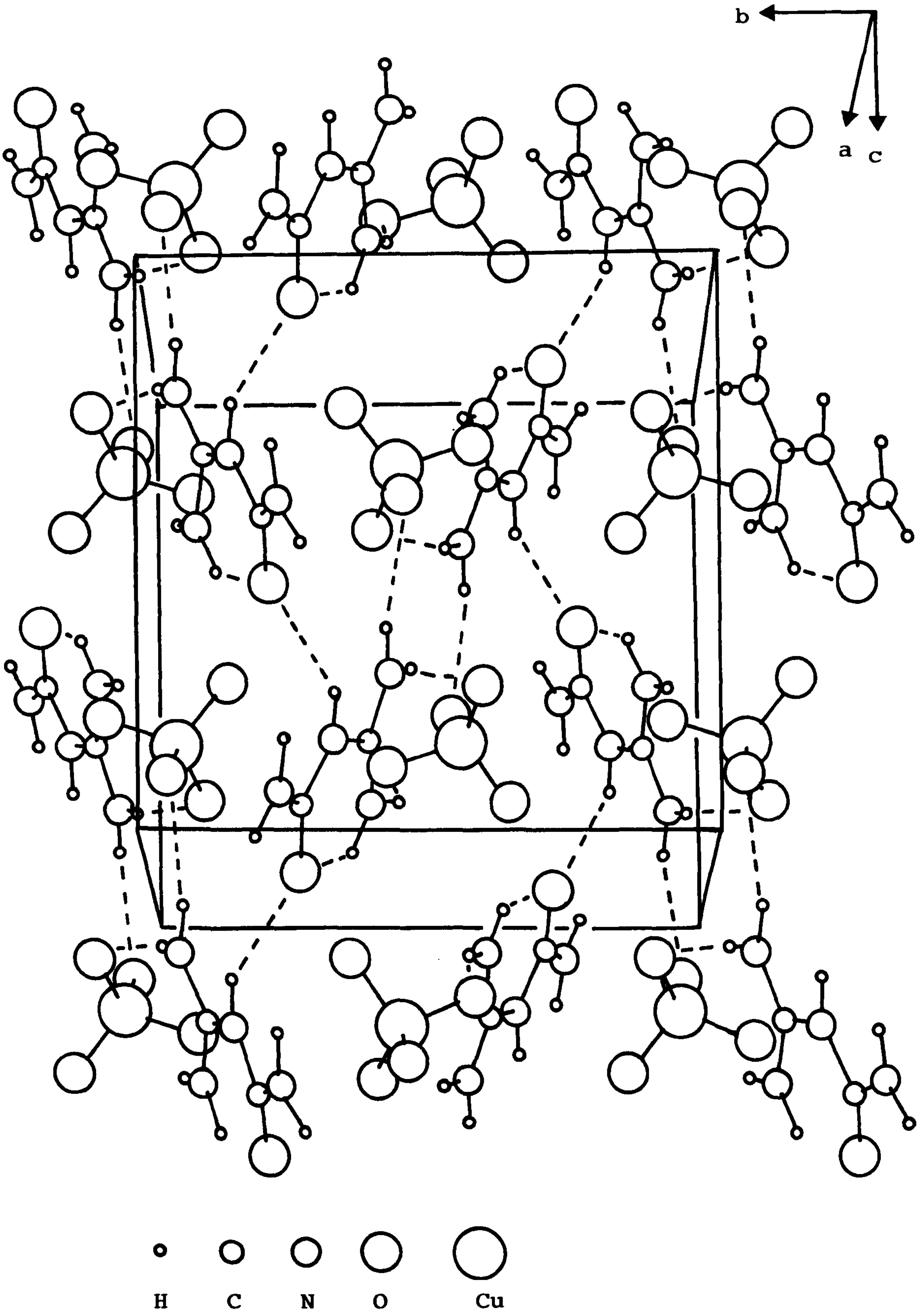


FIGURE 4.2 View of the structure of [clgeH](ClO_4) perpendicular to the (100) plane

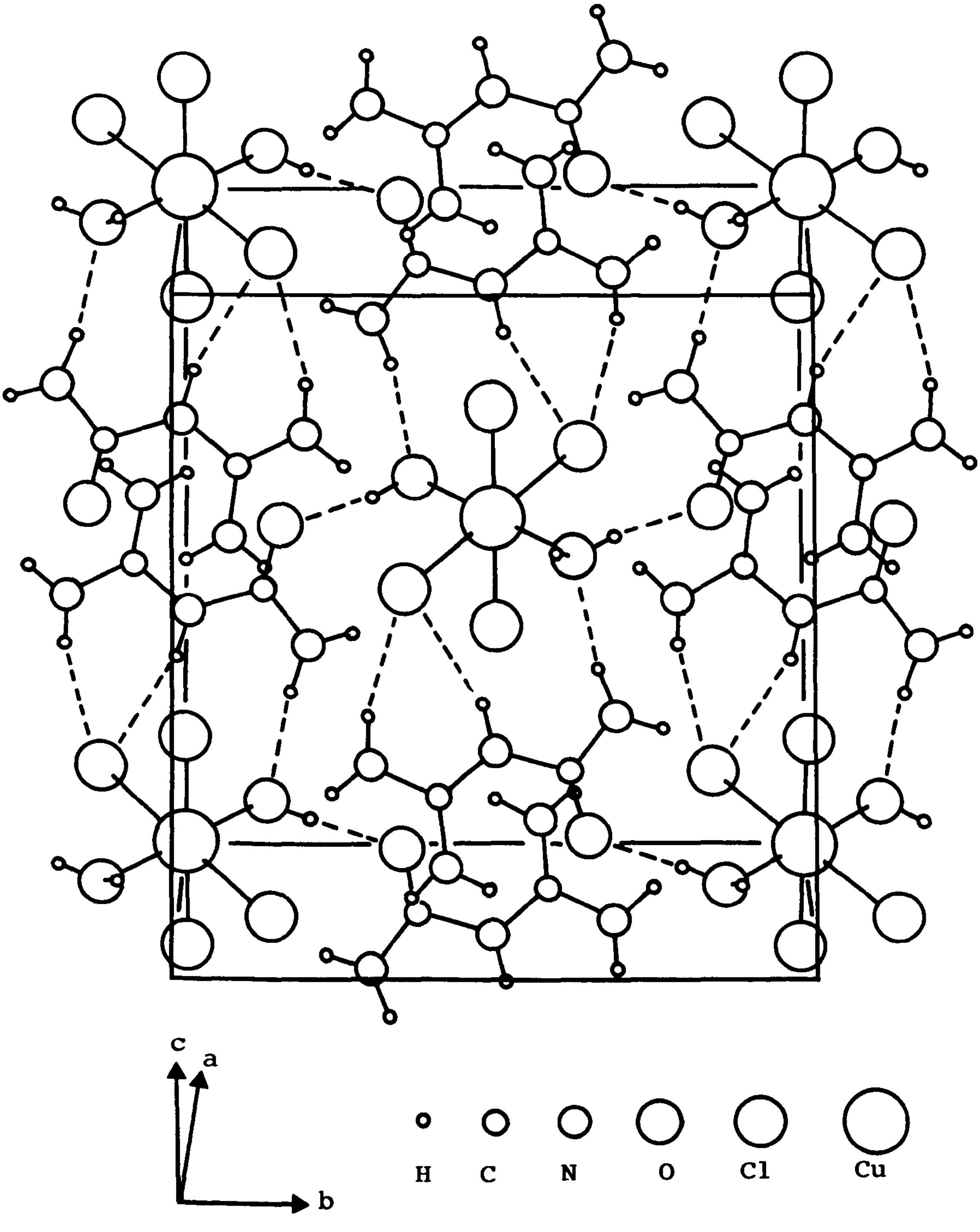


FIGURE 4.3 View of the structure of $[\mathrm{clgeH}]_2[\mathrm{CuCl}_4(\mathrm{H}_2\mathrm{O})_2]$ perpendicular to the (100) plane

TABLE 4.9 Intermolecular contacts of less than 3.30 Å in [clgeH]ClO_4; hydrogen bond and electrostatic interactions

Interaction X-H...X'	Symmetry Properties of X'	r(X...X') /Å	r(X-H) /Å	r(H...X') /Å	XHX' /°
N(1)-H(1)...O(3)	$-x,-y,-z$	3.130	0.78	2.39	158
N(1)-H(2)...O(3)	$-x,\frac{1}{2}+y,\frac{1}{2}-z$	3.072	0.85	2.32	147
N(1)........O(2)	$-1+x,y,z$	3.041	-	-	-
N(1)........O(5)	$-1+x,\frac{1}{2}-y,-\frac{1}{2}+z$	3.147	-	-	-
N(2)-H(3)...O(1)	$x,\frac{1}{2}-y,\frac{1}{2}+z$	2.851	0.90	2.06	146
N(3)-H(4)...O(4)	$x,\frac{1}{2}-y,\frac{1}{2}+z$	3.054	0.87	2.30	145
N(3)-H(5)...O(2)	$1-x,\frac{1}{2}+y,\frac{1}{2}-z$	3.193	0.84	2.37	165
N(3)........O(1)	$x,\frac{1}{2}-y,\frac{1}{2}+z$	3.236	-	-	-
N(3)........O(2)	$x,\frac{1}{2}-y,\frac{1}{2}+z$	3.252	-	-	-
N(3)........O(4)	$-x,\frac{1}{2}+y,\frac{1}{2}-z$	3.290	-	-	-
N(3)........O(5)	x,y,z	3.175	-	-	-
N(4)-H(6)...O(3)	$1-x,\frac{1}{2}+y,\frac{1}{2}-z$	3.004	0.68	2.38	154
N(4)-H(7)...O(5)*	$x,\frac{1}{2}-y,-\frac{1}{2}+z$	2.945	0.82	2.46	119
<u>Intramolecular hydrogen bond</u>					
N(4)-H(7)...O(1)	x,y,z	2.658	0.82	2.04	131

* For this interaction the angle at H(7) is very low owing to the N(4)-H(7)...O(1) hydrogen bond interactions.

TABLE 4.10 Intermolecular contacts of less than 3.50 Å* in $[clgeH]_2[CuCl_4(H_2O)_2]$; hydrogen bond and electrostatic interactions

Interaction X-H...X'	Symmetry Properties of X'	r(X...X') /Å	r(X-H) /Å	r(H...X') /Å	XHX' /°
N(1)-H(1)...Cl(1)	$1-x,\frac{1}{2}+y,\frac{1}{2}-z$	3.447	0.85	2.62	164
N(1)-H(2)...O(2)	$1+x,y,z$	2.941	0.92	2.04	165
N(2)-H(3)...Cl(2)	$1+x,y,z$	3.360	0.90	2.54	153
N(3)-H(4)...Cl(2)	$1+x,y,z$	3.277	0.86	2.39	161
N(3)-H(5)...Cl(2)	$1+x,-\frac{1}{2}-y,\frac{1}{2}+z$	3.214	0.88	2.46	154
N(4)-H(6)...Cl(2)	$1+x,\frac{1}{2}-y,\frac{1}{2}+z$	3.254	0.82	2.53	148
O(2)-H(8)...O(1)	$-1+x,\frac{1}{2}-y,-\frac{1}{2}+z$	2.638	0.84	1.81	167
O(2)-H(9)...Cl(2)	$-1-x,-y,-z$	3.102	0.80	2.30	147
<u>Intramolecular hydrogen bond</u>					
N(4)-H(7)...O(1)	x,y,z	2.647	0.89	2.02	127

* A value of 3.50 Å was chosen owing to the larger van der Waals radius of chlorine than other previous hydrogen bond acceptor atoms.

charge delocalisation is less prevailent and there are no cation-cation interactions. The closest approach is between a water oxygen of the anion and the carbonyl oxygen of the cation [r(O(2)-H(8)...O(1)) = 2.638 Å; Table 4.10]. This hydrogen bond is the shortest that has been observed in the series of compounds discussed in this thesis.

The copper(II) ion is in a centrosymmetric distorted octahedral geometry. It is surrounded equatorially by a pair of oxygens of the water molecules [r(Cu(1)-O(2)) = 1.992 Å] and a pair of chlorine atoms [r(Cu(1)-Cl(1)) = 2.305 Å], another pair of chlorine atoms lying in the axial positions [r(Cu(1)-Cl(2)) = 2.791 Å]. Further details of the $[CuCl_4(H_2O)_2]^{2-}$ fragment are given in Table 4.11.

TABLE 4.11 Molecular geometry of the $[CuCl_4(H_2O)_2]^{2-}$ anionic fragment of $[clgeH]_2[CuCl_4(H_2O)_2]$

Bond Distances/Å		Bond Angles/°	
Cu(1)-Cl(1)	2.305(1)	Cl(1)Cu(1)Cl(2)	88.07(3)
Cu(1)-Cl(2)	2.791(1)	Cl(1)Cu(1)O(2)	89.46(8)
Cu(1)-O(2)	1.992(3)	Cl(2)Cu(1)O(2)	81.57(8)
O(2)-H(8)	0.841	H(8)O(2)H(9)	106(7)
O(2)-H(9)	0.854		

Unfortunately, it was not possible to obtain $[\text{clgeH}]_2[\text{CuCl}_4]$ in a crystalline form suitable for structure determination. However, the coordination geometry of the $[\text{CuCl}_4]^{2-}$ anion may be inferred from the colour changes that occur upon dehydration of $[\text{clgeH}]_2[\text{CuCl}_4(\text{H}_2\text{O})_2]$.

The anion of the hydrated complex has been shown to have a distorted octahedral geometry analogous to that observed for $[\text{Cu(H}_2\text{O)}_6]^{2+}$, both moieties exhibiting a similar blue-green colour (arising from the $^2E_g \rightarrow {}^2T_{2g}$ transition). The loss of two water molecules from the $[\text{CuCl}_4(\text{H}_2\text{O})_2]^{2-}$ moiety leads to the formation of a yellow complex. The copper chromophore is probably a flattened tetrahedral $[\text{CuCl}_4]^{2-}$ anion analogous to that in $[\text{Me}_4\text{N}]_2\text{CuCl}_4$ [58] and $\text{Cs}_2[\text{CuCl}_4]$ [59] which are a similar yellow colour (arising from the $^2T_2 \rightarrow {}^2E$ transition).

The molecular geometry of the perchlorate anion is unremarkable. Data are given in Table 4.12.

TABLE 4.12 Geometry of the perchlorate anion in $[\text{clgeH}]\text{ClO}_4$

Bond Distances/Å		Bond Angles/°	
Cl(1)-O(2)	1.423(2)	O(2)Cl(1)O(3)	107.9(2)
Cl(1)-O(3)	1.448(2)	O(2)Cl(1)O(4)	109.8(2)
Cl(1)-O(4)	1.432(2)	O(2)Cl(1)O(5)	110.6(2)
Cl(1)-O(5)	1.414(2)	O(3)Cl(1)O(4)	108.4(2)
		O(3)Cl(1)O(5)	110.2(2)
		O(4)Cl(1)O(5)	109.9(2)

4.4 Spectroscopic Properties

Extensive mixing of the internal coordinates of a planar skeleton makes assignment of the vibrational spectra of species such as $[\mathrm{clgeH}]^+$ difficult. $[\mathrm{clgeH}]^+$ has C_s symmetry and should have 36 (25A' and 11A") vibrational modes, all of which are infrared active. The vibrations of $[\mathrm{clgeH}]^+$ are the same as those for clge (Section 3.3.6) but there is an extra N-H stretch as well as one extra in-plane and one extra out-of-plane deformation.

Infrared spectra for the various $[\mathrm{clgeH}]^+$ salts, $[D_7\text{-clgeH}]\mathrm{Cl}$ and $[\mathrm{clgeH}]_2[\mathrm{CuX}_4(\mathrm{H}_2\mathrm{O})_2]$ (where X = Cl, Br), were recorded (4000-400 cm^{-1}) in nujol and halocarbon mulls and KBr discs. They are collated numerically in Table 4.13; bands attributable to the anion have been omitted. The spectrum of the $[\mathrm{clgeH}]_s^+$ cation is virtually independent of anion; that of the $[\mathrm{clgeH}]_c^+$ cation, however, differs with the copper(II)-containing anion.

The spectra of cnge, clge, [clgeH]Cl and $[D_7\text{-clgeH}]\mathrm{Cl}$ (1880-1280 cm^{-1}) are compared in Figure 4.4. The spectrum of the $[\mathrm{clgeH}]_s^+$ cation in this region is markedly different from that of neutral clge. The $[\mathrm{clgeH}]_s^+$ spectrum exhibits better resolution showing distinct peaks, whilst that of clge contains broad bands with several shoulders. By comparison with clge, the bands at 1670, 1640 and 1610 cm^{-1} are assigned to $\delta[\mathrm{NH}_2]$ vibrations. Four peaks (1735, 1585, 1520 and 1460 cm^{-1})

TABLE 4.13a

TABLE 4.13a Infrared spectroscopic data/cm^{-1} for various $[clgeH]^+$ salts

$[clgeH]Br$	$[clgeH]H_2PO_4$	$[clgeH]NO_3$	$[clgeH]HSO_4$	$[clgeH]SO_4.2H_2O$
3400sh 3360 }s,br	3410 s,br	3440sh 3370 }s	3440 3410 } s	
			3340ms	3350 s,br
3250m 3175s,br	3300m 3185s,br	3280ms 3190s,br	3210s,br	3180s,br
1730s	1735s	1735 1725 }s	1745s	1735 1725 } s
1670 1630 }s,br	1690 1635 }s,br	1685 1635 }s,br	1695 1640 } s,br	1690 1630 } s,br
1610m				
1580s,br 1520mw	1595s,br 1520w	1585s,br 1520w	1590s,br 1525w	1600s,br
1460s	1460s	1455m	1460m	1455ms
1380sh 1340 }s	1380sh 1350 }m	*	1380sh 1340 }ms	1380sh 1350 } m,br
1115w	*	*	*	*
1055m	*	*	*	*
	930w	930vw	930vw	930vw
760mw	765w	750w	*	*
715mw	700m	705m	*	*
535w,br	550m			
450m,br	450m	450w	450w	440w

FOOTNOTE

* Masked by anion vibrations.

[clgeH]ClO$_4$	[clgeH]Cl	[D$_7$-clgeH]Cl	Assignment
3475 3455 } ms,br	3410sh 3380 } s,br	2550 2550 } s,br	ν_a[N-H] and ν_s[N-H]
3405sh 3370 } s,br			
3250 3180 } ms,br	3250m 3160s,br	2380 2290 } s,br	
	1735s	1700s	
1725			ν[O(1)C(1)N(1)]
1695 1655 } s,br	1670 1640 s,br	1265m,br	δ[NH$_2$]
	1610m	1610s	
1580s,br 1530mw	1585s 1520mw	1570s 1540 1510sh } s	ν[N(3)C(2)N(4)] ν[N(2)C(2)N(3)]
1465ms	1460s	1430 1370 } s	ν[O(1)C(1)N(1)]
1380sh 1345 } ms	1380sh 1345 } ms		
	1145m		
*	1120m	945w	δ[NH$_2$]
*	1060m	1090vw	
930vw			
765w	735mw	755m	
715w	720m	710vw	γ[NH$_2$]
	660w	655w	
560w	550m,br		
470w	460m,br		

TABLE 4.13b Infrared spectroscopic data/cm^{-1} for copper(II)-[clgeH]$^+$ complexes

[clgeH]$_2$[CuCl$_4$(H$_2$O)$_2$]	[clgeH]$_2$[CuBr$_4$(H$_2$O)$_2$]	Assignment
3475 3400sh ms,br	3540m 3405 3360 s	ν_a[N-H] and ν_s[N-H]
3200ms,br	3260 3190 s	
	1740s	ν[O(1)C(1)N(1)]
1680s	1685s	δ[NH$_2$]
1640m	1670sh,s	ν[O(1)C(1)N(1)]*
1610ms	1630ms	
1565ms	1580s 1520m	ν[N(3)C(2)N(4)] ν[N(2)C(2)N(3)]
1455m	1455m	ν[O(1)C(1)N(1)]
1350m	1335m	
1130w	1110mw	δ[NH$_2$]
1080w	1075w	
	1060w	
755w	760w	
715mw	715mw	
670w	630mw,sh	γ[NH$_2$]
540m,br	580m,br	
	510m	
445m	450m	

* For [clgeH]$_2$[CuCl$_4$(H$_2$O)$_2$] only.

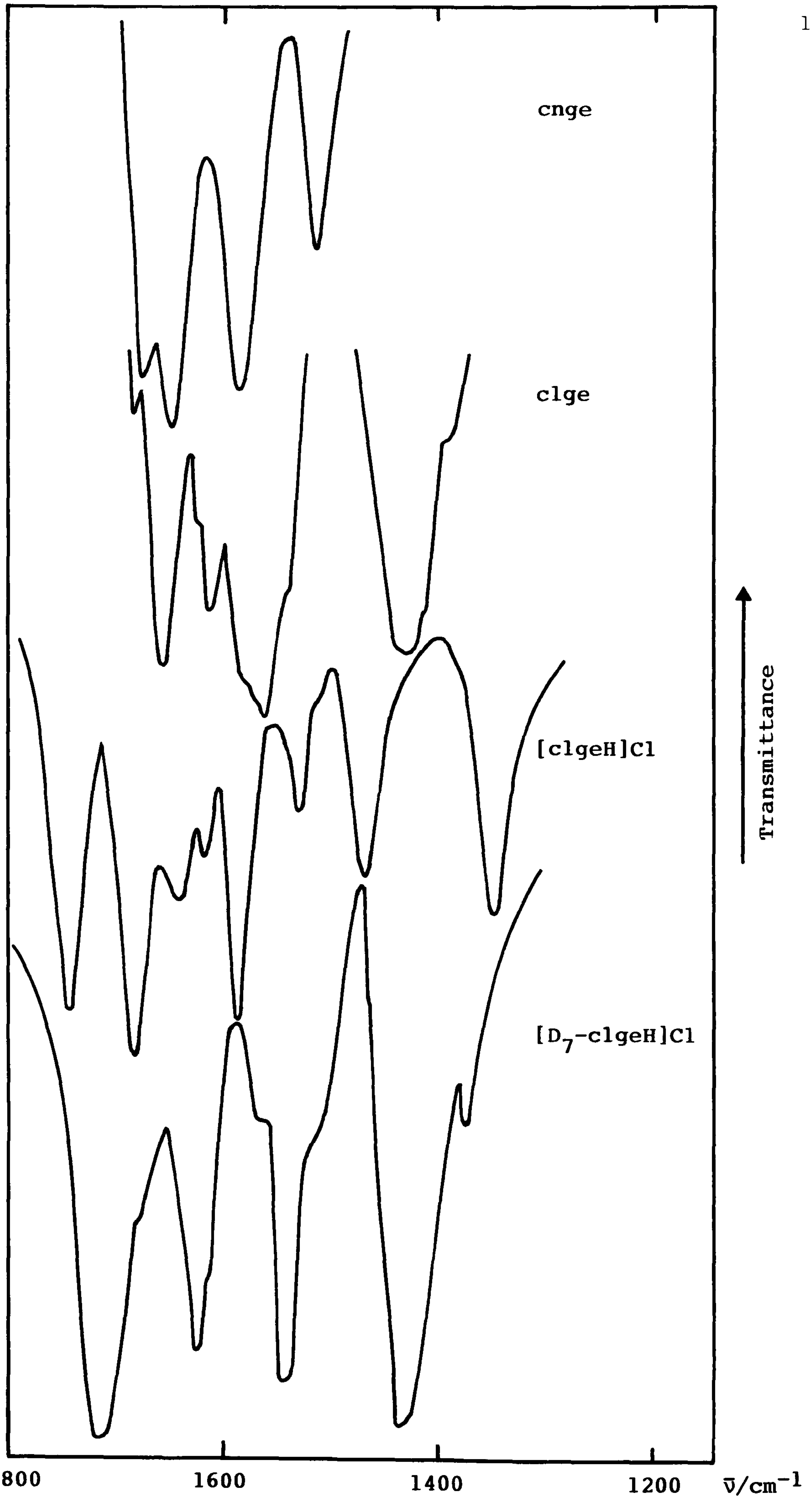


FIGURE 4.4 IR spectra of cnge, clge, [clgeH]Cl and [D_7-clgeH]Cl

remain in this region which can be associated with skeletal vibrations. By analogy with cnge the bands at 1585 and 1520 cm^{-1} are considered to arise primarily from the C-N skeleton, leaving the bands 1735 and 1460 cm^{-1} due to the carbamoyl fragment. These bands occur at higher wavenumbers than in the spectrum of clge (~1550 and 1420 cm^{-1}) and are in agreement with the decreased C(1)-O(1) bond length from 1.251 Å, for clge, to 1.224 Å, for $[clgeH]_s^+$.

The spectra of [clgeH]Cl, $[clgeH]_2[CuCl_4(H_2O)_2]$ and $[clgeH]_2[CuBr_4(H_2O)_2]$ are compared in Figure 4.5.

Although the spectrum of $[clgeH]_2[CuBr_4(H_2O)_2]$ is nearly identical to those of the salts (Table 4.13) that of $[clgeH]_2[CuCl_4(H_2O)_2]$ is different despite the similar geometry of the $[clgeH]_s^+$ and $[clgeH]_c^+$ cations. Most significantly in the 1800-1500 cm^{-1} region, no absorption greater than 1680 cm^{-1} is observed for $[clgeH]_2[CuCl_4(H_2O)_2]$. The 1735 cm^{-1} absorption observed for $[clgeH]_s^+$, assigned to a vibration of the carbamoyl fragment, must be reduced in energy. Consideration of the structural data for the two species reveals that the carbamoyl moiety of the $[clgeH]^+$ cation is involved in an exceedingly strong hydrogen bond in the structure of the complex [O(1)...H(7)-O(2), r(O(1)-O(2)) = 2.638 Å] but not in that of the salt [O(1)...H(3)-N(2), r(O(1)-N(2)) = 2.851 Å]. Presumably such a strong interaction leads to a weakening of the carbonyl bond and hence explains the reduction in the frequency of the ν(C-O) absorption band.

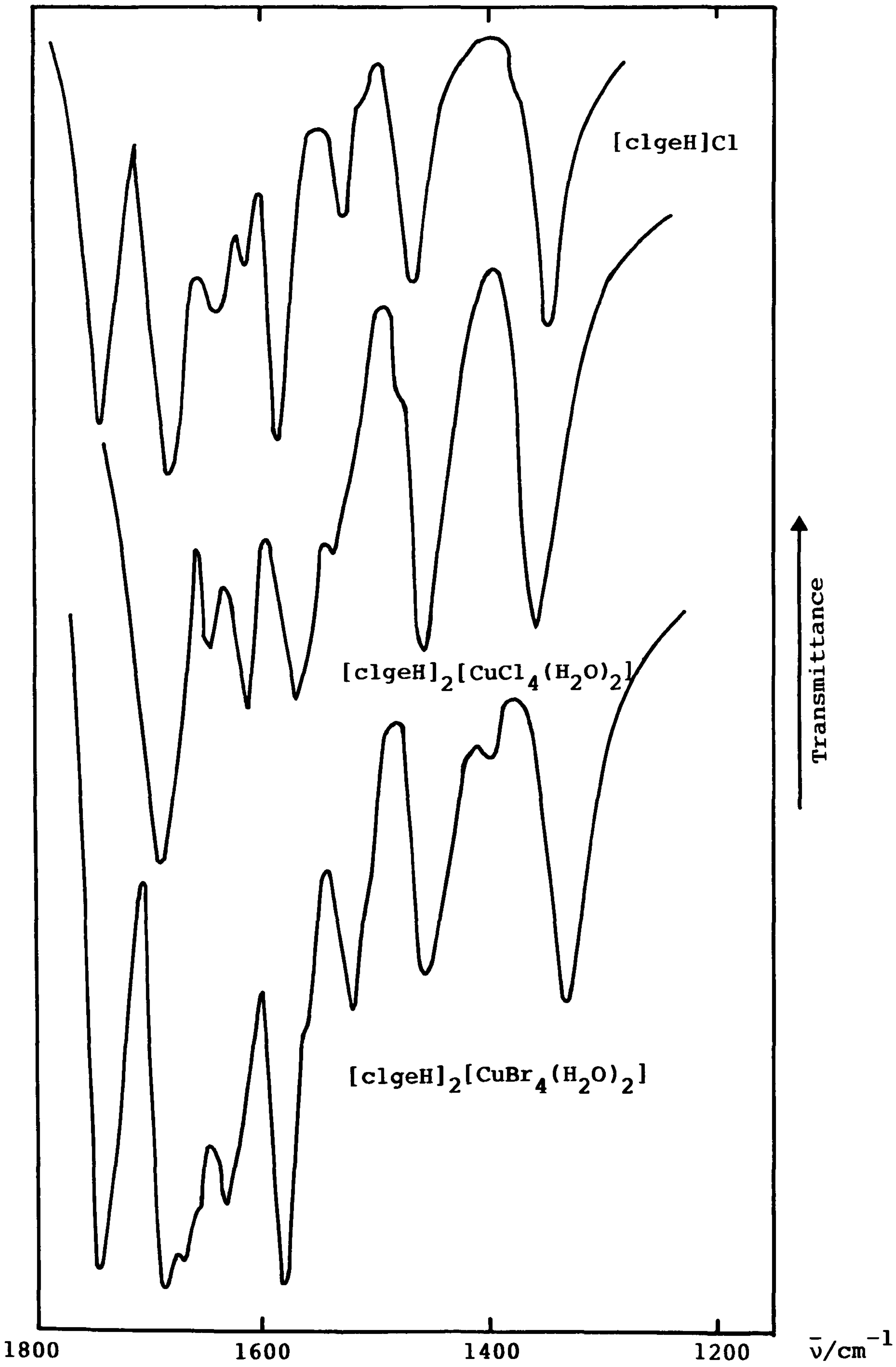


FIGURE 4.5 IR spectra of [clgeH]Cl, $[clgeH]_2[CuCl_4(H_2O)_2]$ and $[clgeH]_2[CuBr_4(H_2O)_2]$

A second reason for the different spectra of the $[\mathrm{clgeH}]^+$ cation in the salts and the chloro complexes, is the fact that hydrogen bonds from $[\mathrm{clgeH}]_s^+$ are exclusively to oxygen atoms (Table 4.9), whilst those from $[\mathrm{clgeH}]_c^+$ are primarily to chlorine atoms (Table 4.10). The latter bonds will be less effective than the former owing to the more diffuse charge of the chlorine atoms. Hence the bands assigned to $\delta[\mathrm{NH_2}]$ vibrations will occur at different frequencies in the two species.

The observation that the spectrum of $[\mathrm{clgeH}]_2$-$[\mathrm{CuBr_4(H_2O)_2}]$ differs from that of the analogous chlorine derivative but is similar to those of the salts is difficult to understand. The presence of the 1735 cm^{-1} absorption in the spectrum of the bromo complex implies the absence of a strong hydrogen bond to the carbonyl oxygen; while the similarities in the spectra of the bromo complex and the salts indicate similar hydrogen bonding networks. The former may be attributable to steric effects of the bromine atoms; the latter to their near non-existent hydrogen bond acceptor properties. Confirmation of these hypotheses can, however, only be achieved by a full structural analysis.

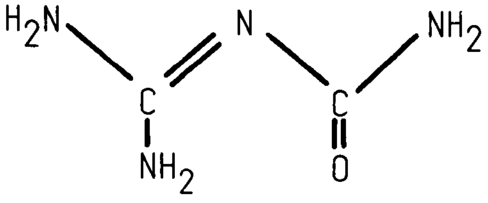
C H A P T E R F I V E

COPPER(II) COMPLEXES OF THE 1-CARBAMOYLGUANIDATE ANION

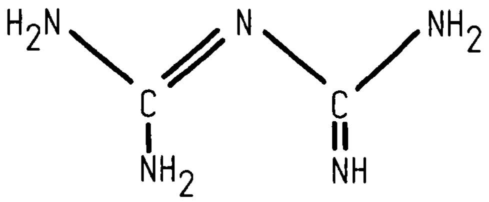
5.1 Introduction

To complete the study of the amphoteric 1-carbamoylguanidine molecule and its coordination properties towards the copper(II) ion, an investigation similar to those undertaken for neutral and cationic 1-carbamoylguanidine (clge; $C_2H_6N_4O$, Chapter Three and $[\text{clgeH}]^+$; $C_2H_7N_4O^+$, Chapter Four) was attempted for the 1-carbamoylguanidate anion ($[\text{clge}]^-$; $C_2H_5N_4O^-$).

In 1862 Haag[11] prepared a distinctive rose-red copper(II) complex from copper(II) sulphate and di(1-carbamoylguanidinium) sulphate ($[\text{clgeH}]_2SO_4$) under alkaline conditions and formulated it to be $Cu[\text{clge}]_2.2H_2O$. Eighty years later Dubsky and Strnad[51] verified this formula by chemical analysis, and shortly afterwards $[\text{clgeH}]_2SO_4$ was noted as a precipitant for the gravimetric determination of copper;[60] the precipitate produced being the highly water insoluble $Cu[\text{clge}]_2.2H_2O$ complex. The complex was next noted by Ray and Bandopadhyay.[52] Their interest stemmed from the close analogy of clge (5.1) to biguanide (bg; 5.2) a compound from which they had produced several copper(II) complexes.

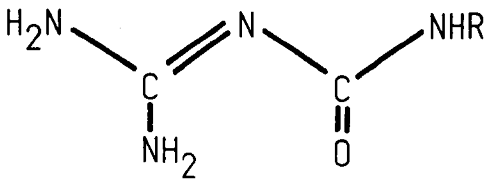


5.1



5.2

Ray's interest in the rose-red complex continued as he and fellow workers prepared a series of what were thought to be copper(II) complexes for both neutral and anionic alkyl substituted clge species.[24] These ligands were termed alkylguanylureas or amidino-3-alkylureas (a3au; 5.3). Since the complexes of their anions can best be represented by the general formula Cu[a3au]$_2$, the complex Cu[clge]$_2$ was considered to be the unsubstituted first member of the series. However, it was later proposed,[27] and has since been proven unequivocally (Chapter Six), that Ray's substituted clge species were 1-amidino-O-alkylureas (aOau; 5.4).



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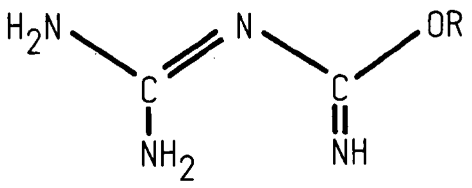
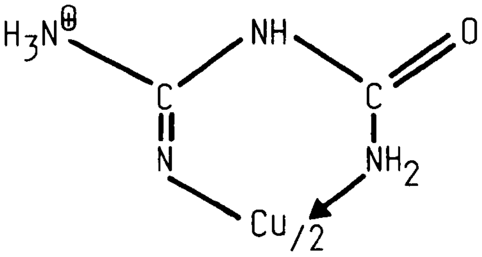


5.4

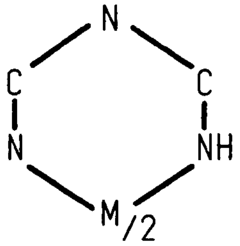
R = alkyl

During the course of this work, it has been found that there is often considerable confusion in the literature as to the identity of the clge species in question (i.e. anion, cation or neutral molecule). Indeed, Ray envisaged the rose-red complex to consist of clge ligands coordinated to the copper(II) cation, best described by form 5.5, with hydroxyl anions balancing the charge [i.e. Cu(clge)$_2$(OH)$_2$; where clge = $C_2H_6N_4O$].[48] This confusion was further compounded by Syamal[53] who,



5.5

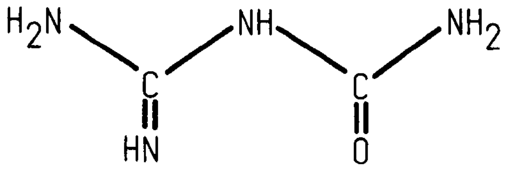
following Ray's work, investigated the structure of three complexes, which he described as Cu(clge)$_2$X$_2$ (where X = OH,Cl,$\frac{1}{2}$SO$_4$) using infrared and UV-visible spectroscopy. Syamal's 'chloride and sulphate complexes' were quoted as being purple with λ_{max} values of 500 and 520nm, whilst the 'hydroxy complex' was rose-red with a λ_{max} value of 510nm. He assumed the similarity in the UV-visible spectra to suggest similar structural formulae and concluded that these complexes contained the fragment 5.6 giving rise to a CuN$_4$ square planar chromophore.



5.6

However, some of these results should be treated with caution as complexes of the form Cu(clge)$_2$Y$_2$ (where Y = NO$_3$,Cl,Br) where synthesized in the work described in Chapter Three and the structure of [Cu(clge)$_2$(NO$_3$)$_2$] elucidated. The structure consisted of [Cu(clge)$_2$]$^{2+}$ moieties, containing a CuO$_2$N$_2$ chromophore, and nitrate anions. All three complexes were blue in appearance with λ_{max} values of 610nm and differed significantly in appearance from the rose-red 'hydroxy complex' which absorbed at 505nm. This difference is further supported by the conditions employed by Syamal and in the present work for the synthesis of the complexes which were (i) precipitation from aqueous solutions at neutral pH for the halides, nitrate and sulphate complexes, and (ii) precipitation from an aqueous solution at alkaline pH for the 'hydroxy complex'. These observations suggest that Syamal's 'hydroxy complex' formulation is incorrect and should be replaced by $Cu[clge]_2.2H_2O$ and that his spectroscopic data for the chloride and sulphate are in error.

The most recent report to examine the rose-red complex, that published by Babykutty et al,[49] describes the complex by the $Cu[clge]_2.2H_2O$ notation and investigates its structure spectroscopically. Their infrared spectra were assigned by comparison with those of what were supposed to be free clge and other structurally similar molecules, such as bg and urea. However, Babykutty et al's spectrum of free clge is in fact that of a $[clgeH]^+$ salt (see Sections 3.3.6 and 4.4). They propose that free clge has structure 5.7 or 5.8 and from these derive the structures 5.9 to 5.12 as possible modes of coordination for $[clge]^-$. They consider that the UV-visible data (λ_{max} = 505nm) and infrared data are most consistent with 5.9 and that the copper(II) ion is coordinated by the four donor atoms of two [clge]$^-$ ligands occupying a square plane, with two remote water molecules situated in the axial positions of the coordination sphere.



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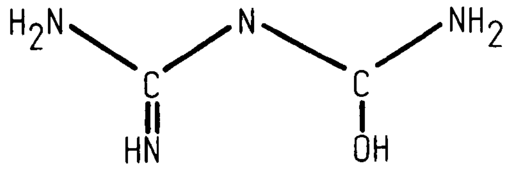

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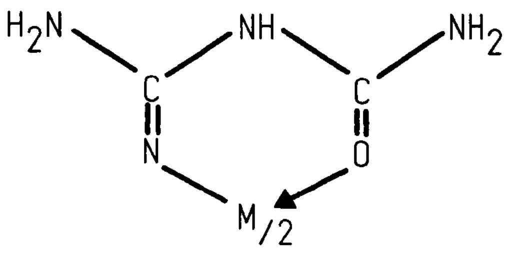

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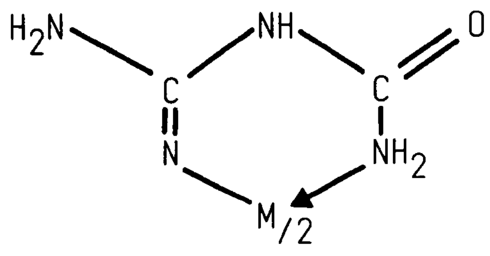

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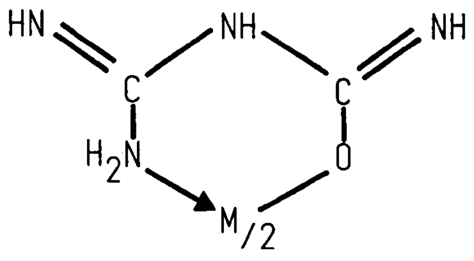

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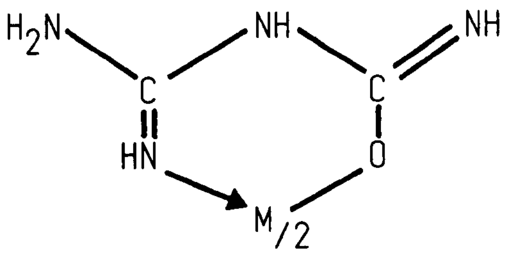


5.12

By analogy with the investigations of copper(II) complexes of clge and [clgeH]$^+$, a determination of the structural chemistry of a copper(II)-[clge]$^-$ complex might best be effected using X-ray crystallographic techniques. This, however, necessitates the synthesis of suitable crystalline material. Williams method[3] of preparation of $Cu[clge]_2.2H_2O$, by the deprotonation of $[clgeH]^+$ in the presence of copper(II) ions dissolved in aqueous ammonium hydroxide solution, gave high yields of product, but only in the form of a microcrystalline precipitate.

$$Cu^{2+} + 2[clgeH]^+ \xrightarrow[(aq.NH_4OH)]{NaOH} Cu[clge]_2.2H_2O\downarrow$$

Varying the conditions for this reaction by slow addition of base, either sodium hydroxide (in solution and solid phases) or lithium hydroxide (generated in situ via hydrolysis of lithium metal) were fruitless, such reactions resulting in only a fine suspension of $Cu[clge]_2 2H_2O$. Crystallization from solutions of $Cu[clge]_2.2H_2O$ by slow evaporation or cooling was not possible since the complex was found to be highly insoluble in every solvent tested. Dissolution was only possible in acidic media, but such solutions only resulted in clge or $[clgeH]^+$ complexes, depending on the molar ratio of acid to $[clge]^-$. Slow neutralisation of these acidic solutions over a period of several days was accomplished using the hydrolysis of urea[61] but, as before, proved to be unsuccessful in producing crystalline material. Finally, to try to influence the precipitation process, attempts were made to incorporate an uncharged stereochemically bulky ligand into the copper(II) ion's coordination sphere. Triphenyl phosphine (PPh_3) was chosen as a candidate ligand but, unfortunately could not be incorporated into a copper(II)-[clge]$^-$ complex, either by direct reaction of an ethanol solution of PPh_3 with Cu[clge]$_2$.2H_2O, or by the basification of an ethanol solution containing copper(II) chloride, clge, and PPh_3 in the molar ratio 1:2:2.

Due to time constraints it was not possible to continue the attempts to crystallize a copper(II)-[clge]$^-$ complex and, therefore, in the absence of crystallographic data, it has only been possible to base an analysis of the structure of Cu[clge]$_2$.2H_2O on infrared and UV-visible spectroscopic and thermogravimetric analytical results.

5.2 **Experimental**

Synthesis of Cu[clge]$_2$.2H_2O[3] and Cu[clge]$_2$

An equimolar ratio of $CuSO_4.5H_2O$ and [clgeH]$_2SO_4$.2H_2O were dissolved in the minimum of hot dilute ammonium hydroxide solution (3M). Addition of excess dilute sodium hydroxide solution (2M) precipitated a rose-red product which, after washing with deionised water and drying over silica gel, was analysed for Cu[clge]$_2$.2H_2O. Yield 98%.

Isothermal dehydration at 100°C for 2 hours gave the anhydrous complex.

Analytical Data

Product	Experimental/Theoretical %		
	C	H	N
$Cu[clge]_2.2H_2O$	15.97/15.92	4.59/4.64	36.89/37.15
$Cu[clge]_2$	18.08/17.97	3.84/3.77	41.88/42.18

$[clge] = C_2H_5N_4O$

Thermogravimetric analysis (tga) was effected using a Stanton Redcroft TG750 instrument (~10mg sample; 1°$Cmin^{-1}$ heating rate).

Infrared spectra were recorded (4000-400cm^{-1}) in KBr discs using a PE680 spectrometer. UV-visible spectra of solid samples were recorded using a PE Lambda 5 spectrometer with a diffuse reflectance facility.

5.3 **Results and Discussion**

A tga curve (0-120°C) for $Cu[clge]_2.2H_2O$ is shown in Figure 5.1. Dehydration occurred in a single step in the 40-100°C region giving the anhydrous complex. Further decomposition commenced at 150°C and was complete by 600°C. Isothermal dehydration (T = 100°C) of larger samples confirmed the facile loss of two water molecules per $Cu[clge]_2$ unit, implying that the complex was composed of tightly bound $[clge]^-$ ligands and more weakly held water molecules.

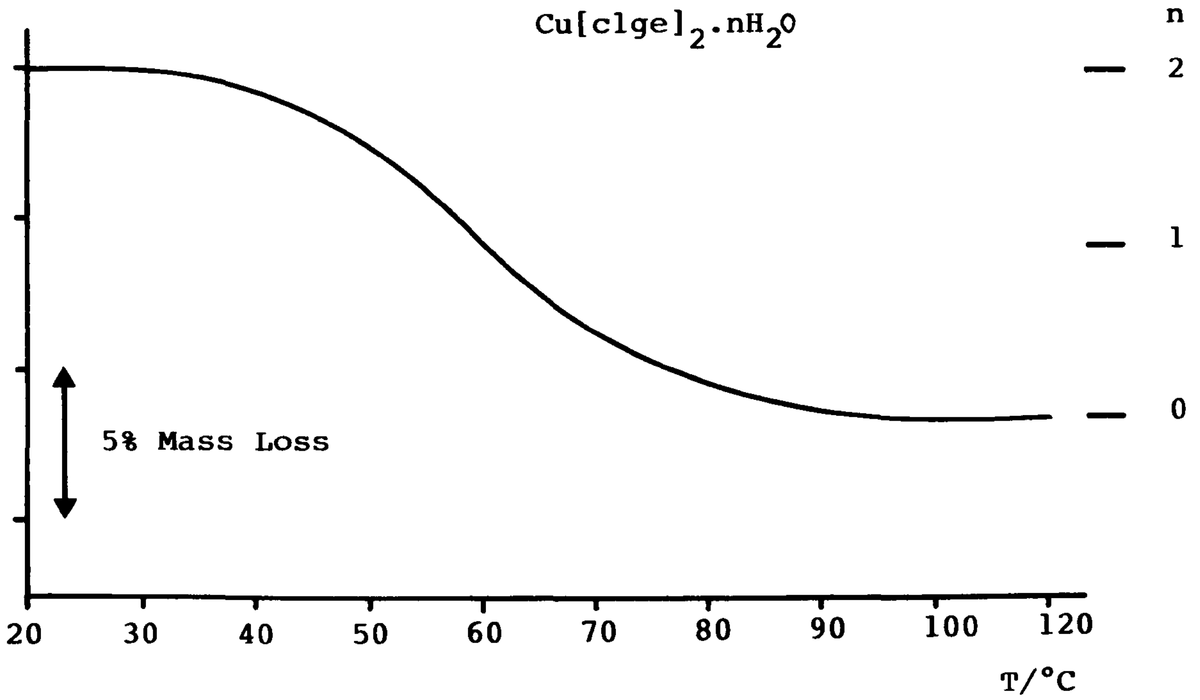


FIGURE 5.1 Tga curve for $Cu[clge]_2.2H_2O$

The infrared spectra of $Cu[clge]_2$ and $Cu[clge]_2.2H_2O$ are collated numerically in Table 5.1 and shown in Figure 5.2 (1800-1200cm^{-1}). The spectral data for the latter complex is in agreement with those recorded by Babykutty et al.[49] There are, however, significant differences between the spectra of the former and latter complexes. These occur in the regions associated with O-H and N-H stretches. The anhydrous complex exhibits slightly better resolution and fewer bands in the 3500-3000, 1700-1600 and 850-450cm^{-1} regions, presumably due to the loss of the O-H vibrations and a reduced level of hydrogen bonding arising from the loss of the water molecules from the crystal structure.

TABLE 5.1 Infrared Spectroscopic Data/cm^{-1} for Cu[clge]$_2$ and Cu[clge]$_2$.2H$_2$O

Cu[clge]$_2$		Cu[clge]$_2$.2H$_2$O		Assignment
		3440		N-H stretches
3400ms		3400		
3360m	br	3350	msbr	O-H stretches^a
3200ms		3270		
1695ms		1680ssh		
	br	1650s	br	N-H deformation
1630s		1620ssh		
1540ms		1535ms		O-H deformation^a
1430mw		1440mw		skeletal
1380m		1400m		stretches
1250ms		1260ms		
1105w		1110w		
960w		965w		
775		845mw		
755	mw	770m		skeletal deformations
725				
700m		705mw		
630	mw,br			N-H deformations
600				O-H deformations^a
525		530		
510	mw	510	mw	
490		495		

^{a}: for Cu[clge]$_2$.2H$_2$O only.

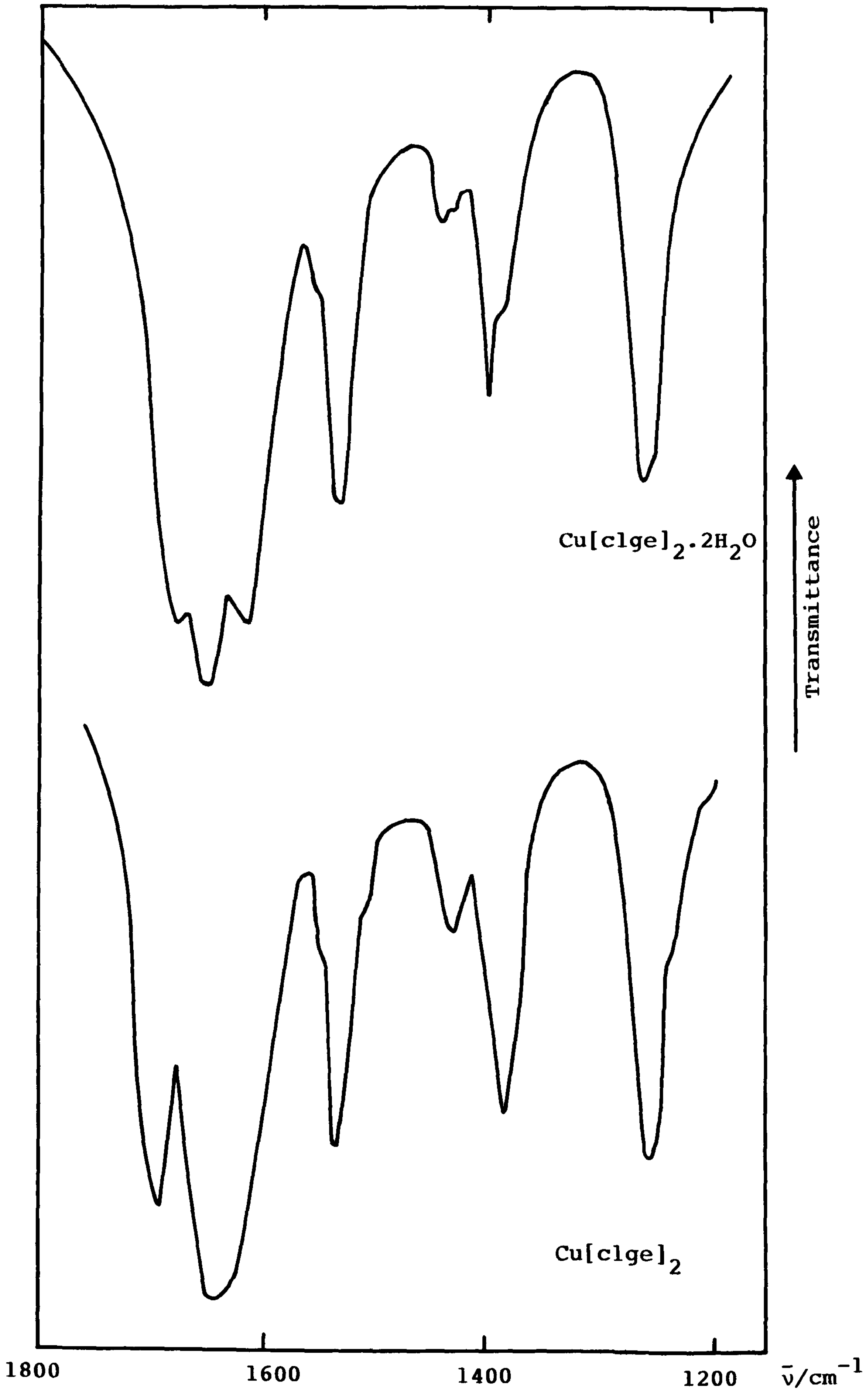
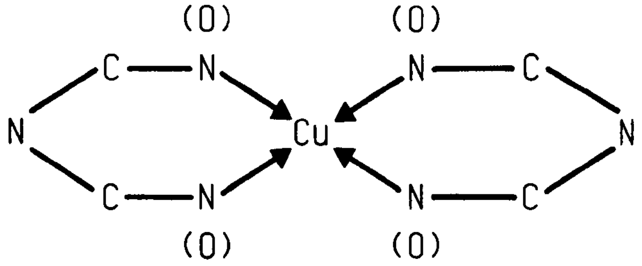


FIGURE 5.2 IR spectra of $Cu[clge]_2.2H_2O$ and $Cu[clge]_2$

The broad assignments noted in Table 5.1 are made by comparison with the spectra of the complexes of 1-cyanoguanidine (cnge), clge and in the light of structural data given in previous chapters. The vibrational spectra are useful in distinguishing between the various ionic forms of clge and its complexes (Figure 5.3) but from these data it is not possible to establish the mode of coordination of the ligand in Cu[clge]$_2$ since extensive mixing of internal coordinates prevents precise assignment of the vibrational spectra. Several authors have attempted a more detailed analysis, but without a full normal coordinate analysis, the results have been inconclusive.

Throughout the course of this thesis it has been observed that the ligands found in copper(II) complexes of neutral and/or anionic clge, bg and bu exhibit extensive electron delocalisation about an essentially planar skeleton. In all the complexes the copper(II) ion lies at the centre of two planar six membered rings to give a fragment typified by form 5.13, with the ligating



5.13

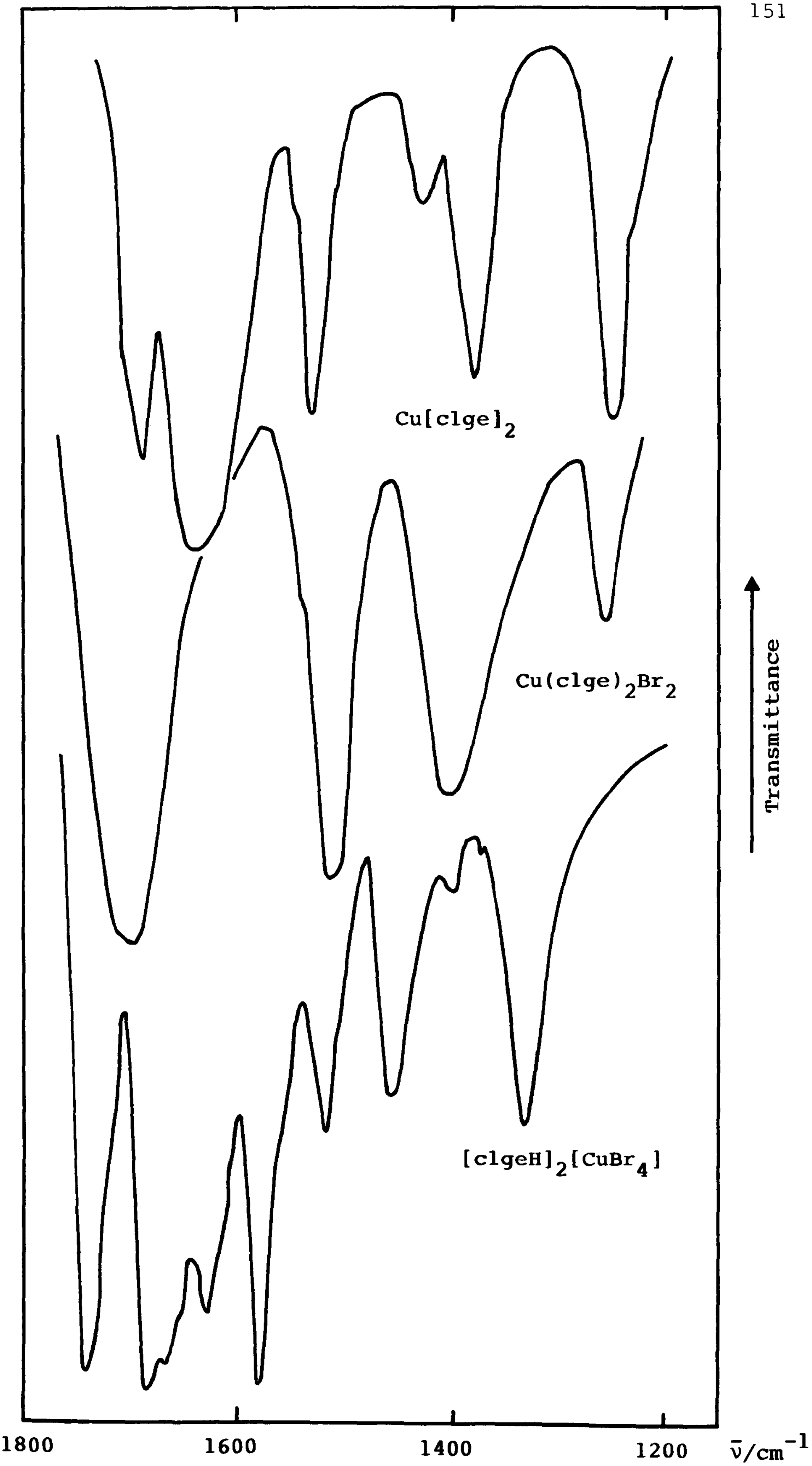
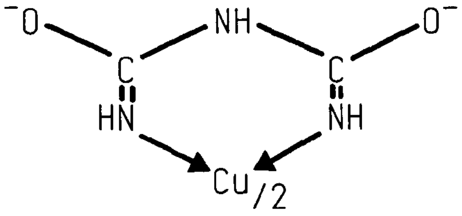
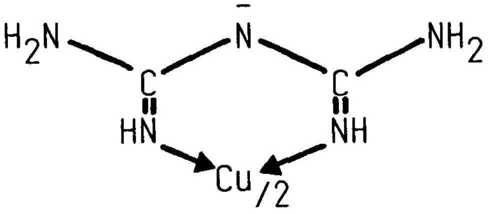
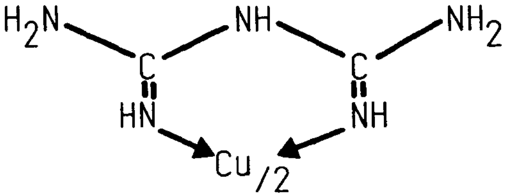
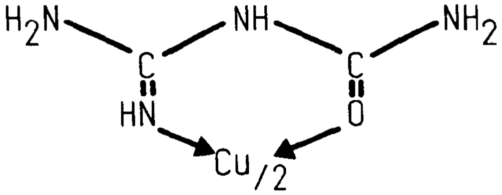
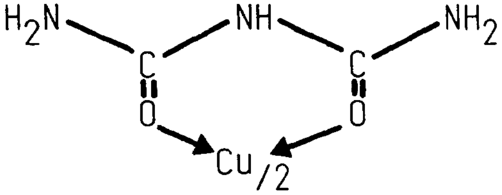


FIGURE 5.3 IR spectra of Cu[clge]$_2$, Cu(clge)$_2$Br$_2$ and [clgeH]$_2$[CuBr$_4$]

atoms of the two chelating ligands lying close to the corners of a square plane. Thus it is logical to suppose that [clge]$^-$ will adopt a similar planar arrangement and by consideration of the electronic structures of structurally characterised copper(II)-clge, bg and bu complexes, it is possible to predict several probable coordination modes.

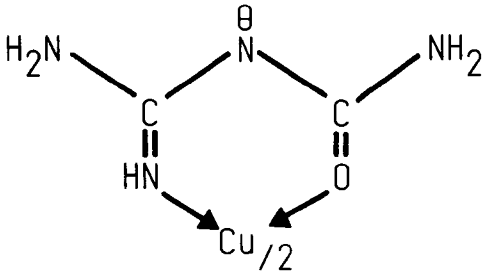
Table 5.2 shows the Lewis structures which describe the bonding of the ligands in the copper(II) complexes of clge, bg, [bg]$^-$ and [bu]$^{2-}$. Structures of cations have not been included since the cations do not coordinate the copper(II) ion (Chapter Four). Coordination via amine residues is not observed; since the ligands are planar the delocalised π-system extends over the whole of the molecule resulting in sp^2 hybridisation of the amine groups. Thus, these groups do not have lone pairs of electrons to direct towards the metal ion. Only imine nitrogen atoms or carbonyl oxygen atoms act as coordinating centres. Non-ligating oxygen atoms only occur as anionic oxy residues, whilst non-ligating nitrogen atoms, except the bridging nitrogen atom, are only found as amine residues. The bridging nitrogen is protonated, giving a C-NH-C bridge, in all forms but that for [bg]$^-$ (5.13) in which a $C{=}\overset{\ominus}{N}{-}C$ bridge exists. By consideration of these observations, two tautomers for the [clge]$^-$ ligand that are consistent with the structures in Table 5.2 are proposed. Form 5.18 is obtained by substitution of a carbonyl group for an imine

TABLE 5.2 Tautomeric Forms Observed in bg, clge and bg Complexes

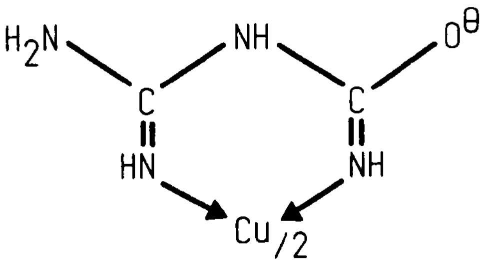
	Biguanide	1-Carbamoyl guanidine	Biuret
L^{2-}			 5.16[d]
L^{-}	 5.13[a]		
L	 5.14[b]	 5.15[c]	 5.17[e]

a: Reference 15
b: Reference 21
c: Chapter Three
d: Reference 18
e: Reference 22

group in form 5.13, whilst substitution of an amine group for an oxy moiety in form 5.16 gives form 5.19.



5.18



5.19

Coordination of a copper(II) ion by a pair of [clge]$^-$ ligands adopting either form 5.18 or 5.19 would result in two isomeric complexes with CuO_2N_2 and CuN_4 chromophores respectively.

A possible method to distinguish between the two possible isomers is UV-visible spectroscopy, the visible spectrum of the copper(II) ion being determined by the number and nature of the ligating species. Table 5.3 shows spectroscopic data for all structurally characterised copper(II) complexes containing ligands analogous to clge. The ligating atoms which form the chromophore are those lying in the equatorial positions of the copper atoms square planar or tetragonally elongated octahedral coordination sphere. The distortion of the latter geometry is such that ligating atoms in the axial positions are so distant that they can be assumed to play no part in the chromophore. The solid state spectra of the complexes all exhibit a broad

TABLE 5.3 Structural and Spectroscopic Data for Copper(II) Complexes of bu, clge, bg, $[bg]^-$, $[bu]^{2-}$ and aOeu

Complex	Chromophore	λ_{max}
$Cu(bu)_2Cl_2$	CuO_4[22]	760[62]
$[Cu(clge)_2(NO_3)_2]$	CuO_2N_2	610
$[Cu(bg)_2]Cl_2.2H_2O$	CuN_4[21]	505[53]
$Cu[bg]_2.2H_2O$	CuN_4[15]	500[63]
$K_2Cu[bu]_2.4H_2O$	CuN_4[18]	485[18]
$[Cu(aOeu)_2]Cl_2.2H_2O$	CuN_4	515
$[Cu(aOeu)_2]Br_2$	CuN_4	515

unsymmetrical absorption band in the visible region. The wavelength of maximum absorbance, λ_{max}, correlates remarkably well with the three types of chromophore. For the CuO_4 chromophore λ_{max} occurs at ~760nm. Replacing two oxygen atoms by two nitrogen atoms results in a CuO_2N_2 chromophore for which λ_{max} is ~610nm. Complete substitution of oxygen atoms by nitrogen atoms gives a CuN_4 chromophore for which λ_{max} is between 480 and 515nm. As noted earlier, both Cu[clge]$_2$ and its dihydrate have λ_{max} values of 505nm and hence, in line with the data in Table 5.3, it can be predicted that both Cu[clge]$_2$ and its dihydrate contain a CuN_4 chromophore. This necessitates that the [clge]$^-$ ligands exist in a form which is described by tautomer 5.19. Unfortunately, however, for Cu[clge]$_2$.2H_2O it is not possible to distinguish between a square planar coordination geometry with the water molecules merely held in the crystal lattice or a distorted octahedral coordination geometry in which the water molecules are distant from the copper(II) ion but lie axially above and below the CuN_4 square plane.

CHAPTER SIX

COPPER(II) COMPLEXES OF 1-AMIDINO-O-ETHYLUREA

6.1 Introduction

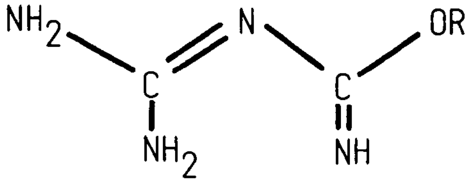
In the course of the examination of the spectroscopic and structural properties of coordinated 1-cyanoguanidine (cnge) (see Chapter Two) the preparation of the anhydrous copper(II)-cnge complexes $Cu(cnge)_2Cl_2$ and $Cu(cnge)_4Cl_2$ was attempted. A method reported by Panda et al[28] was followed in which the requisite molar quantities of an anhydrous copper(II) halide (chloride or bromide) and cnge were reacted in ethanol. Although the appearance, UV-visible absorption spectra and magnetic properties of the products were very similar to those reported for the anhydrous copper(II)-cnge complexes (Table 6.1) the infrared spectra of the former did not contain absorption bands characteristic of the stretching vibrations of the nitrile group of cnge coordinated to copper(II) (see Section 2.6 and Table 6.18). Furthermore, chemical analysis (see Section 6.2) indicated that the products contained cnge and ethanol in a 1:1 molar ratio. The absence of absorption bands attributable to the nitrile stretching vibration of cnge suggested that solvolysis of the nitrile group had occurred with subsequent formation of copper(II)-amidinoethylurea complexes.

These preliminary experiments yielded a mixture containing pink and blue powders, for the chloride complexes, or ruby red and dark green powders for the bromide complexes. By controlling the copper(II) halide:cnge molar ratio, the order of addition of the reactants and the concentration of the reaction solution, it was possible to produce pure products. Analytical data showed them to be 1:1 and 1:2 molar adducts.

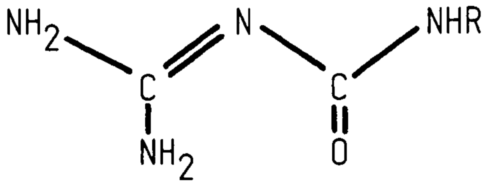
TABLE 6.1 Products of the Reaction between cnge and Copper(II) Halides in Refluxing Ethanol

Product	Appearance	UV-visible spectra λ_{max}/nm
Present Results		
$Cu(aOeu)_2Cl_2.2H_2O$	pink	515
$Cu(aOeu)Cl_2$	blue	650
$Cu(aOeu)_2Br_2$	ruby red	515
$Cu(aOeu)Br_2.2H_2O$	dark green	660
$Cu[aOeu]_2$	pink-red	540
Panda's Results[28]		
$Cu(cnge)_2Cl_2$	pink	530
$Cu(cnge)_4Cl_2$	blue	675
$Cu(cnge)_2Br_2$	pink	525
$Cu(cnge)_4Br_2$	blue	665

Examination of the literature revealed that alcoholysis of cnge in the presence of a copper(II) salt is well known; there is, however, some confusion over the molecular structure of the product amidinoalkylurea and its coordination mode to copper(II). The reaction was first reported by Dutta and Ray[24] who assumed reaction proceeded through 1-amidino-O-alkylurea (aOau; 6.1) intermediates to the isomeric 1-amidino-3-alkylurea (a3au; 6.2) products. Subsequently, Baker and Daniels[25] emphasised the role of the metal cation, proposing a reaction mechanism sequentially involving copper(II)-cnge, copper(II)-aOau and copper(II)-a3au complexes. Meanwhile, Kawano and Odo[26] proposed that the reaction products were 1-amidino-O-alkylureas and that the geometrical rearrangement did not occur; they also recognised the significance of copper(II)-cnge complexes as intermediates. Diana et al,[29] by synthesising the two isomers via alternative unambiguous routes, resolved this dichotomy showing chemically that the ligands produced in the alcoholysis reaction were 1-amidino-O-alkylureas.



6.1

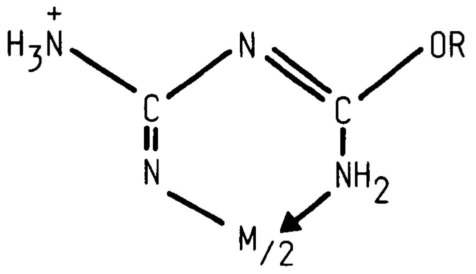


6.2

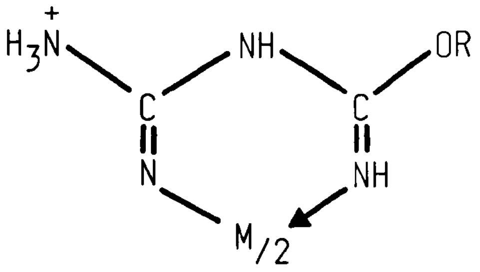
R = alkyl

These tautomeric forms are assumed by analogy with biguanide, 1-carbamoylguanidine and biuret; they have not been confirmed experimentally.

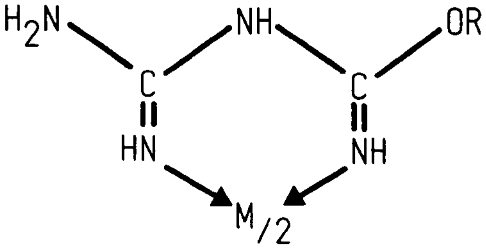
Although this conclusion has since been generally accepted, the coordination mode of aOau to copper(II) has not been established, numerous tautomeric forms being suggested. Initially Diana et al[27] and Dutta and Syamal[64] favoured structure (6.3); Wasson and Trapp[38] then proposed structure (6.4). Subsequently, after detailed infrared studies, Syamal and Ghanekar[65] preferred structure (6.5).



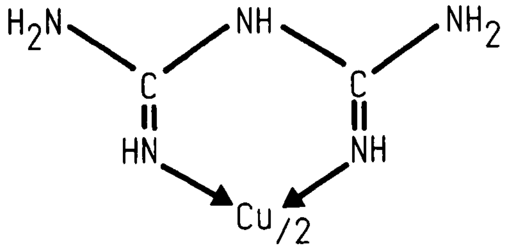
6.3



6.4



6.5



6.6

In the absence of structural verification, comparison with the more extensively studied, analogous ligand, biguanide (bg) indicates coordination probably occurs through two imine groups as in structure (6.5). The tautomeric form adopted by bg (6.6) when coordinated to copper(II) was elucidated in a recent high precision single crystal X-ray diffraction study of the structure of $[Cu(bg)_2]Cl_2.2H_2O$.[21]

To verify the identity of the products generated by this present work and to ascertain the coordination geometry of the chelating ligand, their crystal and molecular structures have been determined. The results reported in this Chapter identified the complexes as $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2.2H_2O$. However, although the solution of the structure of the former complex was satisfactory, that of the latter complex was disappointing owing to the presence of several elements of twinning. Consequently, whereas detailed geometrical parameters could be quoted with confidence for the structure of $[Cu(aOeu)Cl_2]_2$, only gross aspects of the structure could be described for $Cu(aOeu)_2Cl_2.2H_2O$. Hence a determination of the structure of the analogous complex $[Cu(aOeu)_2]Br_2$ was attempted. This proved to be very successful, enabling a complete analysis of the aOeu ligand.

To characterise further the aOeu molecule, the preparation of the cationic and anionic forms ($[aOeuH]^+$ and $[aOeu]^-$ respectively) and of neutral uncoordinated aOeu was attempted. Microcrystalline samples of [aOeuH]Cl and $Cu[aOeu]_2$ were obtained, however, the neutral species could not be synthesised. The methods employed to try to produce this molecule involved either neutralisation of aqueous solutions of [aOeuH]Cl with NaOH or deprotonation of [aOeuH]Cl in aqueous or ethanolic solution using an ion exchange resin in a manner similar to that used for the preparation of 1-carbamoylguanidine (see Section 3.2). Unfortunately, these efforts only produced cnge and ethanol, presumably due to the decomposition of uncoordinated neutral aOeu.

The infrared spectra of the aOeu compounds produced in this work have been recorded but detailed assignment has not been possible owing to the complexity of the vibrations associated with the aoeu ligand.

6.2 **Experimental**

The complexes and the cation were produced as follows. Analytical data for all the products are given in Table 6.2

(a) $[Cu(aOeu)Cl_2]_2$

Cnge (2.52g, 30mmol) and copper(II) chloride (4.04g, 30mmol) were dissolved in the minimum of hot ethanol. The cnge solution was added slowly to the refluxing copper(II) chloride solution and the dark blue complex precipitated after several minutes. It was filtered off, washed with ethanol and air dried. Yield 7.5g, 95%.

(b) $[Cu(aOeu)_2]Cl_2.2H_2O$

An ethanol solution of copper(II) chloride (4.04g, 30mmol in 150cm^3) was added in small aliquots to a refluxing ethanol solution of cnge (5.04g, 60mmol in 250cm^3). The solution was refluxed for 15 minutes and then reduced to one quarter of its volume. It was cooled in ice for 2 hours and the pink complex precipitated was filtered off, washed with cold ethanol and air dried. Yield 11.1g, 86%. [Cu(aOeu)$_2$]Cl$_2$ was obtained upon isothermal dehydration of [Cu(aOeu)$_2$]Cl$_2$.2H$_2$O at 85°C.

(c) Cu(aOeu)Br$_2$.2H$_2$O

As (a), but copper(II) bromide (6.70g, 30mmol) was substituted for copper(II) chloride and for blue read green. Yield 10.5g, 90%. Cu(aOeu)Br$_2$ was obtained upon isothermal dehydration of Cu(aOeu)Br$_2$.2H$_2$O at 90°C.

(d) Cu(aOeu)$_2$Br$_2$

As (b), but copper(II) bromide (6.70g, 30mmol) was substituted for copper(II) chloride and for pink read ruby-red. Yield 10.9g, 75%.

(e) [aOeuH]Cl

H$_2$S gas was bubbled through an aqueous solution of [Cu(aOeu)$_2$]Cl$_2$.2H$_2$O (4.30g, 10mmol in 500ml water) until the blue solution became colourless. Air was drawn through the solution for several minutes to remove traces of H$_2$S. The black precipitate of CuS was filtered off and the filtrate evaporated under vacuum until the onset of precipitation. The precipitate was collected, washed with ice cold water and dried over silica gel under vacuum. Yield 2.99g, 90%.

(f) $Cu[aOeu]_2$

Dilute NaOH (2M) was added to an aqueous solution of $[Cu(aOeu)_2]Cl_2.2H_2O$ (4.30g, 10mmol in 500ml water) until the solution became colourless. The pink-red precipitate was filtered off, washed with water and dried over silica gel. Yield 3.11g, 96%.

TABLE 6.2 Analytical Data for the Products

Product	Experimental/Theoretical %		
	C	H	N
$[Cu(aOeu)Cl_2]_2$	18.37/18.15	3.86/3.78	21.63/21.17
$[Cu(aOeu)_2]Cl_2.2H_2O$	22.23/22.30	5.51/5.57	26.50/26.02
$[Cu(aOeu)_2]Cl_2$	24.45/24.33	5.28/5.07	28.36/28.39
$Cu(aOeu)Br_2.2H_2O$	12.25/12.33	3.63/3.60	14.30/14.38
$Cu(aOeu)Br_2$	13.45/13.59	2.94/2.83	15.61/15.85
$Cu(aOeu)_2Br_2$	19.93/19.86	4.01/4.14	22.99/23.17
[aOeuH]Cl	29.01/28.83	6.80/6.61	33.77/33.63
$Cu[aOeu]_2$	29.76/29.86	5.91/5.60	34.91/34.84

aOeu = $C_4H_{10}N_4O$ $[aOeuH]^+$ = $C_4H_{11}N_4O$ $[aOeu]^-$ = $C_4H_9N_4O$

Infrared spectra (4000-400cm^{-1}) were recorded in KBr discs using a P.E.598 spectrometer. UV-visible spectra were recorded using a P.E. Lambda 5 spectrometer with a diffuse reflectance facility.

6.3 Crystal and Molecular Structures of the Bis(1-amidino-O-ethylurea)dichlorodi-μ-chlorodicopper(II) dimer,of Bis(1-amidino-O-ethylurea)copper(II) Dichloride Dihydrate and of Bis(1-amidino-O-ethylurea)copper(II) Dibromide

6.3.1 Structure solution and crystal data for $[Cu(aOeu)Cl_2]_2$

Deep blue crystals of $[Cu(aOeu)Cl_2]_2$ were obtained by slow evaporation of an ethanolic solution. Microscopic examination of the crystals showed them to have the shape of an arrowhead, implying twinning. Since the crystals were too small for cleavage, an apparently twinned crystal (0.2x0.1x0.05mm) was mounted in a Lindemann tube for preliminary study. Oscillation and Weissenberg photographs revealed cell parameters, space group and twinning about the (100) plane. Moreover, as a/c.cos β = 3.04 (≃3) there was approximate overlap of the (3kl) and (6kl) reflections of the twinned crystals. Cell parameters space group and X-ray diffraction data were collected for one component of the twinned crystal as described in Section 1.6.1. Allowance was made at a later stage for the twinning of the crystal. Of the 1751 intensities collected 1075 were deemed to be observed.

The copper atom was located from a Patterson function. The chlorine atoms and the carbon, nitrogen and oxygen atoms were then located from successive difference Fourier syntheses. The identities of the skeletal atoms of the chelating ligand were confirmed by equating their atomic scattering factor to that of carbon and then determining their isotropic temperature factors. Those atoms with factors between 0.03906 and 0.06154, between 0.02553 and 0.02808 and equal to 0.01506 were designated carbon, nitrogen and oxygen, respectively. Full matrix least squares refinement with anisotropic temperature factors for all these atoms converged at R = 0.098. Analysis of F_{obs} and F_{calc} values showed this disappointingly high R value to be due to poor agreement for the (0kl), (3kl) and (6kl) reflections, presumably owing to the twinning. Although (0kl) reflections could be corrected by a layer scale factor, incomplete overlap within the (3kl) and (6kl) reflections made allowance for the twinning impossible despite many attempts. The 285 reflections of the type (3kl) and (6kl) were therefore removed, leaving 790 for the calculations. Full matrix least squares refinement with anisotropic temperature factors then converged at R = 0.054. A subsequent difference Fourier synthesis indicated the presence of electron density (varying from 0.47 to 0.25 e/Å^3) demonstrating the approximate positions of hydrogen atoms consistent with the amidino-O-ethylurea tautomeric form. The accurate positions of the hydrogen atoms were then defined [r(N-H)=r(C-H) = 1.00Å, U(ISO) = 0.03$Å^2$] using a hydrogen placing routine. Further refinement of the structure with fixed hydrogen atoms converged at R = 0.047. Final positional parameters and thermal parameters are given in Tables 6.3 and 6.4. The refined layer scale factor for the (0kl) reflections was 1.46 corresponding to 47% of the minor twin component. Observed and calculated structure factors are included in Appendix B.

Crystal Data

$C_4H_{10}N_4OCl_2Cu$, M = 264.4, monoclinic, spacegroup $P2_1/c$, a = 7.175(2), b = 16.773(3), c = 8.312(2), β = 106.99(3), U = 956.66$Å^3$, D_m = 1.85gcm^{-3}, D_c = 1.84gcm^{-3} for Z = 4, F(000) = 532, μ (MoK_α) = 28.80cm^{-1}.

6.3.2 Structure solution and crystal data for $[Cu(aOeu)_2]Cl_2.2H_2O$

Small pink crystals of $[Cu(aOeu)_2Cl_2.2H_2O$ were deposited from the mother liquor of the reaction of cnge with copper(II) chloride in ethanol (Section 6.2). A very small crystal (0.2x0.1x0.01mm) was mounted on the end of a glass fibre with 'Araldite' adhesive. Cell parameters, space group and X-ray diffraction data (in the range 1<Θ<20) were obtained as described in Section 1.6.1. Of the 906 intensities collected, 557 had net counts exceeding $2\sigma_I$ and were deemed to be observed.

TABLE 6.3 Final Positional Parameters ($x10^3$) for $[Cu(aOeu)Cl_2]_2$

Atom	x/a	y/b	z/c
Cu(1)	171.7(3)	437.17(7)	428.5(1)
Cl(1)	106.0(6)	321.7(1)	546.0(3)
Cl(2)	236.7(6)	506.6(2)	679.4(3)
C(1)	193(2)	408.9(6)	84(1)
C(2)	269(2)	544.2(6)	188(1)
C(3)	356(2)	680.1(6)	241(1)
C(4)	404(2)	749.4(7)	144(2)
N(1)	164(2)	382.0(4)	222.2(9)
N(2)	177(2)	363.8(5)	-49(1)
N(3)	244(2)	486.4(5)	69.4(9)
N(4)	247(2)	533.3(5)	334(1)
O(1)	317(1)	612.8(4)	128.4(8)
H(1)	137	323	223
H(2)	140	306	-48
H(3)	205	386	-153
H(4)	265	502	-42
H(5)	273	582	410
H(6)	235	693	278
H(7)	465	669	345
H(8)	431	799	214
H(9)	292	760	40
H(10)	522	736	107

TABLE 6.4 Final Thermal Parameters ($x10^3$)/$Å^2$ for $[Cu(aOeu)Cl_2]_2$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cu(1)	55(1)	32.5(6)	23.9(6)	3.0(6)	18.4(6)	3.1(9)
Cl(1)	84(3)	35(1)	37(1)	6(1)	28(2)	1(2)
Cl(2)	69(2)	43(1)	25(1)	0(1)	18(1)	-4(2)
C(1)	54(9)	45(6)	36(5)	6(5)	30(6)	10(6)
C(2)	44(8)	41(6)	26(5)	-2(4)	15(5)	-1(6)
C(3)	70(9)	36(6)	45(6)	1(5)	19(71	-14(7)
C(4)	80(9)	44(6)	67(8)	3(6)	24(9)	-11(8)
N(1)	79(9)	27(4)	32(4)	5(3)	21(6)	3(5)
N(2)	110(9)	39(5)	25(4)	-9(4)	32(6)	-9(7)
N(3)	70(8)	39(5)	26(4)	-1(4)	23(5)	-6(5)
N(4)	90(9)	34(5)	31(4)	-4(4)	32(6)	-14(6)
O(1)	80(7)	39(4)	34(4)	5(3)	29(5)	-12(5)

In the form: $[\exp -2\pi^2\ U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)l^2c^{*2}$
$+2U(12)hka^*b^*+2U(13)hla^*c^*+23)klb^*c^*)]$

Consideration of the molecular formula within the context of the crystal symmetry indicated that the copper atom must be situated in a special position (0,0,0) of the $P2_1/c$ space group and that pairs of aOeu molecules, chlorine atoms and water molecules must be located in centrosymmetrically related positions. Consequently, subsequent to the data reduction stage, the positions of the chlorine atoms and then the positions of the carbon, nitrogen and oxygen atoms were determined in successive difference Fourier syntheses. Full matrix least squares refinement with anisotropic temperature factors for all the atoms converged at $R = 0.148$. A subsequent difference Fourier synthesis showed there was considerable residual electron density, the larger peaks (largest 0.15 e/Å^3) being related to Cl(1) by twinning operations. The twinned elements, permitted by the β angle close to 90°, together with the limited intensity data owing to the small size of the crystal, were thought to contribute to the disappointingly high R value. Attempts to refine the structure with sets of coordinates for all the twinned atoms resulted in but minor improvements in R-value, presumably owing to the limited intensity data. It was then decided to discontinue refinement at $R = 0.148$. Final positional parameters and thermal parameters are given in Tables 6.5 and 6.6 respectively. Observed and calculated structure factors are included in Appendix B.

TABLE 6.5 Final Positional Parameters ($\times 10^3$) for $[Cu(aOeu)_2]Cl_2.2H_2O$

Atom	x/a	y/b	z/c
Cu(1)	0	0	0
Cl(1)	-823(2)	212(1)	-293(1)
C(1)	-444(7)	132(3)	12(3)
C(2)	-231(6)	89(3)	187(3)
C(3)	-104(8)	82(3)	360(3)
C(4)	-187(9)	132(5)	461(4)
N(1)	-297(6)	87(2)	-39(3)
N(2)	-655(5)	182(2)	-22(2)
N(3)	-435(5)	137(2)	118(2)
N(4)	-78(7)	33(2)	150(2)
O(1)	-295(5)	111(2)	279(2)
O(2)	-310(4)	88(2)	-273(2)

TABLE 6.6 Final Thermal Parameters ($\times 10^3$)/Å^2 for

$[Cu(aOeu)_2]Cl_2.2H_2O$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cu(1)	1.3(3)	3.5(3)	5.7(4)	-0.5(4)	-0.4(2)	0.8(3)
Cl(1)	5.6(7)	9.2(9)	9.5(9)	-2.6(7)	0.8(6)	1.1(6)
C(1)	5(3)	2(2)	5(3)	-1(2)	1(2)	-3(2)
C(2)	3(2)	3(2)	6(3)	-3(2)	-1(2)	1(2)
C(3)	8(3)	9(3)	5(3)	-1(2)	-3(2)	2(2)
C(4)	6(3)	21(7)	10(4)	-3(4)	-1(3)	4(4)
N(1)	3(2)	5(2)	9(3)	-2(2)	0(2)	-1(2)
N(2)	1(1)	5(2)	10(3)	0(2)	-2(2)	3(1)
N(3)	6(2)	3(2)	7(3)	0(2)	0(2)	0(2)
N(4)	11(3)	1(2)	6(2)	-1(1)	-1(2)	-1(2)
O(1)	5(2)	8(2)	6(2)	-2(2)	0(1)	1(1)
O(2)	4(2)	7(2)	8(2)	-1(1)	0(1)	-1(1)

In the form: $[\exp -2\pi^2 U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)l^2c^{*2}$

$+2U(12)hka^*b^*+2U(13)hla^*c^*+23)klb^*c^*)]$

Crystal Data

$C_8H_{24}N_8O_4Cl_2Cu$, M = 430.4, monoclinic, space group $P2_1/c$, a = 5.299(2), b = 13.739(3), c = 12.806(3)Å, β = 89.89(3)°, U = 932.31Å^3, D_m = 1.55gcm^{-3}, D_c = 1.53gcm^{-3} for Z = 2, F(000) = 446, μ(MoK_α) = 15.33cm^{-1}.

6.3.3 Structure solution and crystal data for $Cu(aOeu)_2Br_2$

Ruby red crystals of $[Cu(aOeu)_2]Br_2$ were obtained from an ethanol solution of $Cu(cnge)_2Br_2$ (5x10^{-2}M) allowed to stand for several days at room temperature. A suitable crystal (0.3x0.1x0.1mm) was mounted in a Lindemann tube for preliminary study. Cell parameters, space group and X-ray diffraction data were obtained as described in Section 1.6.1. Of the 1510 intensities collected, 1079 were deemed to be observed.

Consideration of the molecular formula within the context of the crystal symmetry indicated that the copper atom must be situated in a special positon (0,0,0) of the $P2_1/c$ space group and that pairs of aOeu molecules and bromide atoms must be located in centrosymmetrically related positions. A Patterson function confirmed the position of the copper atom and revealed the position of the bromine atoms. A subsequent difference Fourier synthesis located the carbon, nitrogen and oxygen atoms. Full matrix least squares refinement with anisotropic temperature factors converged at R = 0.041. The top nine peaks (density 0.79 to 0.48 eÅ^3) and the eleventh peak (density 0.46 e/Å^3) of a subsequent difference Fourier synthesis gave the positions of the hydrogen atoms of the aOeu molecule. Further refinement of the structure using isotropic temperature factors for all the atoms including the hydrogens was totally successful but for the fact that five of the hydrogen atoms [H(1),(2),(3),(5) and (6)] gave virtually zero (i.e. less than their standard deviations) U(ISO) values. Thus for the last few cycles of refinement these hydrogen atoms were refined with a fixed U(ISO) value (0.001Å^2) whilst the other hydrogens had both their positions and U(ISO) values refined. This final refinement converged at R = 0.031. Final positional parameters and thermal parameters are given in Tables 6.7 and 6.8. Structure factors are included in Appendix B.

Crystal Data

$C_8H_{20}N_8O_2Br_2Cu$, M = 483.3, monoclinic, space group $P2_1/c$, a = 5.221(2), b = 12.306(3), c = 12.703(3)Å, β = 95.94(3)°, U = 811.78Å^3, $D_m = 1.97gcm^{-3}$, $D_c = 1.98gcm^{-3}$ for Z = 2, F(000) = 478, $\mu(MoK_\alpha) = 66.33cm^{-1}$.

6.3.4 Coodination geometry of the copper(II) cation and intermolecular contacts for $[Cu(aOeu)Cl_2]_2$, $[Cu(aOeu)_2Cl_2.2H_2O$ and $[Cu(aOeu)_2]Br_2$

The basic unit in the structure of $[Cu(aOeu)Cl_2]_2$ is the centrosymmetric chlorine bridged $[Cu(aOeu)Cl_2]_2$ dimer (Figure 6.1). The Cu^{2+} ion is located 0.118Å above

TABLE 6.7 Final Positional Parameters $(\mathrm{x}10^3)$ for $[\mathrm{Cu(aOeu)_2}]\mathrm{Br_2}$

Atom	x/a	y/b	z/c
Cu(1)	0	0	0
Br(1)	746.2(1)	316.29(4)	157.70(5)
C(1)	-400.3(9)	-5.3(4)	145.0(4)
C(2)	-259.2(9)	-184.6(4)	89.8(4)
C(3)	-197(1)	-374.4(4)	59.6(4)
C(4)	59(1)	-398.1(5)	116.6(5)
N(1)	-251.1(8)	49.4(3)	90.1(3)
N(2)	-572.4(9)	39.8(4)	202.6(4)
N(3)	-398.2(8)	-115.9(3)	147.1(3)
N(4)	-101.4(8)	-150.9(3)	27.5(3)
O(1)	-322.8(7)	-285.6(2)	110.0(3)
H(1)	-275(9)	118(4)	100(4)
H(2)	-573(9)	109(4)	203(4)
H(3)	-650(10)	3(4)	238(4)
H(4)	-490(1)	-143(5)	190(5)
H(5)	-30(10)	-193(4)	-2(4)
H(6)	-196(9)	-360(4)	-3(4)
H(7)	-300(10)	-431(5)	64(5)
H(8)	120(20)	-458(7)	97(6)
H(9)	180(20)	-346(8)	104(8)
H(10)	50(10)	-401(6)	188(6)

TABLE 6.8 Final Thermal Parameters $(\mathrm{x}10^3)/\text{Å}^2$ for $[\mathrm{Cu(aOeu)_2}]\mathrm{Cl_2.2H_2O}$

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)	U(ISO)
Cu(1)	28.2(4)	21.3(4)	29.1(4)	1.9(3)	16.6(3)	-1.5(3)	
Br(1)	69.9(4)	31.6(3)	47.0(3)	-2.4(3)	34.3(3)	3.4(3)	
C(1)	33(2)	26(2)	28(2)	0(2)	12(2)	0(2)	
C(2)	30(2)	24(2)	29(2)	0(2)	8(2)	-3(2)	
C(3)	45(3)	25(2)	36(3)	-6(2)	16(2)	-3(2)	
C(4)	46(3)	37(3)	49(4)	-1(3)	15(3)	3(3)	
N(1)	35(2)	25(2)	40(2)	2(2)	19(2)	2(2)	
N(2)	45(3)	28(2)	49(3)	2(2)	33(2)	2(2)	
N(3)	34(2)	27(2)	34(2)	0(2)	24(2)	-2(2)	
N(4)	41(3)	24(2)	41(2)	1(2)	24(2)	2(2)	
O(1)	39(2)	22(2)	45(2)	-2(1)	24(2)	-4(1)	
H(1)							1
H(2)							1
H(3)							1
H(4)							20(10)
H(5)							1
H(6)							1
H(7)							20(20)
H(8)							50(90)
H(9)							90(30)
H(10)							50(20)

the base of a square pyramidal coordination sphere typical of 5-coordinate copper(II).[59] The equatorial plane is composed of the two imine nitrogen atoms of the chelating bidentate aOeu ligand [r(Cu-N(1)) = 1.935Å; r(Cu-N(4)) = 1.940Å] and two chlorine atoms [r(Cu-Cl(1)) = 2.227Å; r(Cu-Cl(2)) = 2.314Å]; the axial position is occupied by a more remote chlorine atom centrosymmetrically related to Cl(2) [r(Cu-Cl(2)') = 2.957Å]. Full details of the copper(II) cations coordination sphere are given in Table 6.9.

TABLE 6.9 Coordination Sphere of the Cu^{2+} Cation and Planarity of the Ligating Atoms for $[Cu(aOeu)Cl_2]_2$; Bond Distances/Å and Angles/°

Cu(1)-Cl(1)	2.279(3)	Cu(1)N(1)C(1)	130(1)
Cu(1)-Cl(2)	2.314(3)	Cu(1)N(4)C(2)	129(1)
Cu(1)-Cl(2)'	2.957(4)	Cl(1)Cu(1)Cl(2)	93.1(1)
Cu(1)-N(1)	1.935(8)	Cl(1)Cu(1)Cl(2)'	95.2(1)
Cu(1)-N(4)	1.940(8)	Cl(1)Cu(1)N(1)	91.0(2)
		Cl(1)Cu(1)N(4)	175.9(4)
		Cl(2)Cu(1)Cl(2)'	91.9(1)
		Cl(2)Cu(1)N(1)	170.2(4)
		Cl(2)Cu(1)N(4)	86.6(3)
		Cl(2)'Cu(1)N(1)	96.5(4)
		Cl(2)'Cu(1)N(4)	89.0(4)
		N(1)Cu(1)N(4)	88.6(4)

symmetry properties of Cl(2)' -x,1-y,1-z

Ligating atom	Deviation from plane/Å
Cl(1)	0.037
Cl(2)	-0.038
N(1)	-0.046
N(4)	0.047

Cu(1) is 0.118Å above the Cl(1)Cl(2)N(1)N(4) plane

Equation of best plane: -6.59858x+4.3394y-0.11507z = 0.597

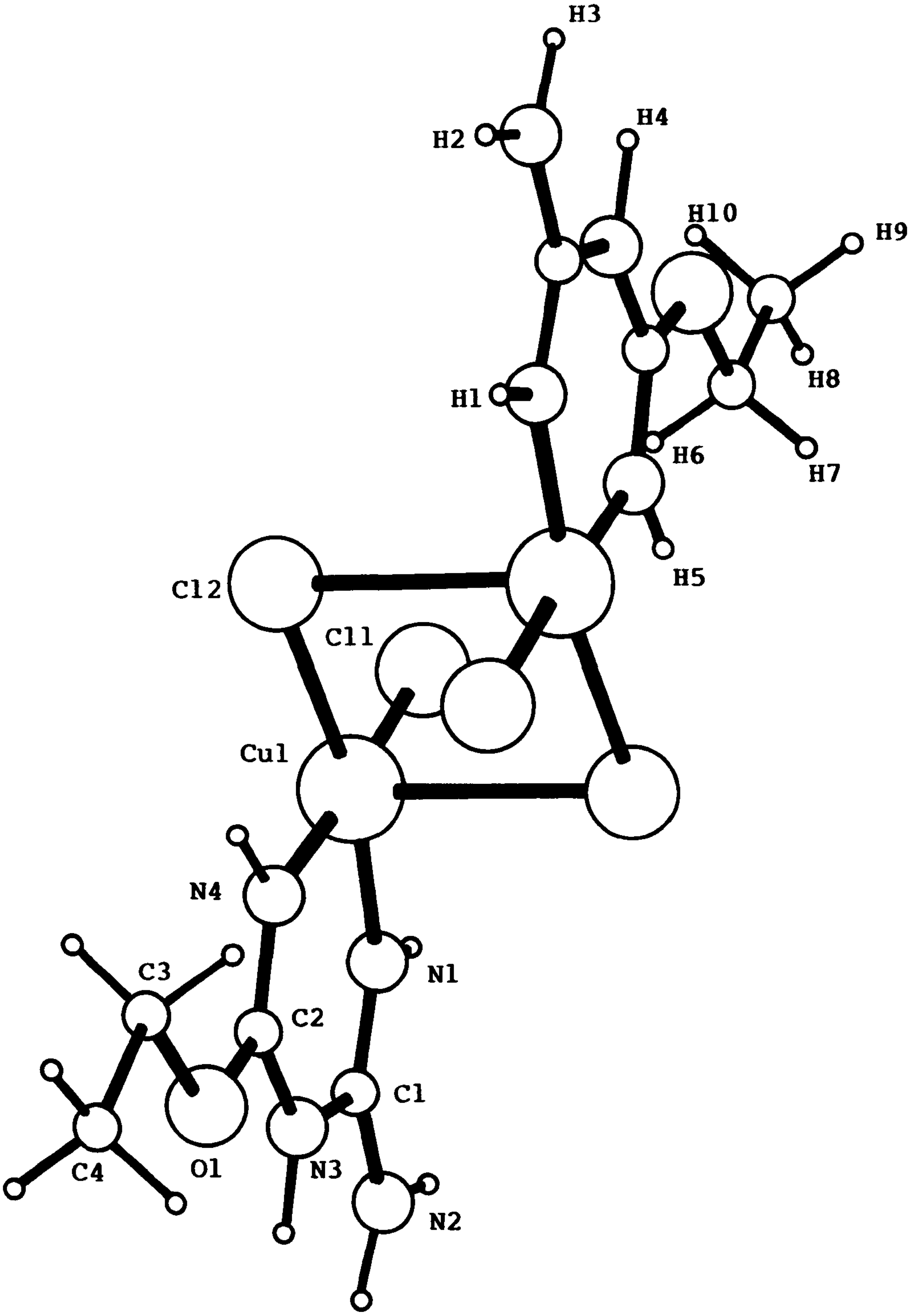


FIGURE 6.1 Molecular geometry of the $[Cu(aOeu)Cl_2]_2$dimer

The dimers form part of pairs of corrugated planes which run parallel to (100) (Figure 6.2). Intermolecular contacts of less than 3.30Å only occur within these planes (Table 6.10, Figure 6.3). They arise between nitrogen and chlorine atoms and can be classified into two types; those with a geometry consistent with an intermolecular hydrogen bond, N(2)-H(2)...Cl(1) and N(3)-H(4)...Cl(2), and those within the CuN_2Cl_2 square plane, N(1)...Cl(1) and N(4)...Cl(2).

TABLE 6.10 Intermolecular Contacts of Less than 2.30Å # for $[Cu(aOeu)Cl_2]_2$: Hydrogen Bond and Electrostatic Interactions

Interaction	Symmetry properties of X'	r(X...X') Å	r(H-H) Å	r(H...X') Å	XHX' °
N(1)-H(1)...Cl(1)*	x,y,z	3.02	1.01	2.76	95
N(2)-H(2)...Cl(1)	x,½+y,-½-z	3.29	1.00	2.32	161
N(3)-H(4)...Cl(2)	x,y,-1+z	3.24	1.01	2.27	161
N(4)-H(5)...Cl(2)*	x,y,z	2.93	1.01	2.65	96

There are two other contacts to N(2) over 3.30Å, $r(N(2)...Cl(1)^a)$ = 3.33Å, $r(N(2)-Cl(2)^a)$ = 3.40Å, symmetry of $Cl(1)^a$ and $Cl(2)^a$ x,y,-1+z. Hydrogen H(3) lies on a line bisecting the angle $Cl(1)^a$-Cu(1)-$Cl(2)^a$.

* These contacts are within the CuN_2Cl_2 square plane giving rise to the small XHX' angle.

Both the structures of $[Cu(aOeu)_2]Cl_2.2H_2O$ and $Cu(aOeu)_2Br_2$ consist of essentially planar cationic fragments (Table 6.11) and chloride or bromide anions as

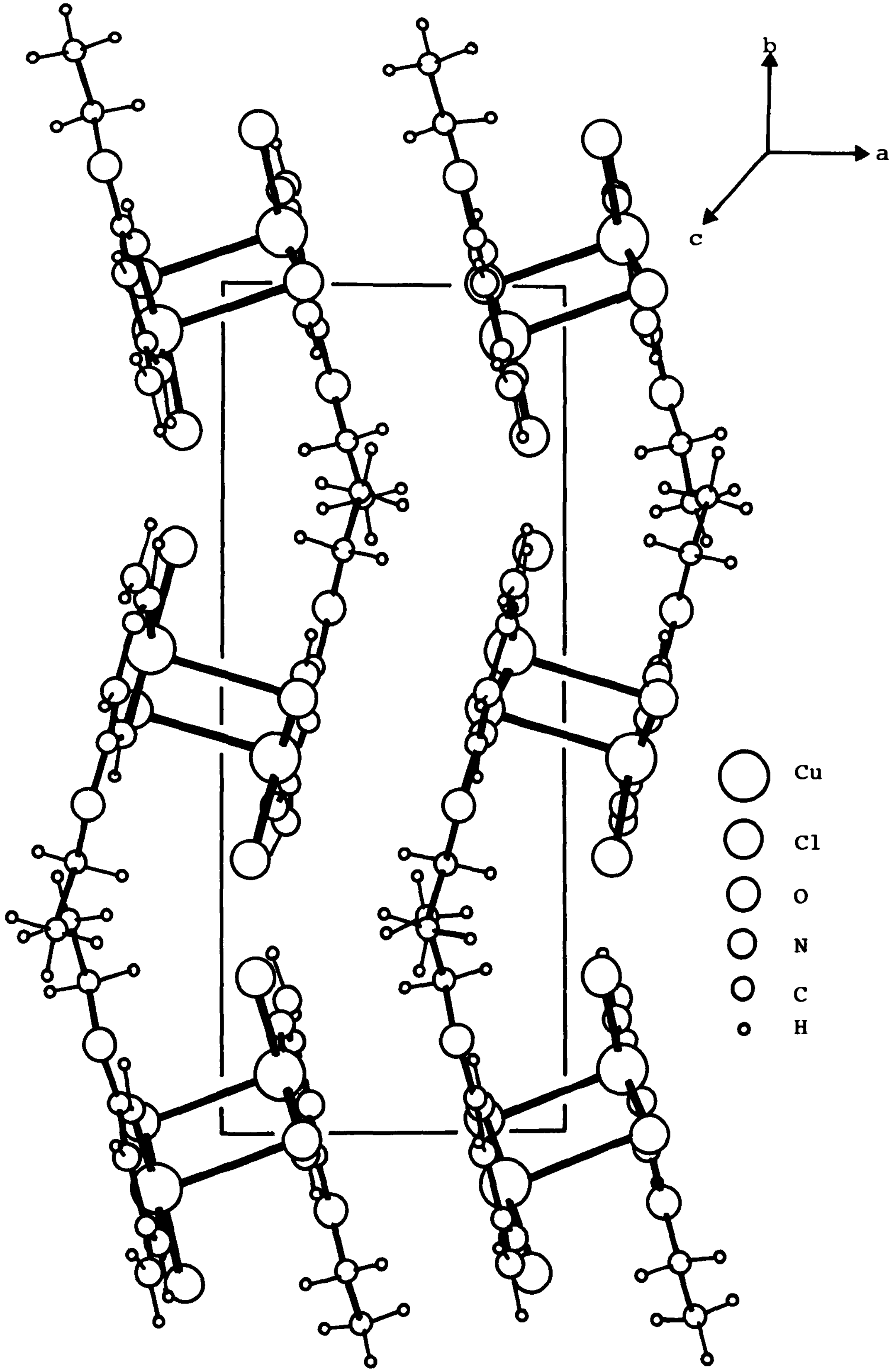


FIGURE 6.2 Projection of the structure of $[Cu(aOeu)Cl_2]_2$ onto the (001) plane

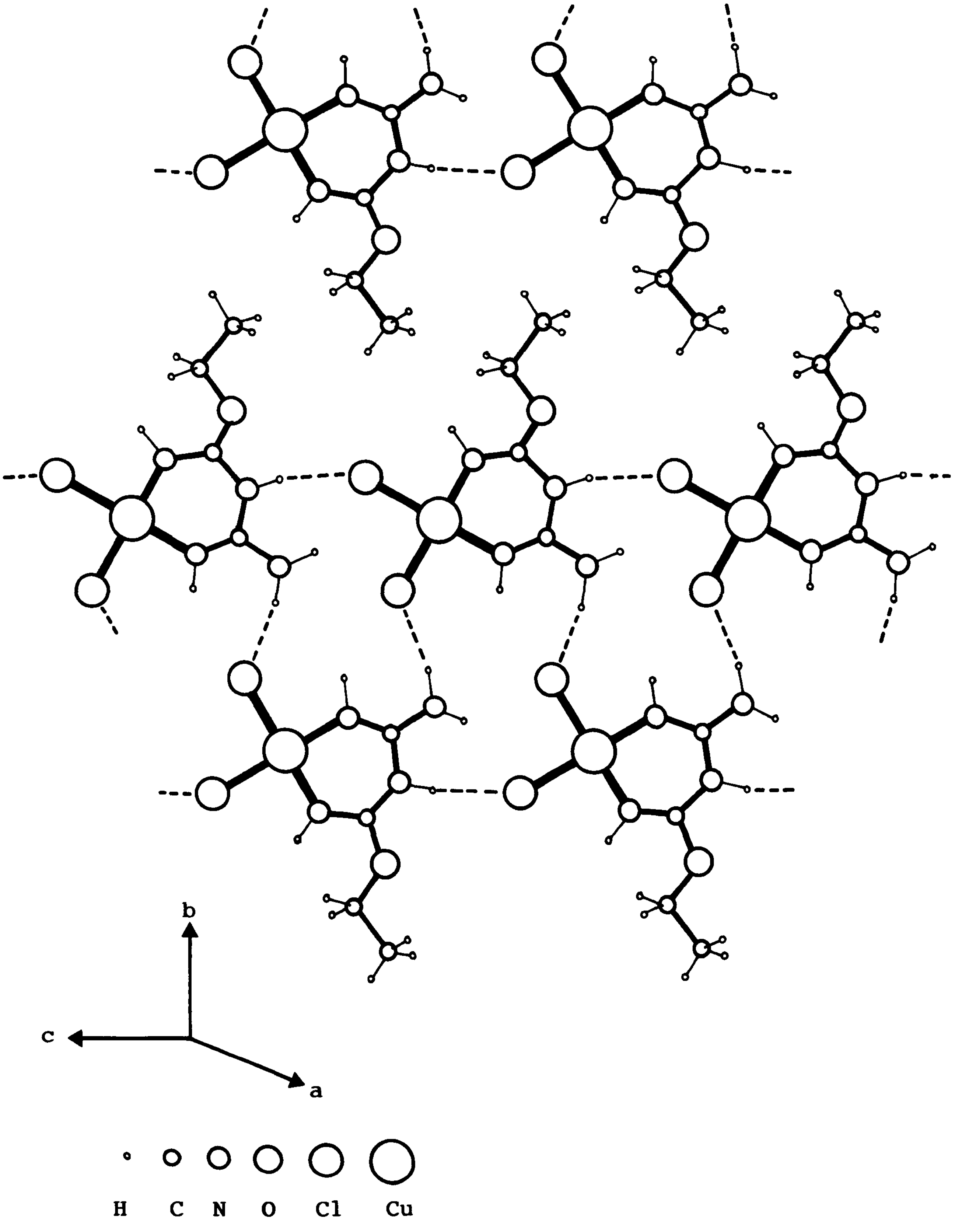


FIGURE 6.3 Projection of the structure of $[Cu(aOeu)Cl_2]_2$ onto the (100) plane

appropriate. The cationic fragments of the former complex are $\{[Cu(aOeu)_2]^{2+}.2H_2O\}$ units which form two sets of interlinked ribbons which lie parallel to (120) and ($\bar{1}$20) (Figure 6.4). The cationic fragments of the latter complex are $[Cu(aOeu)_2]^{2+}$ units and they form a set of planes parallel to (102) (Figure 6.6). In both fragments the copper(II) ion is coordinated by two centrosymmetric bidentate aOeu ligands with the water molecules in $\{[Cu(aOeu)_2]^{2+}.2H_2O\}$ being hydrogen bonded to pairs of ligating atoms of the two (aOeu) ligands (Figure 6.5).

TABLE 6.11 Planarity of the $\{[Cu(aOeu)_2]^{2+}.2H_2O\}$ fragment in $[Cu(aOeu)_2]Cl_22H_2O$ and of the $[Cu(aOeu)_2]^{2+}$ fragment in $[Cu(aOeu)_2]Br_2$

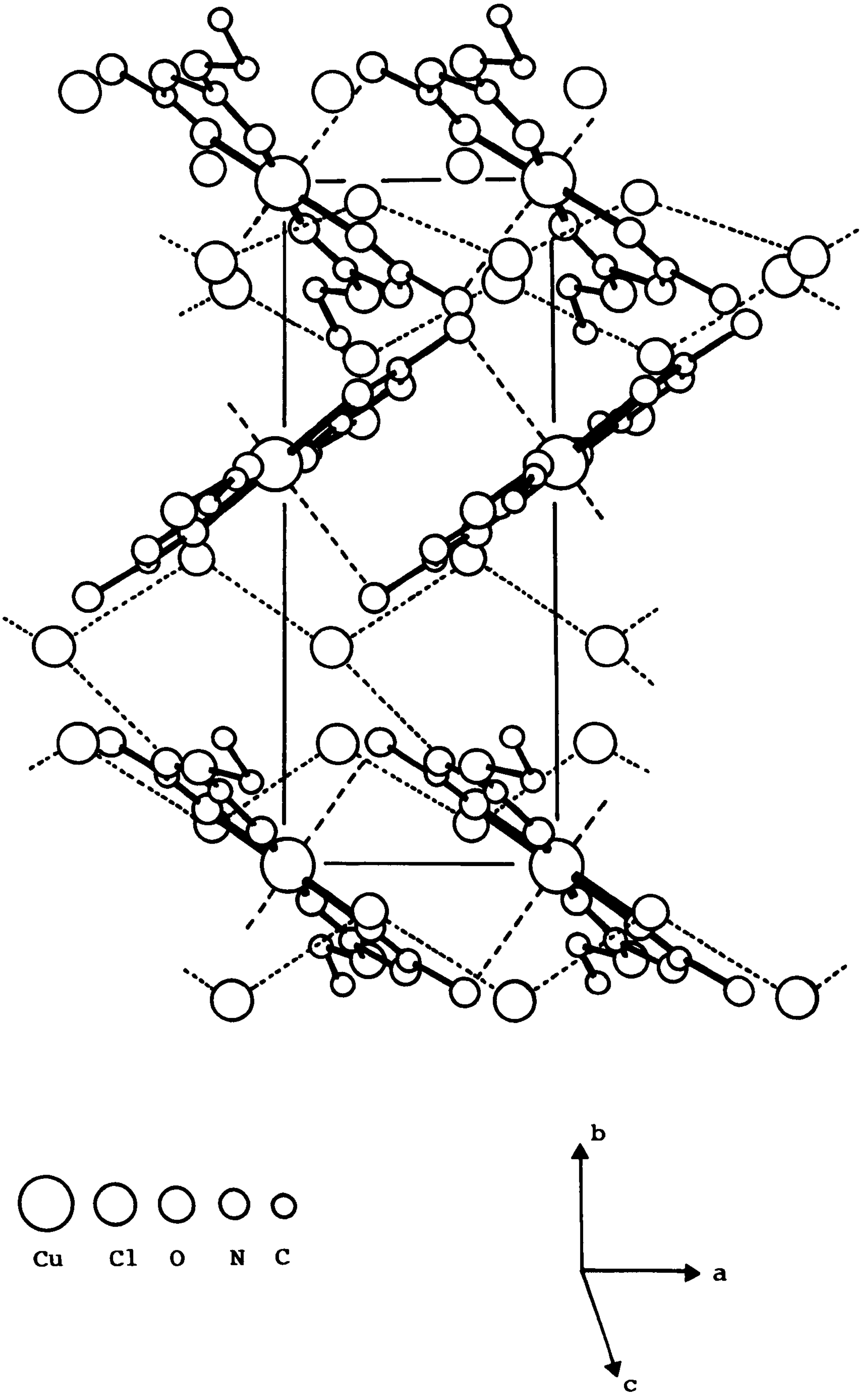
Atom	$\{[Cu(aOeu)_2]^{2+}2H_2O\}$ Deviation from plane/Å[b]	$[Cu(aOeu)_2]^{2+}$ Deviation from plane/Å[c]
Cu(1)	-0.084	-0.017
C(1)	-0.020	-0.011
C(2)	-0.038	-0.012
C(3)	0.060	0.018
C(4)	0.242	see footnote (a)
O(1)	-0.114	-0.005
N(1)	-0.002	0.005
N(2)	-0.087	0.043
N(3)	-0.066	-0.058
N(4)	-0.141	0.038
O(2)	0.250	-

(a) C(4) lies 1.339Å below the plane.

(b) Equation of best plane: $3.10780x+11.05139y-1.20068z = 0.084$

(c) Equation of best plane: $-3.27956x+0.19590y-9.00324z = 0.017$

FIGURE 6.4 Projection of the structure of $[Cu(aOeu)_2]Cl_2.2H_2O$ onto the (001) plane



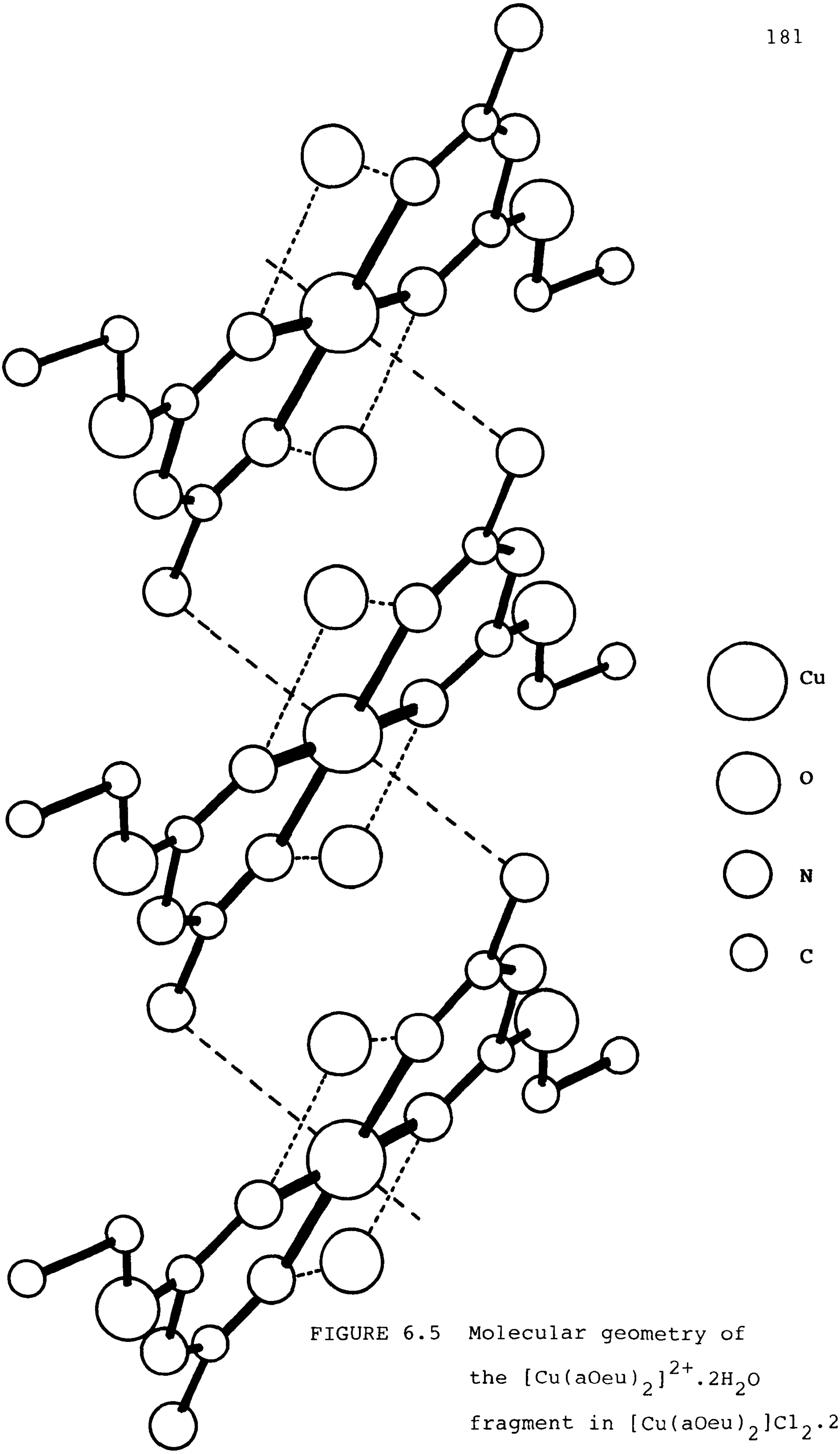


FIGURE 6.5 Molecular geometry of the $[Cu(aOeu)_2]^{2+}.2H_2O$ fragment in $[Cu(aOeu)_2]Cl_2.2H_2O$

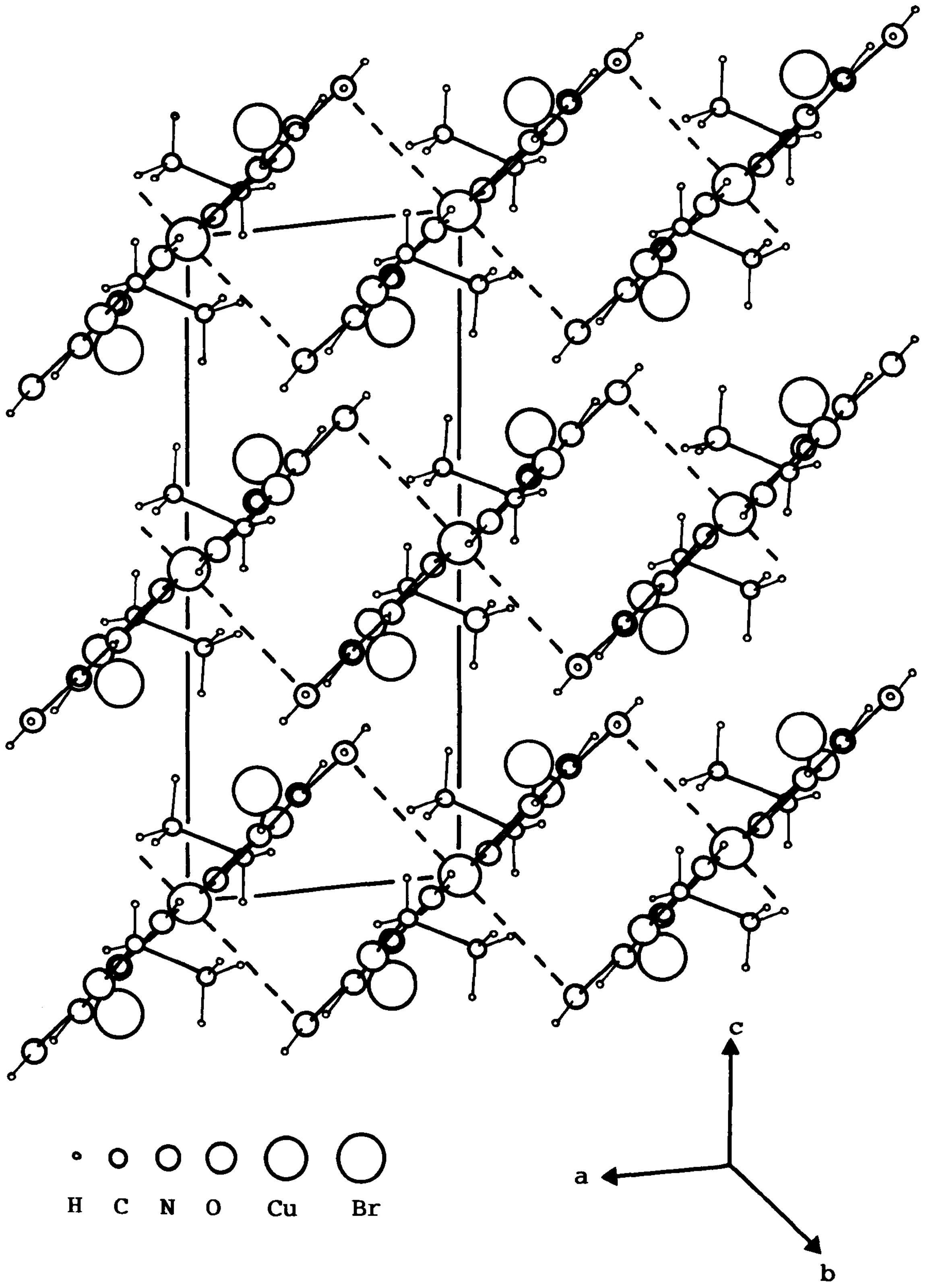


FIGURE 6.6 Projection of the structure of $[Cu(aOeu)_2Br_2$ onto the (010) plane

Whereas for $[Cu(aOeu)_2]Cl_2.2H_2O$ there is inter-ribbon hydrogen bonding between chlorine and either ligand nitrogen or water oxygen (Figure 6.4, Table 6.12), for $[Cu(aOeu)_2]Br_2$ hydrogen bonding only occurs between bromine and ligand nitrogen atoms within the planes. Full details of intermolecular bonding are given in Tables 6.12 and 6.13.

In both complexes the copper(II) ion is surrounded by four imine nitrogens, which lie at the corners of a square plane, of the two chelating aOeu ligands (Table 6.14; Figures 6.5 and 6.7).

TABLE 6.14 Coordination sphere of the Cu^{2+} cation for $[Cu(aOeu)_2]Cl_2.2H_2O$ and $[Cu(aOeu)_2]_2Br_2$; Bond distances/Å and angles/°

	$[Cu(aOeu)_2]Cl_2.2H_2O$	$[Cu(aOeu)_2]_2Br_2$
Cu(1)-N(1)	2.03(4)	1.926(4)
Cu(1)-N(4)	2.02(4)	1.972(4)
Cu(1)-N(2)'	3.11(3)	3.265(5)
N(1) Cu(1) N(4)	87(2)	88.8(2)
N(1) Cu(1) N(2)'	88(1)	86.3(2)
N(4) Cu(1) N(2)'	92(1)	100.1(2)
Cu(1) N(2)' C(1)'	93(1)	87.1(3)

Symmetry of N(2)' and C(1)' 1+x,y,z

By consideration of the structural data it can also be inferred that a bonding interaction, albeit weak, occurs between the copper(II) ion and two $[Cu(aOeu)_2]^{2+}$

TABLE 6.12 Intermolecular contacts of less than 3.30Å; Hydrogen bond and electrostatic interactions for $[Cu(aOeu)_2]Cl_2 2H_2O$

Interaction X...X'	Symmetry Properties of X'	r(X...X') Å	Angle °	
N(1)...O(2)	x,y,z	3.00	C(1)-N(1)-O(2)	122
			Cu(1)-N(1)-O(2)	106
N(3)...Cl(1)	x,½-y,½+z	3.14	C(1)-N(3)-Cl(1)	112
			C(2)-N(3)-Cl(1)	122
N(4)...O(2)	-x,-y,-z	3.08	C(2)-N(4)-O(2)	126
			Cu(1)-N(4)-O(2)	103
O(2)...Cl(1)	x,y,z	3.22	O(2)-Cl(1)-O(2)	114
O(2)...Cl(1)	1+x,y,z	3.10	Cl(1)-O(2)-Cl(1)	114

TABLE 6.13 Intermolecular contacts of less than 3.60Å; Hydrogen bond and electrostatic interactions for $[Cu(aOeu)_2]Br_2$

Interaction X-H...X'	Symmetry Properties of X'	r(X...X') Å	r(X-H) Å	r(H...X') Å	XHX' °
N(1)-H(1)...Br(1)	x-1,-y,z	3.395(4)	0.86(5)	2.55(5)	167(4)
N(2)-H(3)...Br(1)	-x,-½-y,½-z	3.445(5)	0.78(6)	2.73(5)	154(5)
N(3)-H(4)...Br(1)	-x,-½-y,½-z	3.329(4)	0.84(6)	2.51(6)	166(5)
N(4)-H(5)...Br(1)	1-x,y,z	3.6+	0.74(5)	3.02(5)	166(5)

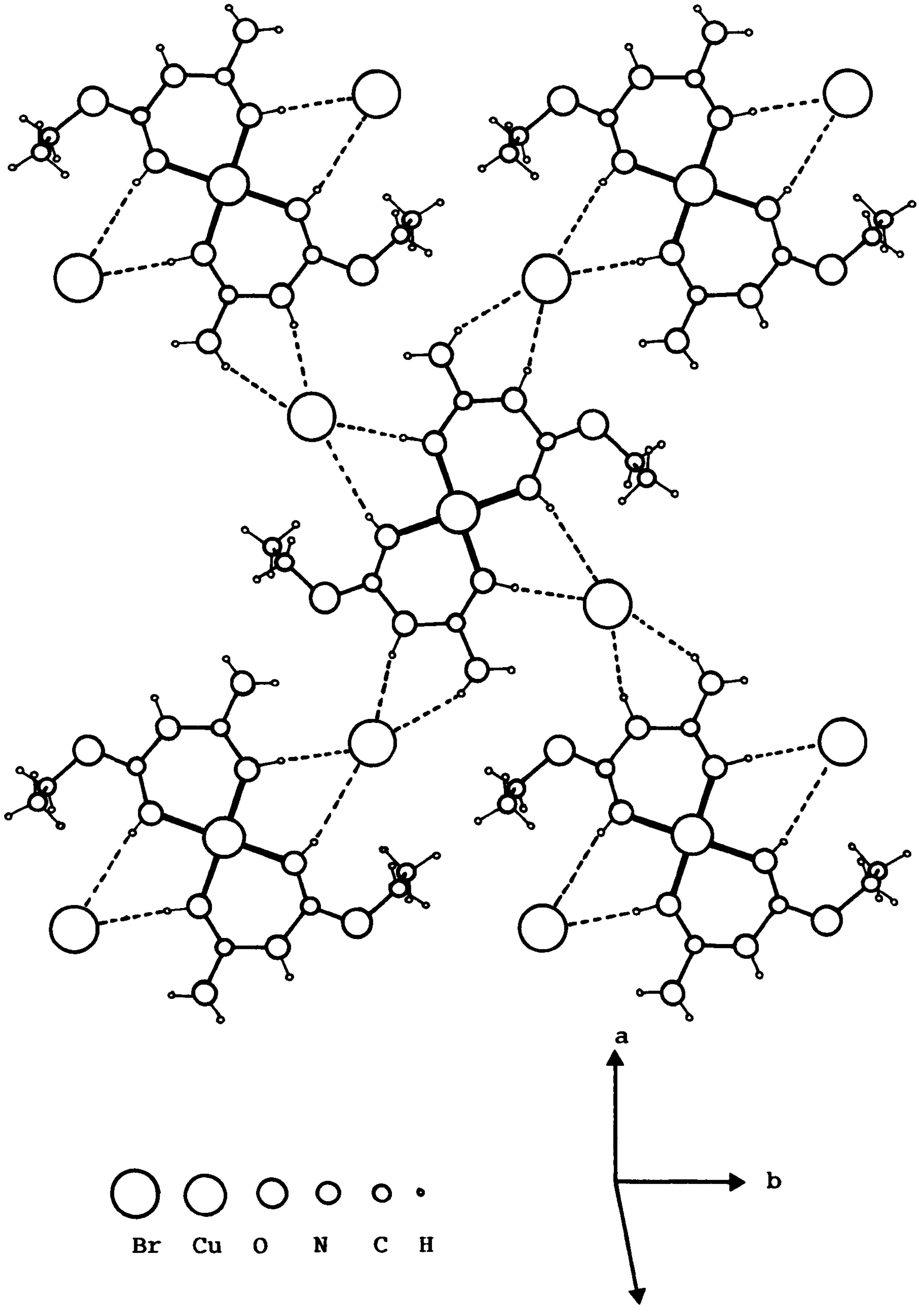


FIGURE 6.7 Projection of the structure of $[Cu(aOeu)_2]Br_2$ onto the (102) plane

fragments in adjacent ribbons, for$[Cu(aOeu)_2]Cl_2.2H_2O$, or planes, for $[Cu(aOeu)_2]Br_2$. The fragments are related by translations of $\pm a$ such that the terminal amine nitrogens N(2)' are located in the axial positions above and below the CuN_4 plane close to the limit of the copper(II) ions coordination sphere (Figures 6.5 and 6.6). Whereas for the chloride complex this contact [r(Cu(1)-N(2)') = 3.11Å] is only marginally greater than the sum (2.98Å) of Van der Waals radii for copper (1.43Å) and nitrogen (1.55Å) that in the bromide complex [r(Cu(1)-N(2)') = 3.265Å] is markedly larger. Evidence for an interaction arises from the location and electronic structure of the ligand. The amine nitrogen N(2)' can be considered to be sp^2 hybridised (see Section 6.3.5 for details) and lies in such a position {Cu(1)N(2)'C(1)' bond angle = 93° for $[Cu(aOeu)_2]Cl_2.2H_2O$ or 87.1° for $[Cu(aOeu)_2]Br_2$} that its $2p_z$ orbital, and hence a lone pair of electrons, can be directed towards the copper(II) ion.

The coordination geometry around the copper(II) ion in both the chloride and bromide complexes could be described as either a square plane or an axially distorted octahedron, both of which are typical of d^9 systems. The tetragonal distortion parameters (0.65 and 0.58 respectively), however, lie within the range (0.66-0.56) allocated to square coplanar complexes.[59] Similar tetragonal distortion parameters (0.62; 0.64) are found for analogous complex $[Cu(aebg)(cnge)]SO_4.H_2O$ (aebg = 1-(2-aminoethyl)biguanide)[40] in which the copper(II) ion is situated in a CuN_4 square planar chromophore derived from three nitrogen atoms of the tridentate aebg ligand [r(Cu-N) = 1.93, 1.93, 2.01Å] and the nitrile nitrogen atom of cnge [r(Cu-N) = 1.96Å]. Remotely located in the axial positions of the CuN_4 chromophore are the nitrile [r(Cu-N) = 3.06Å] and imine [r(Cu-N) = 3.14Å] nitrogen atoms of cnge molecules in adjacent complexes. As in the present complexs, the ligands providing the axial ligating atoms lie parallel to the square plane of the copper(II) ions coordination sphere.

6.3.5 Molecular geometry of the aOeu ligand in $[Cu(aOeu)Cl_2]$, $[Cu(aOeu)_2]Cl_2.2H_2O$ and $[Cu(aOeu)_2]Br_2$

In all three complexes the bidentate aOeu ligand chelates the copper(II) ion adopting the di-imine tautomeric form 6.5. The C-N and C-O bond distances, which are intermediate between single and double bonds, the NCN, CNC and NCO bond angles, which are close to 120° (Table 6.15), and the planarity of the skeletal atoms C(1), C(2), N(1), N(2), N(3), N(4) and O(1) (Table 6.16) infer sp^2 hybridisation of, and the presence of a delocalised π-system over, the ligand excluding the ethyl moiety.

Whereas both the carbon atoms of the ethyl moiety, C(3) and C(4), are effectively coplanar with the other skeletal atoms of the ligand for the two chloro complexes the terminal ethyl carbon atom, C(4), of the ligand in the

TABLE 6.15 Geometry of the aOeu ligand in $[Cu(aOeu)Cl_2]_2$, $[Cu(aOeu)_2]Cl_2.2H_2O$ and $[Cu(aOeu)_2]Br_2$; bond distances/Å and angles/°

	$[Cu(aOeu)Cl_2]_2$	$[Cu(aOeu)_2]Cl_2.2H_2O$	$[Cu(aOeu)_2]Br_2$
C(1)-N(1)	1.30(2)	1.20(5)	1.288(6)
C(1)-N(2)	1.32(2)	1.38(5)	1.337(6)
C(1)-N(3)	1.37(2)	1.35(5)	1.362(6)
C(2)-N(3)	1.36(2)	1.54(5)	1.371(6)
C(2)-N(4)	1.28(2)	1.21(5)	1.269(6)
C(2)-O(1)	1.34(2)	1.26(5)	1.319(5)
C(3)-O(1)	1.44(2)	1.50(5)	1.458(6)
C(3)-C(4)	1.51(2)	1.53(7)	1.481(8)
N(1) C(1) N(2)	123(1)	128(4)	124.0(4)
N(1) C(1) N(3)	122(1)	123(4)	122.0(4)
N(2) C(1) N(3)	115(1)	109(4)	114.1(4)
C(1) N(3) C(2)	126(1)	126(4)	127.5(4)
N(3) C(2) N(4)	124(1)	121(4)	122.9(4)
N(3) C(2) O(1)	110(1)	105(3)	108.8(4)
N(4) C(2) O(1)	126(1)	133(4)	128.4(4)
C(2) O(1) C(3)	117(1)	114(3)	119.1(4)
O(1) C(3) C(4)	107(1)	106(4)	111.0(4)

bromide complex lies 1.341Å below the plane of the other skeletal atoms (Table 6.16). This anomally in conformation about the O(1)-C(3) bond is presumably a manifestation of the location of the stereochemically bulky bromide anion and the minimization of interactions between the ethyl moiety and the anion.

TABLE 6.16 Planarities of the aOeu ligand in $[Cu(aOeu)Cl_2]_2$, $[Cu(aOeu)_2]Cl_2.2H_2O$ and $[Cu(aOeu)_2Br_2$

Atom	$[Cu(aOeu)Cl_2]_2$ Deviation from Plane/Å[b]	$[Cu(aOeu)_2]Cl_2.2H_2O$ Deviation from Plane/Å[c]	$[Cu(aOeu)_2Br_2$ Deviation from Plane/Å[d]
C(1)	-0.003	0.053	-0.013
C(2)	-0.004	-0.017	-0.014
C(3)	0.028	0.013	0.019
C(4)	-0.008	0.128	see footnote (a)
O(1)	-0.012	-0.148	0.000
N(1)	0.006	0.009	-0.009
N(2)	0.005	-0.029	0.049
N(3)	0.001	-0.043	-0.056
N(4)	-0.012	-0.075	0.024

(a) C(4) lies 1.341Å below the plane
(b) Equation of best plane: $6.4764x-4.14202y+0.60884z = -0.392$
(c) Equation of best plane: $3.19713x+10.180675y-1.66831z = 0.066$
(d) Equation of best plane: $-3.31213x+0.15246y-8.93169z = 0.043$

As noted in Section 6.3.4 for $[Cu(aOeu)_2]Cl_2.2H_2O$ and $[Cu(aOeu)_2]Br_2$ a weak bonding interaction may occur between the amine nitrogens, N(2)', of two translationally related $[Cu(aOeu)_2]^{2+}$ fragments and the copper(II) ion. Such an interaction would be expected to result in a reduction of the electron density of the π-system over the N(2)'-C(1)' bond and hence in a lengthening of the bond. Unfortunately, the poor quality of data precludes such an analysis for $[Cu(aOeu)_2]Cl_2.2H_2O$ and it seems that the interaction in $[Cu(aOeu)_2]Br_2$ is so weak that it has no marked effect on the N(2)-C(1) bond length in comparison with that in $[Cu(aOeu)Cl_2]_2$.

The coordination geometry of aOeu is consistent with those of coordinated biguanide (bg)[21] and ethylenediaminebiguanide (edbg),[66] all three ligands forming $\overline{\text{Cu-NH=C(R)-NH-C(R)=N}}\text{H}$ chelate rings. The formation of bridging C-NH-C fragments, C=N-C bridges existing in the free molecules, leads to a decrease in the π character of the bridging C-N bonds and an increase in that of the terminal C-N bonds. These changes, which also occur for 1-carbamoylguanidine (clge; see Chapters Three and Four for detailed discussion) are manifest in shorter terminal than bridging C-N bonds. Comparison of data for aOeu, bg, edbg and clge coordinated to copper(II) is effected in Table 6.17.

TABLE 6.17 Significant features of the molecular geometries of aOeu, bg, edbg and clge coordinated to copper(II)

Ligand	Free Molecule		Coordinated to Copper(II)	
	Average $r(C-N_{bridge})$ /Å	Average $r(C-N_{terminal})$ /Å[c]	Average $r(C-N_{bridge})$ /Å	Average $r(C-N_{terminal})$ /Å[c]
aOeu[a]	-	-	1.365	1.320
aOeu[b]	-	-	1.367	1.337
bg[13,21]	1.356	1.358	1.374	1.349
edbg[66]	-	-	1.410	1.372
clge	1.352	1.348	1.370	1.315

(a) For $[Cu(aOeu)Cl_2]_2$

(b) For $[Cu(aOeu)_2]Br_2$

(c) This average does not include those contacts formally defined as double bonds between carbon and terminal imine groups.

6.4 Spectroscopic Properties

6.4.1 Vibrational spectra

As has been shown in previous chapters, extensive mixing of internal coordinates occurs in molecules with planar skeletons making assignment of the vibrational spectra difficult. However, the spectra are of value in distinguishing between the compounds examined in this chapter. Where possible approximate assignments have been made by comparison with structurally similar molecules described in earlier chapters.

The infrared spectra are collated numerically in Table 6.18. The most striking feature of the spectra which first distinguished aOeu complexes from those of cnge was the absence of absorptions in the 2300-2000cm^{-1} region and the presence of absorptions in the 2990-2980cm^{-1} region. The absorptions in the former region would be attributable for cnge to nitrile stretching vibrations whilst those in the second region arise from the stretching vibrations of the C-H bonds in the ethyl moiety of aOeu.

The stretching and bending vibrations of N-H bonds ν[NH] and δ[NH] will give rise to absorptions in the 3500-3000cm^{-1} and 1700-1500cm^{-1} regions. All the compounds exhibit several overlapping bands in both regions (Figures 6.8 and 6.9). For $[Cu(aOeu)_2]Cl_2$, its dihydrate and [aOeuH]Cl the bands in the first region are broad and poorly defined whilst for $[Cu(aOeu)Cl_2]_2$, $[Cu(aOeu)_2]Br_2$ and $Cu[aOeu]_2$ they are more highly

TABLE 6.18

TABLE 6.18 Infrared spectroscopic data/cm^{-1} for copper(II)

$[Cu(aOeu)Cl_2]_2$		$[Cu(aOeu)_2]Cl_2$ and $[Cu(aOeu)_2]Cl_2.2H_2O$		$[Cu(aOeu)_2]Br_2$	
				3420	ms,br
3380	s	3390	ms,br		
3350	ms	3325		3285	
3305					
3260		3205		3190	
3220	m			3030	
3185					
2980	mw	2985	m	2990	m
1665	s	1670	s	1670	s,br
1650		1630	m	1645	s
				1615	ms
1550	ms	1560	m	1560	ms
1495	m	1480	mw	1465	m
1460	m	1465		1440	
1390	mw	1390	mw	1400	
1375					
1340	ms			1345	m
		1275	mw	1275	ms
1230	w	1210	ms	1205	s
1180	ms	1125	mw	1120	m
1115	mw				
		1015	w	1080	mw
1025	mw	1015	w	995	m
980	w	980	w	980	
880	mw	880	mw	870	w
		860	sh		
790	m	790	mw	810	m
755	m	750	sh	760	m
730	ms	735		730	
695	mw			700	mw,br
640	w,br				
560	mw	570	w,br		
530		525	mw	525	mw
505		505	w	495	
405	w	475	mw,br	450	br

(aOeu) complexes and [aOeuH]Cl

$Cu[aOeu]_2$		[aOeuH]Cl		Assignment
3480	ms			
3370		3350	s,br	
3340	m	3300sh		ν[NH]
3260				
		3180		
2980mw		2980m		ν[CH]
		1640	s,br	
1625	s	1620		δ[NH]
1580		1575s		
1520	s,br	1520s,br		
		1480ms		
1445		1430m		ν[NCN]
1380ms		1385m		
				ν[C-N-C]
1350ms		1340ms		
1260s				ν[N-O-C]
1212mw				
1125mw	sh			
1110m				
1090s		1090ms,br		ν[C-C]
1025m				
		935w		
890	mw			
825				
800		845w		$\gamma[NH_2]$
770	mw			
735		740mw		
705				
680mw		595	m	γ[CH]
610mw		565		
		515		
505mw,br				
400w,br		455mw		

FIGURE 6.8 Comparison of the ir spectra (3500-2800cm^{-1}) for copper(II)-(aOeu) and copper-[aOeu] complexes and [aOeuH]Cl

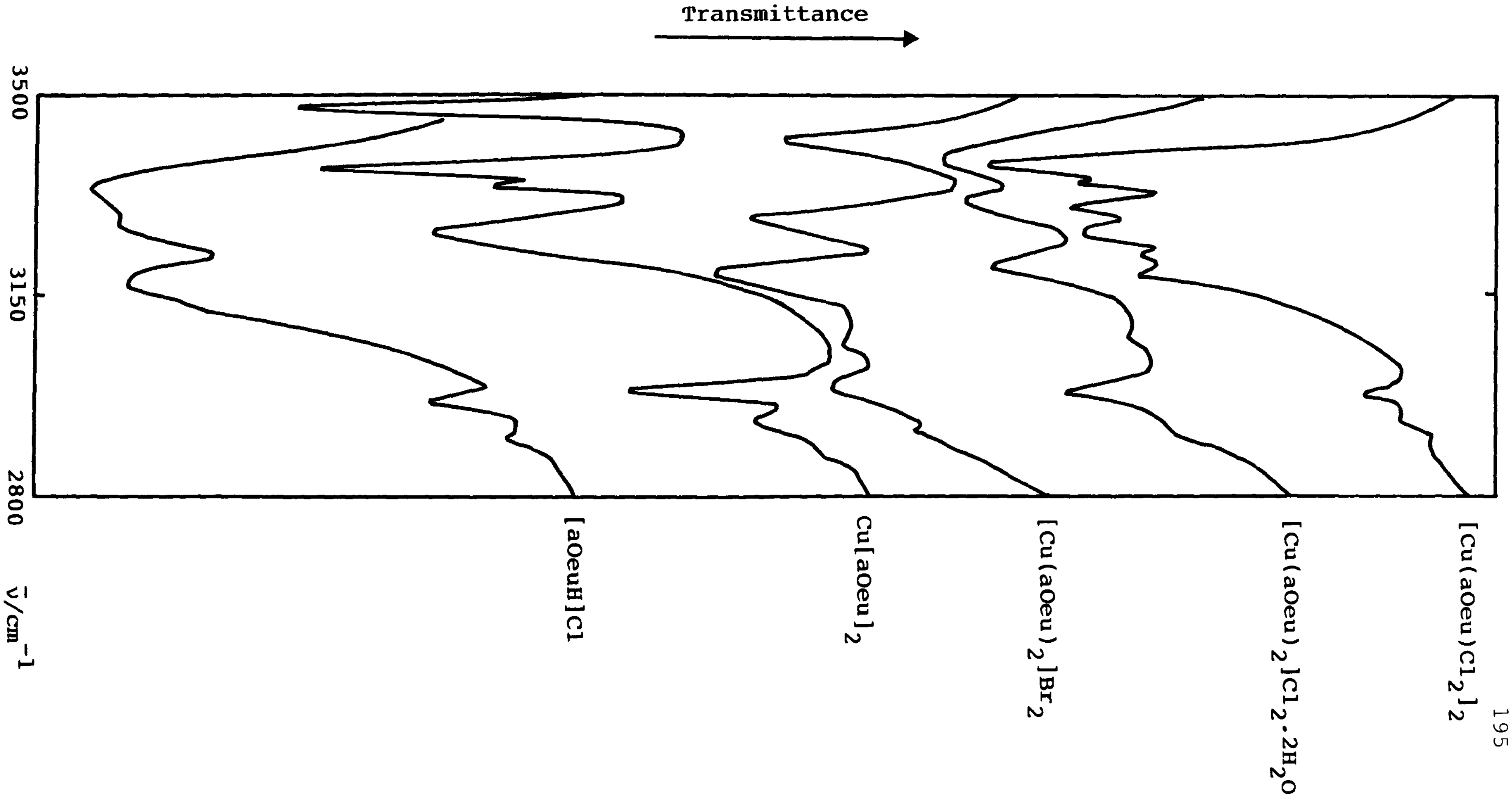
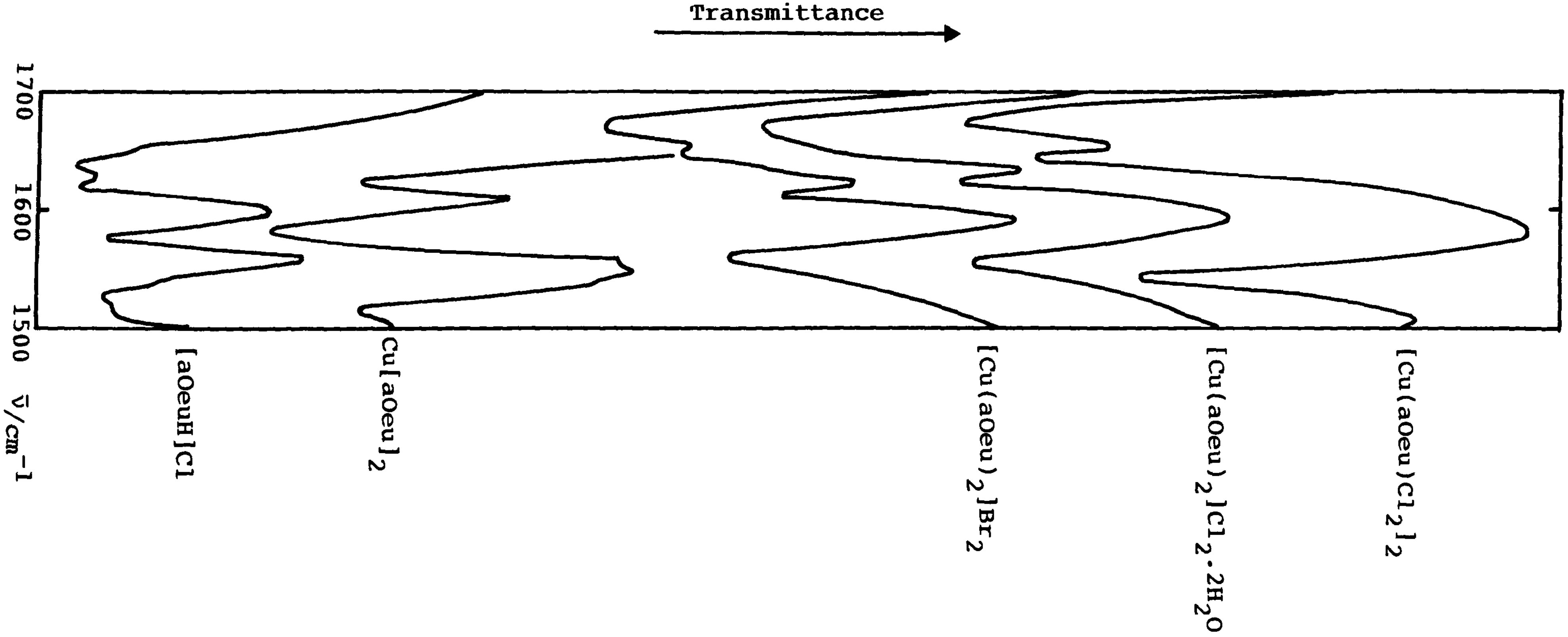


FIGURE 6.9 Comparison of the ir spectra (1700-1500cm^{-1}) for copper(II)-(aOeu) and copper(II)-[aOeu] complexes and [aOeuH]Cl



resolved. In the second region all the compounds exhibit similar resolution but only Cu[aOeu]$_2$ has one band at wavenumbers greater than 1600cm^{-1} whilst all the others have at least two. These difficulties are very difficult to explain in the absence of structural data for all the compounds, however, it is likely that the level of hydrogen bonding and the tautomeric form adopted by the various aOeu moieties will influence the nature of these absorptions. For example, the well resolved band in the ν[NH] absorption region of the spectra of [Cu(aOeu)Cl$_2$]$_2$ and [Cu(aOeu)$_2$]Br$_2$ is consistent with the presence of localised N-H bonds (Tables 6.10 and 6.13).

The number and complexity of the absorptions occurring at lower than 1500cm^{-1} precludes any useful analysis of the spectra in this region. These absorptions are only useful in fingerprinting each compound. It must be noted, however, that the spectra of [Cu(aOeu)$_2$]Cl$_2$ and its dihydrate were identical and cannot be used to distinguish between these complexes.

6.4.2 UV-Visible Spectra

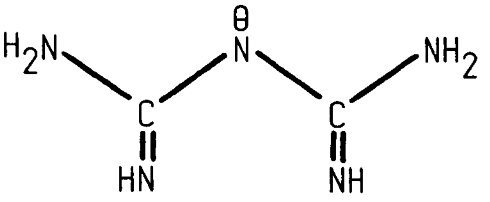
All the complexes give rise to broad absorptions in the visible region which can be used to distinguish complexes with a 1:1 ratio from those with a 1:2 ratio of copper:aOeu. The former class of complexes {[Cu(aOeu)Cl$_2$]$_2$ and Cu(aOeu)Br$_2$.2H$_2$O} give absorptions with a λ_{max} 650-660nm whilst the latter class of complexes {[Cu(aOeu)$_2$]Cl$_2$, its dihydrate, [Cu(aOeu)$_2$]Br$_2$ and

$Cu[aoeu]_2\}$ give absorptions with λ_{max} = 515-540nm (Table 6.1).

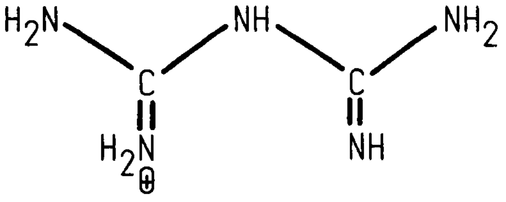
The similarity of the absorptions within each class of compounds suggest similar chromophores. Hence, the copper(II) ion of $Cu(aOeu)Br_2.2H_2O$ may have a square based pyramidal coordination sphere analogous to that of $[Cu(aOeu)Cl_2]$ with bromine atoms in place of chlorine atoms, the water molecules probably occurring as water of crystallization. Also the copper(II) ion of $Cu(aOeu)_2Cl_2$ and $Cu[aOeu]_2$ is likely to have a square planar or highly tetragonally distorted octahedral coordination sphere nearly identical to those found in $[Cu(aOeu)_2]Cl_2.2H_2O$ and $[Cu(aOeu)_2]Br_2$.

6.5 **The Bonding in $Cu[aOeu]_2$ and $[aOeuH]Cl$**

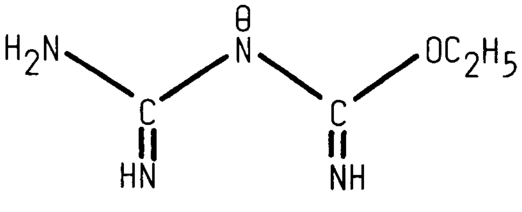
The tautomeric form adopted by the aOeu ligand (6.5) parallels that of the biguanide ligand (6.6). Therefore, it is logical to assume that the tautomeric forms adopted by the anion $[aOeu]^-$ and cation $[aOeuH]^+$ will mirror those of their structurally characterised biguanide equivalents $[bg]^-$ (6.7) and $[bgH]^+$ (6.8). Hence the most probable tautomers for $[aOeu]^-$ and $[aOeuH]^+$ are forms 6.9 and 6.10 respectively.



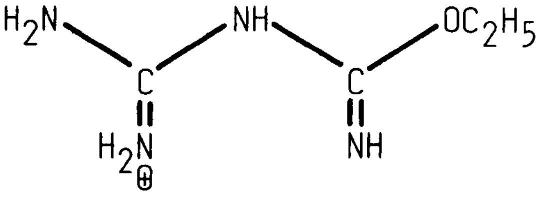
6.7



6.8



6.9



6.10

Evidence for the former correlation may be derived from the similarity of the UV-visible spectra of Cu[aOeu]$_2$ and Cu[bg]$_2$.2H$_2$O. Both complexes exhibit a single broad absorption band centred at 480nm (for Cu[aOeu]$_2$) and at 500nm (for Cu[bg]$_2$.2H$_2$O) confirming the presence of CuN$_4$ chromophores (Section 5.3). This is entirely consistent with the [aOeu]$^-$ ligand adopting tautomeric form 6.9.

CHAPTER SEVEN

THE COPPER(II)CHLORIDE-1-CYANOGUANIDINE-ETHANOL SYSTEM: AN INFRARED SPECTROSCOPIC STUDY

7.1 Introduction

X-ray diffraction studies of the complexes that can be isolated after various time periods and under different conditions from the copper(II)halide-cnge-ethanol system, have shown them to be copper(II)(aOeu)$_n$X$_2$ (where aOeu = 1-amidino-O-ethylurea; n = 1,2; X = Cl,Br) complexes. Copper(II)-cnge complexes were not isolated (Chapter Six). The nature of the species in solution and the reaction mechanisms for such a system have not been examined.

This Chapter describes the use of solution infrared spectroscopy in an investigation of the $CuCl_2$-cnge-EtOH system.

This technique was chosen by analogy to the solid state studies of copper(II)-cnge and copper(II)-aOeu complexes (Sections 2.6 and 6.4 respectively). Although the spectrum of the former complexes showed infrared to be effective in detecting coordination of cnge, those of the latter complexes gave only 'fingerprint' absorptions characteristic of each complex studied.

Unfortunately, ethanol is a poor solvent for infrared spectroscopy as it has many strong and broad absorptions in the 4000 to 400cm^{-1} region (Figure 7.1, n.b. the spectrum is of a liquid film) which could mask

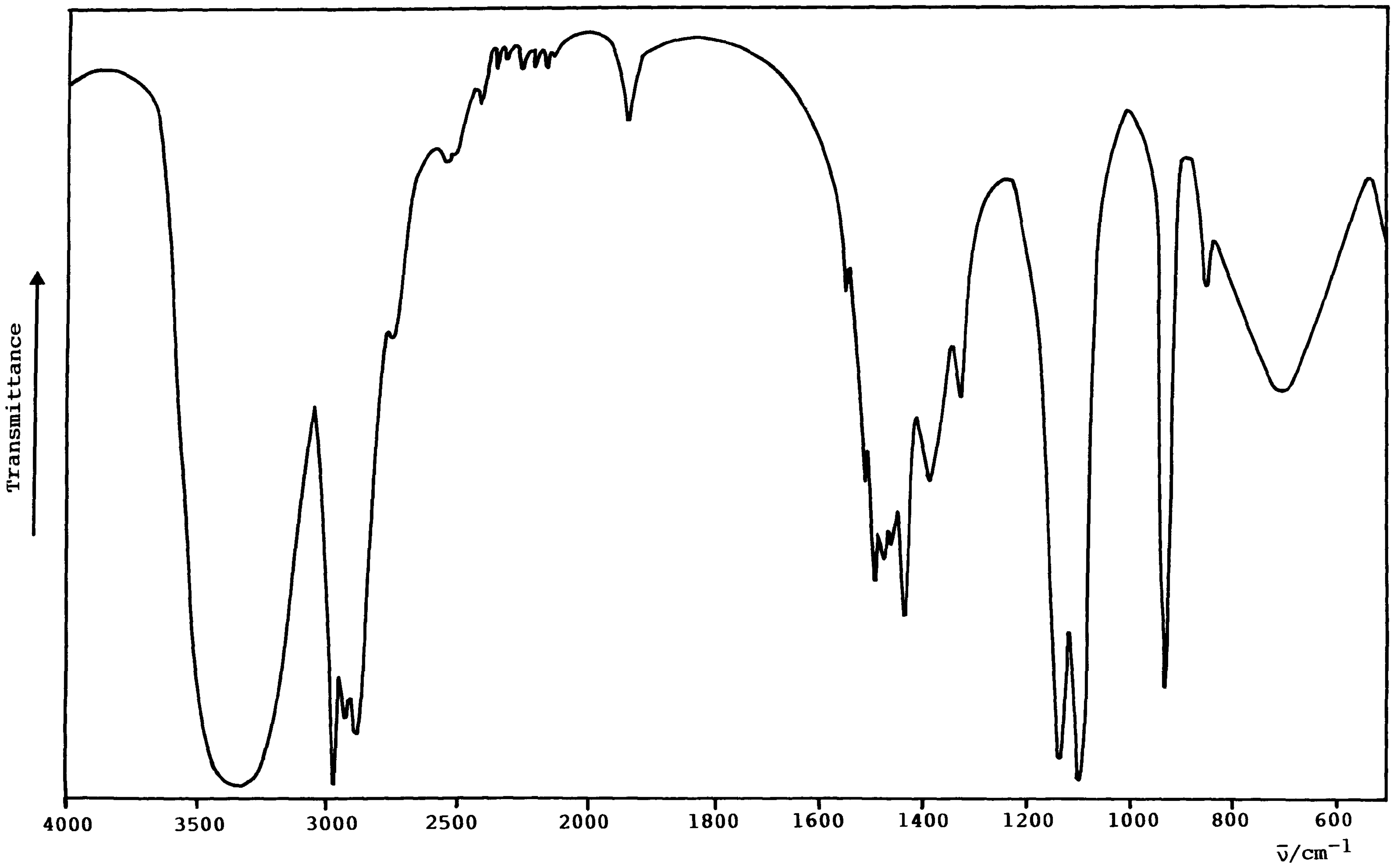


FIGURE 7.1 IR spectrum (4000-400 cm^{-1}) of ethanol (liquid film sample)

solute absorptions. However, the 2300 to 1600cm^{-1} region is comparatively free of strong ethanol absorptions and offers a window in which solute absorptions may be observed. The solute bands can be enhanced by subtraction of the ethanol absorptions using computerised data handling techniques.

Figures 7.2, 7.3 and 7.4 illustrate the use of this technique for the enhancement of the absorptions due to cnge dissolved in ethanol. Figures 7.2 and 7.3 show the spectra (2300 to 1600cm^{-1}) of ethanol and a solution of cnge in ethanol respectively. Differencing these two spectra the absorptions due to cnge alone are obtained (Figure 7.4).

The ethanol absorptions are much more intense in Figures 7.2 and 7.3 than in Figure 7.1 due to the use of an infrared solution cell. This ensured a sufficient amount of the solute in the spectrometer beam to be detected (the samples had relatively low solubilities) but gave a longer path length through the ethanol than for the liquid film (Figure 7.1).

The difference spectra of $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $[Cu(aOeu)_2]Cl_2.2H_2O$ in ethanol solution have also been recorded (2300-1600cm^{-1}) and the changes in the difference spectrum of a 1:1 molar ratio of copper(II) chloride and cnge in ethanol have been monitored as a function of time.

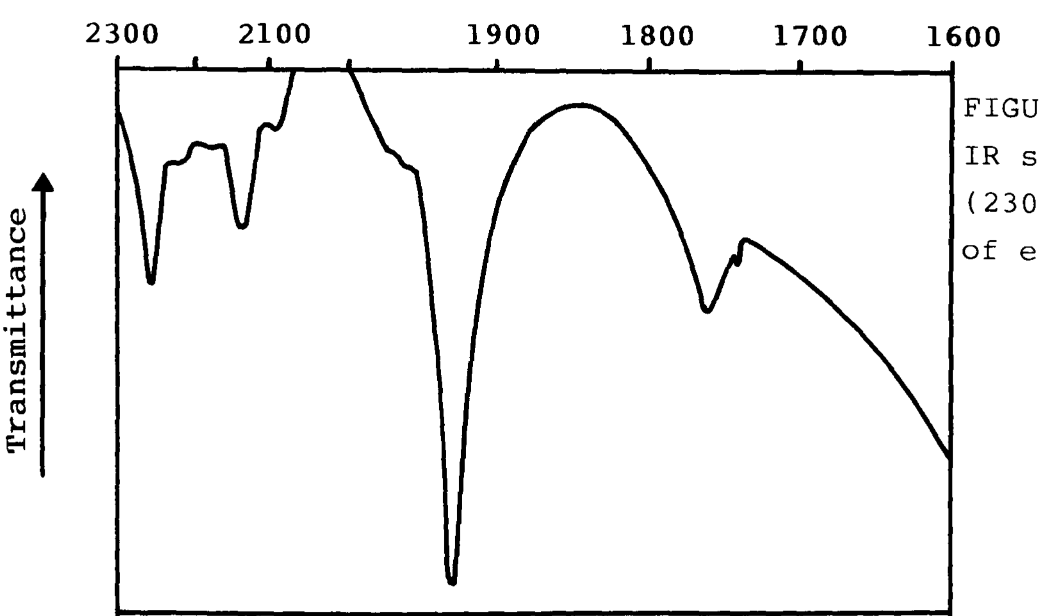


FIGURE 7.2
IR spectrum
(2300-1600cm^{-1})
of ethanol

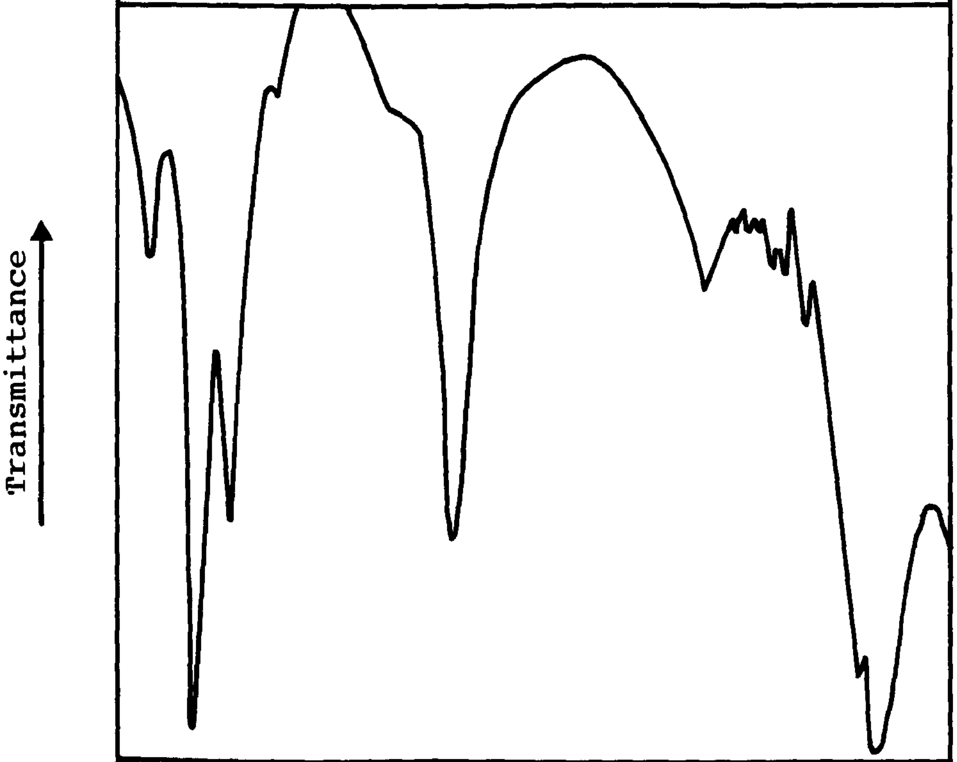


FIGURE 7.3
IR spectrum
(2300-1600cm^{-1})
of cnge in
ethanol
solution

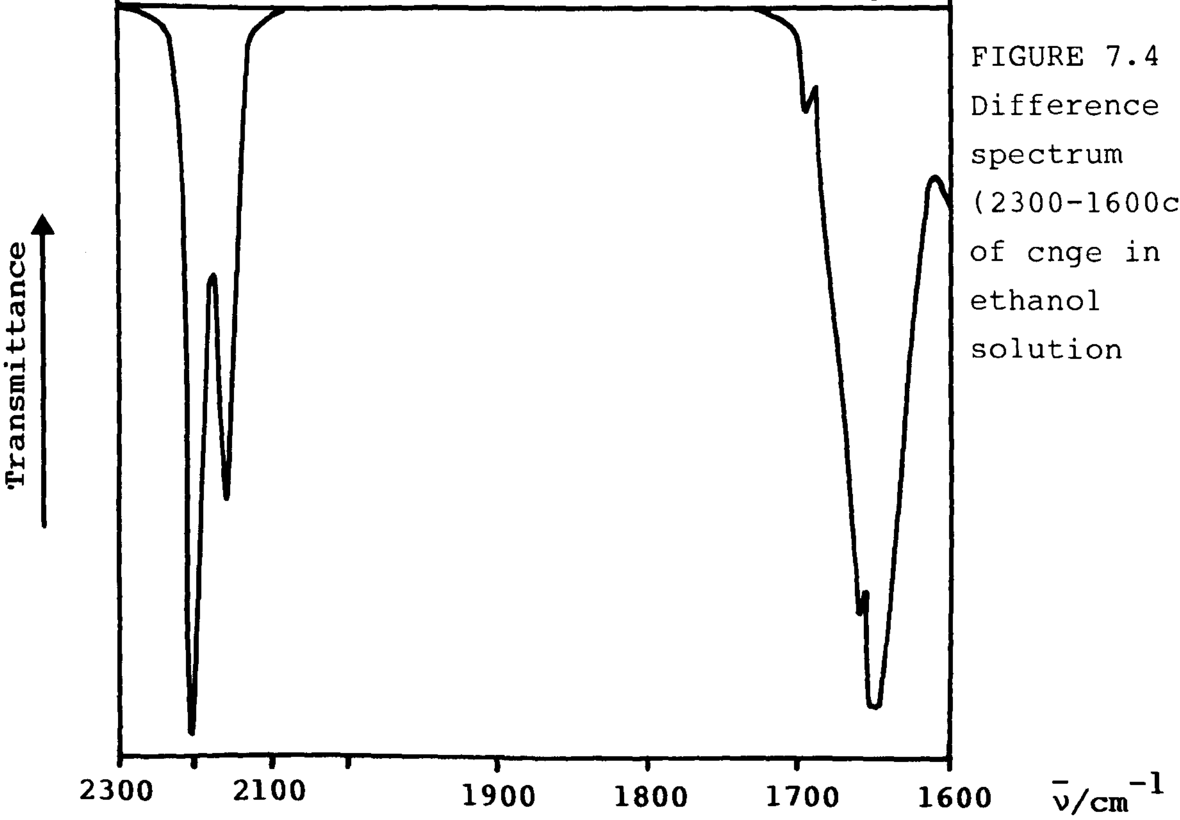


FIGURE 7.4
Difference ir
spectrum
(2300-1600cm^{-1})
of cnge in
ethanol
solution

7.2 Experimental

7.2.1 Infrared solution spectra

All infrared solution spectra (2300-1600cm^{-1}) were recorded using a Perkin Elmer PE680 grating instrument controlled by a PE3600 data station with PE 680 software.

An infrared solution cell (NaCl windows, 0.1mm path length) was filled with samples of ethanol and ethanol solutions of cnge (100mM), $[Cu(cnge)_2Cl_2(H_2O)_2]$ (10mM; freshly prepared) and $[Cu(aOeu)_2]Cl_2.2H_2O$ (5mM) and their spectra recorded. Between samples the cell was flushed with ethanol and dried with a flow of nitrogen gas. Bands due to ethanol were subtracted from the spectra of cnge and the two complexes.

7.2.2 Sequential infrared solution spectra

Aliquots (2cm^3) of ethanol solutions of copper(II) chloride (100mM) and cnge (100mM) were mixed and a sample of the resulting solution used to fill the infrared solution cell. Using an 'OBEY' programme (Appendix A) spectra were recorded at 2 hour intervals for 8 hours. The spectrum of ethanol was subtracted from each of these spectra. The experiment was carried out in duplicate.

7.3 Results and Discussion

7.3.1 Infrared solution spectra of cnge, $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $[Cu(aOeu)_2]Cl_2.2H_2O$ in ethanol

By analogy with solid state spectra, for cnge and its complexes, the bands expected to occur in the

2300-1600cm^{-1} window are a doublet in the 2300-2000cm^{-1} region and a single broad band in the 1700-1600cm^{-1} region. The doublet has been attributed to a Fermi interaction between the asymmetric nitrile stretch ν_a[N(1)C(1)N(2)] and a combination containing, or an overtone of, an N-H vibration. For brevity this doublet will be defined as ν_a(NCN)*. The doublet is particularly sensitive to coordination to copper(II), coordination resulting in a hypsochromic shift of ν_a(NCN)* (Section 2.6). The broad band has been assigned to the $\delta[NH_2]$ vibration and as such is less sensitive to coordination.

For copper(II)-aOeu complexes the solid state spectrum has not been rigorously assigned, however, absorptions characteristic of this ligand do occur in the 1700-1600cm^{-1} region (Section 6.4).

Examination of the 2300-2000cm^{-1} region of the difference spectra of cnge, $[Cu(cnge)_2Cl_2(H_2O)_2]$ and $[Cu(aOeu)_2]Cl_2.2H_2O$ in ethanol solution (Figures 7.4, 7.5 and 7.6 respectively) shows that cnge exhibits two absorptions at 2200 and 2157cm^{-1} whilst the cnge complex exhibits three bands at 2237, 2196 and 2155cm^{-1}. The aOeu complex shows no strong absorptions in this region.

The three absorptions in the solution spectrum of the copper(II)-cnge complex can be assigned to the overlapping of the two ν_a(NCN)* doublets of free and coordinated cnge. The lowest wavenumber absorption (2155cm^{-1}) and a proportion of the middle absorption (2196cm^{-1}) arise from free cnge ν_a(NCN)* absorptions

FIGURE 7.5 Difference ir spectrum (2300-1600cm^{-1}) of $[Cu(cnge)_2Cl_2(H_2O)_2]$ in ethanol solution

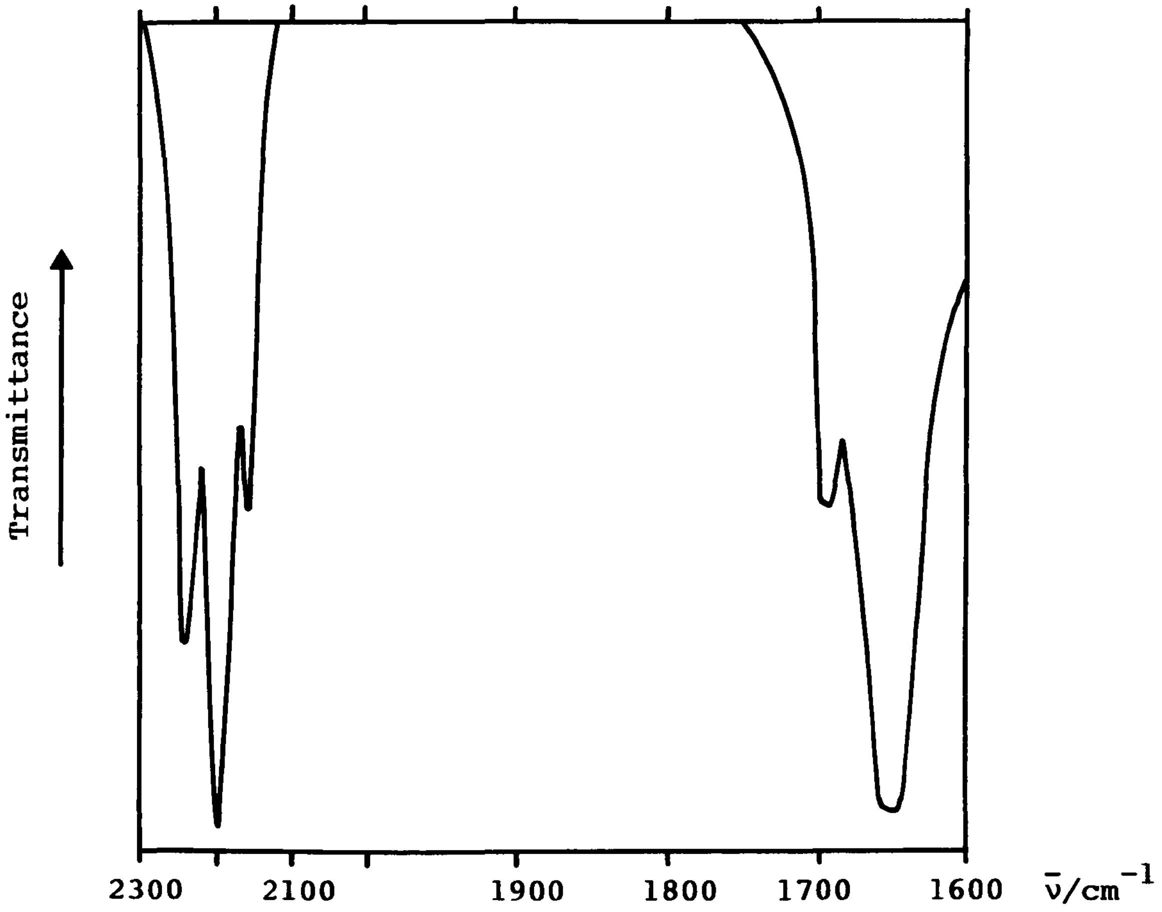
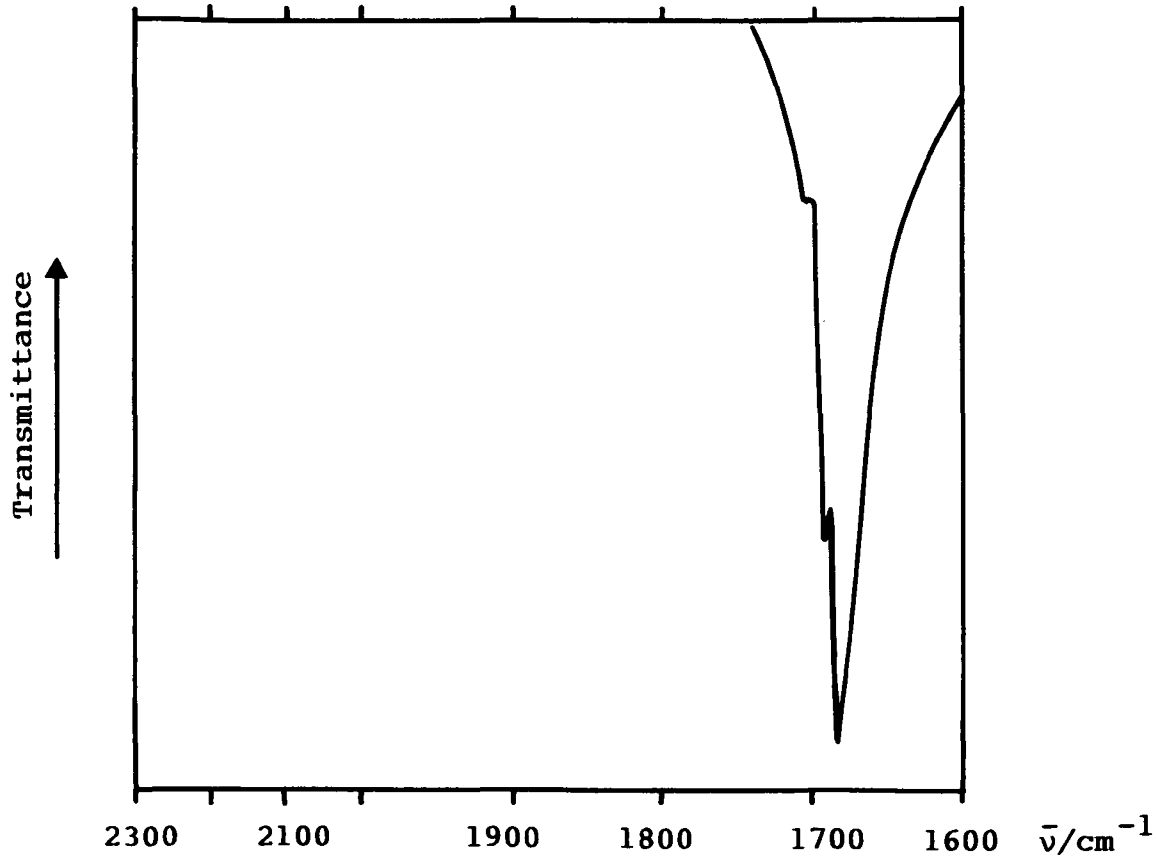


FIGURE 7.6 Difference ir spectrum (2300-1600cm^{-1}) of $[Cu(aOeu)_2]Cl_2.2H_2O$ in ethanol solution



(found at 2157 and 2200cm^{-1}) whilst the highest wavenumber absorptions (2236cm^{-1}) and a proportion of the middle absorption (2196cm^{-1}) arise from the ν_a(NCN)* absorption of coordinated cnge.

These data necessarily imply that some form of dissociation of the copper(II) complex has occurred in ethanol to give an equilibrium between free and coordinated cnge. Some possible equilibria are shown below (ligands other than cnge are omitted for clarity).

$$\mathrm{Cu(cnge)_2}^{2+} \xrightleftharpoons{\mathrm{EtOH}} \mathrm{Cu(cnge)}^{2+} + \mathrm{cnge}$$

$$\mathrm{Cu(cnge)}^{2+} \xrightleftharpoons{\mathrm{EtOH}} \mathrm{Cu}^{2+} + \mathrm{cnge}$$

$$\mathrm{2Cu(cnge)_2}^{2+} \xrightleftharpoons{\mathrm{EtOH}} \mathrm{Cu(cnge)}^{2+} + \mathrm{Cu}^{2+} + \mathrm{3cnge}$$

Although from these data it is not possible to distinguish between the various equilibria, it is clear that the dissociation is quite significant from the similar intensities of the 2236 and 2155cm^{-1} absorptions. Unfortunately, quantitative analysis of the spectra cannot be affected as it is not possible to obtain an ethanol solution spectrum of coordinated cnge alone owing to the existence of the equilibria.

There are significant differences in the solution spectra of cnge, $[\mathrm{Cu(cnge)_2Cl_2(H_2O)_2}]$ and $[\mathrm{Cu(aOeu)_2]Cl_2 \cdot 2H_2O}$

in the 1700 to 1600cm^{-1} region (Figures 7.4, 7.5 and 7.6 respectively).

Both cnge and its copper(II) complex exhibit bands at 1650cm^{-1}. That in the spectrum of the complex, however, is broader, an assumed manifestation of coordination to copper(II).

The spectrum of $[Cu(aOeu)_2]Cl_2.2H_2O$ exhibits only one band at 1683cm^{-1}. It is much sharper than those of cnge and its complex in this region and hence it would be possible to observe the formation of copper(II)-aOeu complexes from an ethanol solution containing copper(II) chloride and cnge.

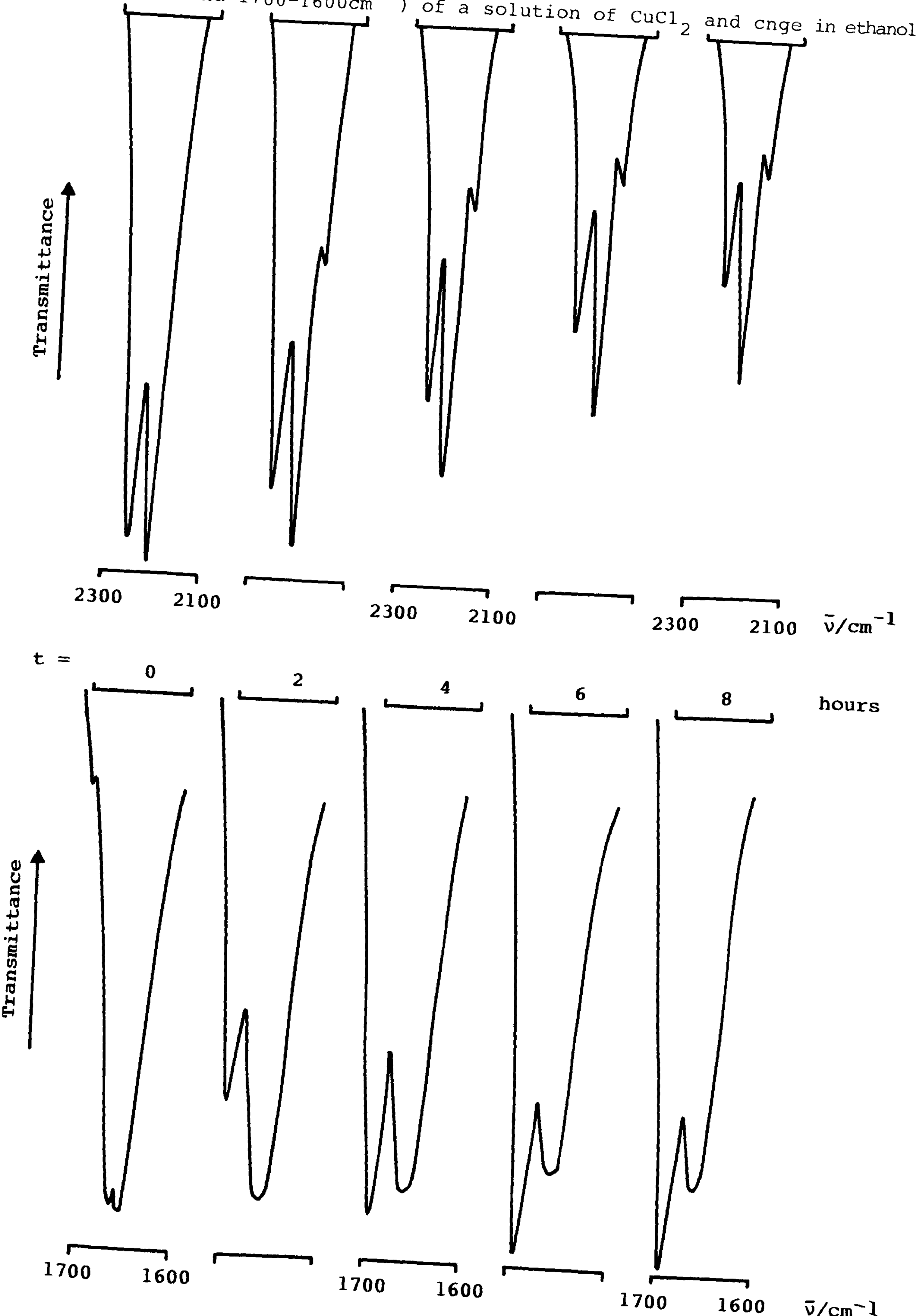
7.3.2 Sequential infrared solution spectra monitoring the copper(II) chloride-1-cyanoguanimidine-ethanol system

Both the 2300 to 2500cm^{-1} and the 1750 to 1600cm^{-1} regions proved to be useful in monitoring changes in this system. The first region showed loss of the starting material whilst the second region showed the formation of the product.

Figure 7.7 shows the changes in the difference spectrum (2300 to 1600cm^{-1}) of a 1:1 molar ratio of copper(II) chloride and cnge in ethanol over an 8 hour period. Monitoring for longer periods was not possible owing to leakage of the reaction solution from the cell and precipitation of products.

Initially in the 2300 to 2000cm^{-1} region two strong absorptions (2238 and 2196cm^{-1}) and a lower

FIGURE 7.7 Sequential ir difference spectra (2300-2100cm^{-1} and 1700-1600cm^{-1}) of a solution of $CuCl_2$ and cnge in ethanol



intensity shoulder (~2155cm^{-1}) were observed. By comparison with the spectrum of [Cu(cnge)$_2$Cl$_2$(H$_2$O)$_2$] in ethanol, it can be inferred that both free and coordinated cnge are present initially in the reaction mixture. Since there is not complete formation of coordinated cnge then free and coordinated cnge must be in equilibrium. The relative intensities of the 2238 and 2155cm^{-1} bands implies that coordinated cnge forms a significant proportion of the equilibrium mixture.

Over the period the reaction was monitored, all three of the absorptions in the 2300-2000cm^{-1} region diminish in intensity inferring loss of both free and coordinated cnge. The lowest wavenumber absorption appears (within the experimental limits) to diminish at a slower rate than the other two absorptions, the shoulder eventually being resolved into a peak at 2155cm^{-1}.

The change in the relative intensities of the absorptions is also consistent with the presence of an equilibrium since loss of cnge from the system will result in an increase in the [cnge]/[Cu(cnge)$^{2+}$] ratio ([X] $\equiv$ concentration of X) according to either of the following equilibria.

$$\mathrm{Cu^{2+} + cnge \rightleftharpoons Cu(cnge)^{2+}} \quad \beta_1 = \frac{[\mathrm{Cu(cnge)^{2+}}]}{[\mathrm{Cu^{2+}}][\mathrm{cnge}]}$$

$$\mathrm{Cu(cnge)^{2+} + cnge \rightleftharpoons Cu(cnge)_2{}^{2+}} \quad \beta_2 = \frac{[\mathrm{Cu(cnge)_2{}^{2+}}]}{[\mathrm{Cu^{2+}}][\mathrm{cnge}]^2}$$

The increase in the [cnge]/[Cu(cnge)] ratio also precludes the copper(II) species acting solely as a catalyst; it must form part of the product. If this were not the case, increase in $[Cu^{2+}]$ would occur which must be countered by a decrease in the $[cnge]/[Cu(cnge)^{2+}]$ ratio.

Examination of the 1700 to 1600cm^{-1} region is also of value. Initially a broad absorption at 1650cm^{-1} is observed. As the reaction proceeds a relatively sharp band at 1690cm^{-1} grows, whilst the 1650cm^{-1} band decreases in intensity inferring formation of aOeu at the expense of cnge.

7.4 Conclusions

These results go someway to identify the species in a solution of copper(II) chloride and cnge in ethanol over a period of time. Initially free cnge and a copper(II)-cnge complex $\{Cu(cnge)^{2+}$ or $Cu(cnge)_2{}^{2+}\}$ are present. With time, ethanolysis occurs and copper(II) aOeu complexes are produced. Loss of both free and coordinated cnge is observed, although the differing rates of loss imply the presence of an equilibrium between free and coordinated cnge.

These results give a qualitative insight into the reaction of cnge with copper(II) chloride in ethanol. A more detailed quantitative analysis of the reaction based on the use of UV-visible spectroscopy has been attempted and this is presented in the next chapter.

CHAPTER EIGHT

THE COPPER(II)CHLORIDE-1-CYANOGUANIDINE-ETHANOL SYSTEM: A UV-VISIBLE SPECTROSCOPIC STUDY

8.1 Introduction and Preliminary Experiments

The work described in the two previous chapters has given some understanding of the $CuCl_2$-cnge-EtOH system. That in Chapter Six unequivocally identified the ligand produced by the ethanolysis of cnge as 1-amidino-O-ethylurea (aOeu) and characterised the crystalline products as $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2$. The work described in Chapter Seven investigated the nature of the species in solution using infrared spectroscopy and demonstrated the formation of one or more copper(II)-cnge species initially and then their decay with subsequent formation of copper(II)-aOeu species. The infrared spectra (2300-1600cm^{-1}) were only sensitive to absorptions arising from ligand vibrations and could not be used to examine the coordination geometry of the copper(II) ion. Also, due to its qualitative nature, it was not possible to determine the stoichiometry of the complexes in solution nor the kinetics of their formation and decay.

It was apparent that a more quantitative technique complementary to vibrational spectroscopy was required to study the $CuCl_2$-cnge-EtOH system in greater detail.

As noted in Chapter Six, the crystalline products that were isolated could be distinguished by their distinctive colours, blue, for $[Cu(aOeu)Cl_2]_2$, and pink, for $[Cu(aOeu)_2]Cl_2$. The solid state visible spectra (400-900nm) of the complexes gave the wavelengths of their maximum absorption (λ_{max}) as 515 and 650nm respectively and illustrated that visible spectroscopy could be used to distinguish between the complexes.

The visible spectra of ethanol solutions of $CuCl_2$, $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2$, all at 2.0mM, are shown in Figure 8.1. Spectra at low concentrations are illustrated since $[Cu(aOeu)Cl_2]_2$ was not particularly soluble. All three spectra exhibit a single broad absorption but with decreasing λ_{max} and ε_{max} (ε_{max} = molar absorptivity at λ_{max}) values (Table 8.1).

Although all three absorptions overlap to varying extents, it is possible to distinguish between the complexes via their spectra.

An ethanol solution of cnge gives no absorption in the visible region. However, addition of cnge in ethanol to $CuCl_2$ or $[Cu(aOeu)Cl_2]_2$ in ethanol immediately shifted the λ_{max} value from 890nm to 820nm or 680nm to 650nm respectively (Table 8.1). The minimum values of λ_{max} were only obtained when the cnge was in great excess. Addition of cnge in ethanol to $[Cu(aOeu)_2]Cl_2$ in ethanol gave no visible change (Table 8.1). Figures 8.2 and 8.3 show the two extremes of the spectra for the addition of cnge to $CuCl_2$ and $[Cu(aOeu)Cl_2]_2$ respectively. These observations indicate the presence of equilibria in solution in which cnge forms complexes with both $CuCl_2$

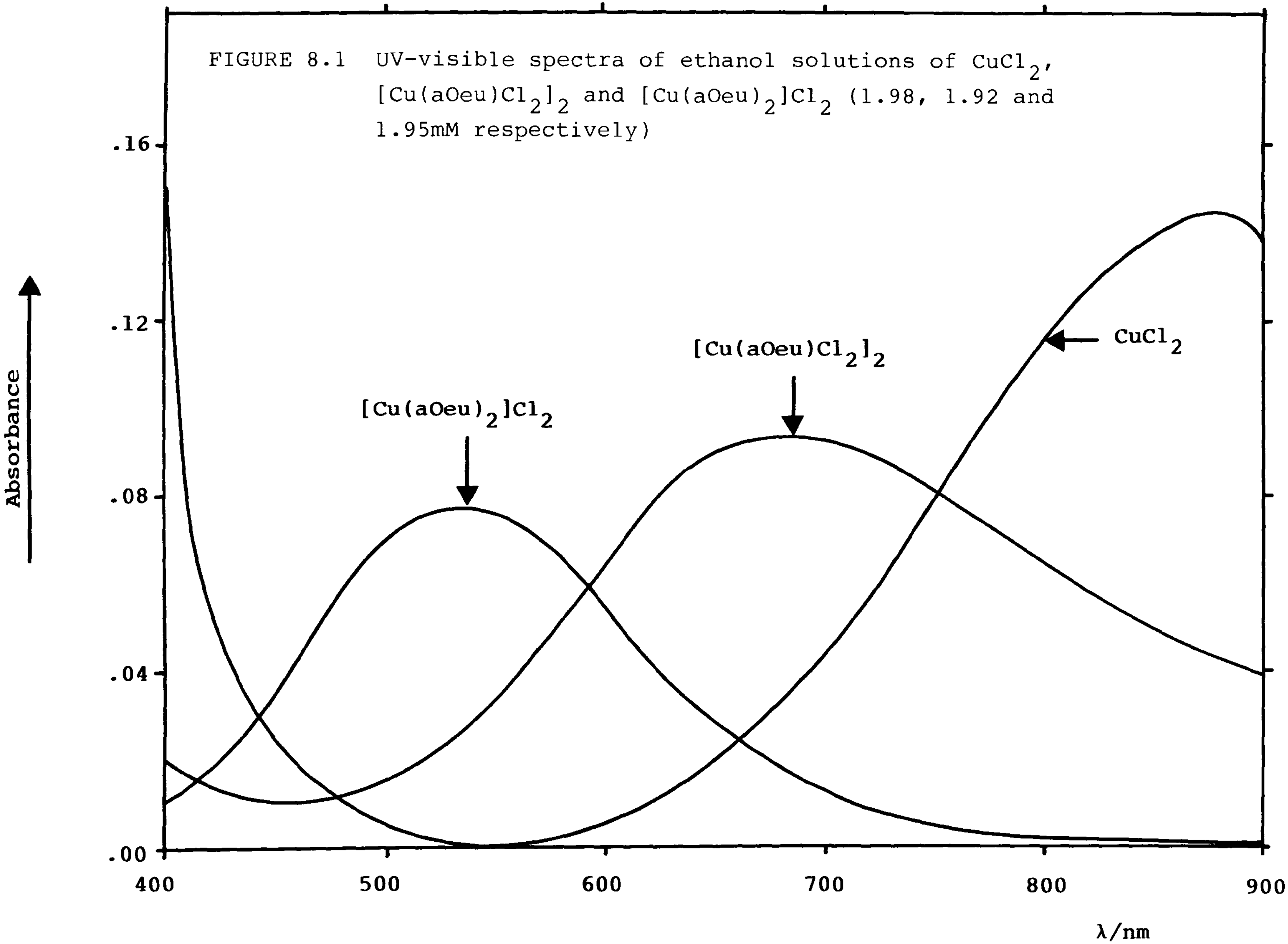


FIGURE 8.1 UV-visible spectra of ethanol solutions of $CuCl_2$, $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2$ (1.98, 1.92 and 1.95mM respectively)

TABLE 8.1 Spectroscopic Data for $CuCl_2$, $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2$

	Solid Phase	Ethanol Solution		Ethanol Solution Containing Excess cnge	
	λ_{max}/nm	λ_{max}/nm	ε_{max}/$lmol^{-1}cm^{-1}$	λ_{max}/nm	ε_{max}/$lmol^{-1}cm^{-1}$
$CuCl_2$	>900	880	71.5	820	90.0
$[Cu(aOeu)Cl_2]_2$	650	680	47.0	650	54.5
$[Cu(aOeu)_2]Cl_2$	515	540	40.0	540	40.0

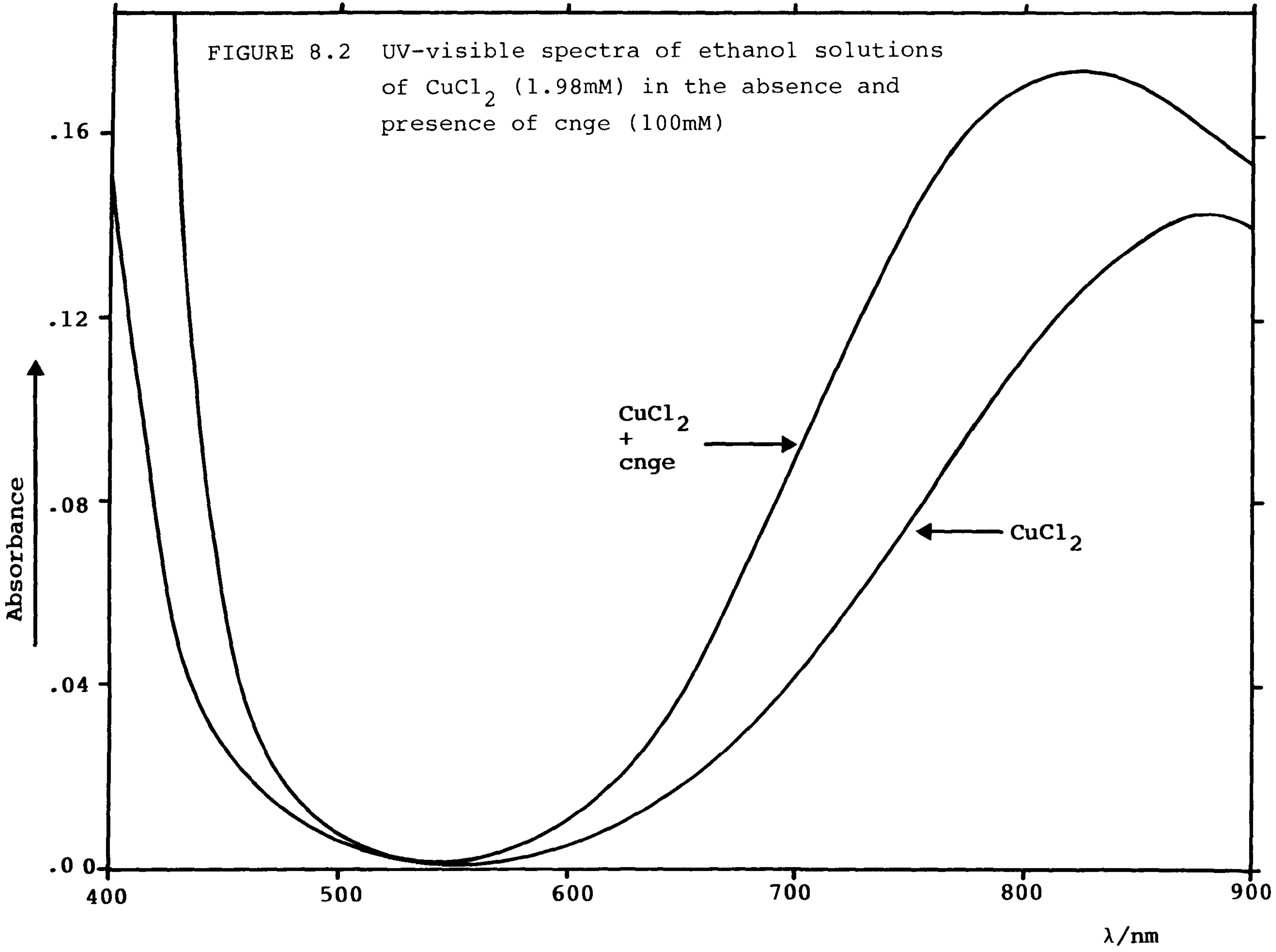
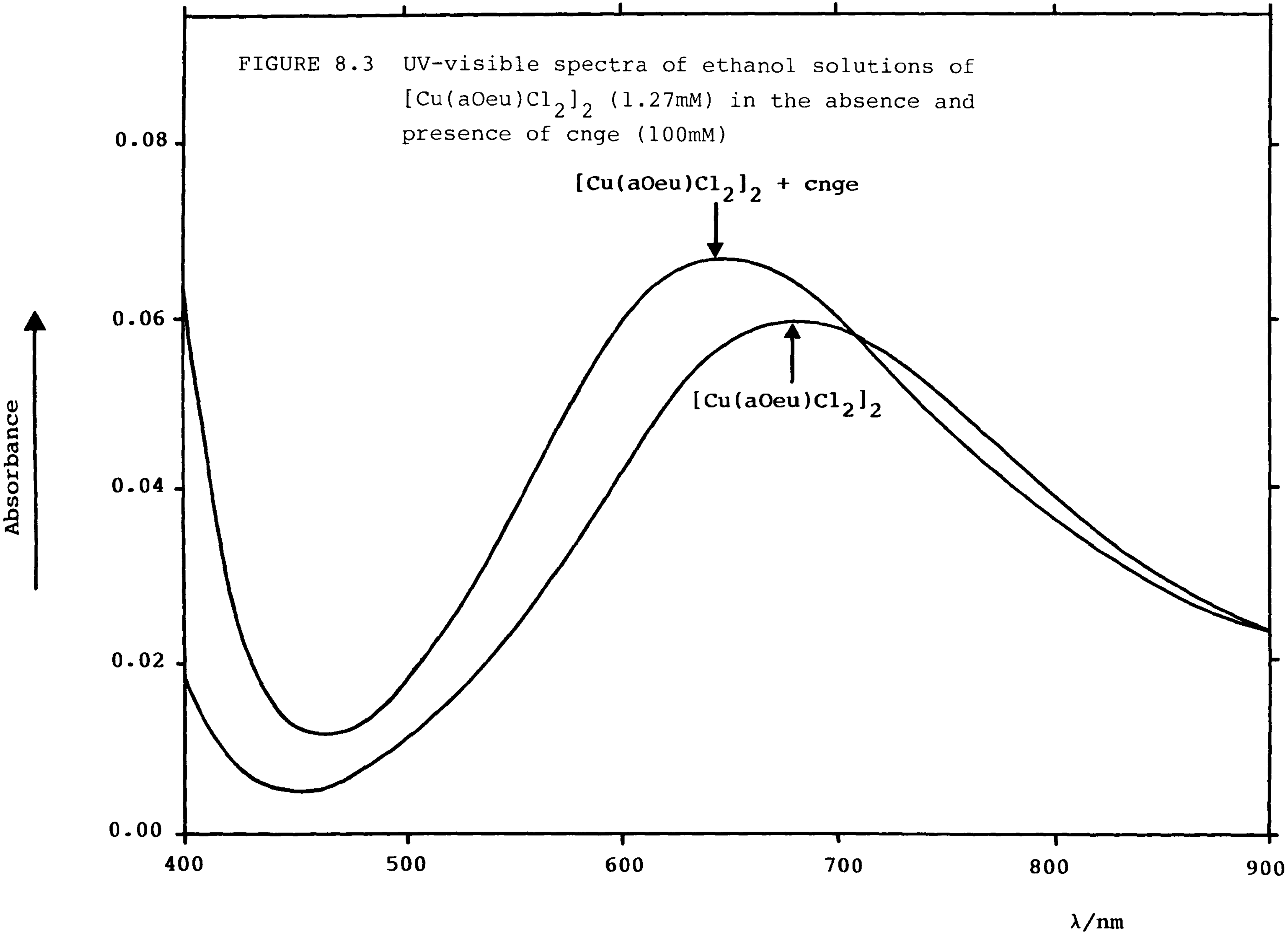


FIGURE 8.2 UV-visible spectra of ethanol solutions of $CuCl_2$ (1.98mM) in the absence and presence of cnge (100mM)

FIGURE 8.3 UV-visible spectra of ethanol solutions of $[Cu(aOeu)Cl_2]_2$ (1.27mM) in the absence and presence of cnge (100mM)



and $[Cu(aOeu)Cl_2]_2$ but not $[Cu(aOeu)_2]Cl_2$. The equilibrium involving $CuCl_2$ and cnge is consistent with the results of the infrared study described in Chapter Seven.

The spectrum of $CuCl_2$ and cnge in ethanol only remained constant for time periods which varied with the concentrations of the two solutes. For all the concentrations studied, the absorbance and λ_{max} gradually decreased in value from 820nm to give a meta stable λ_{max} at 650nm which eventually decreased to a final value of 540nm. Figure 8.4 illustrates this behaviour and shows the overlayed sequential UV-visible spectra of an ethanol solution initially containing copper(II) chloride (2.5mM) and cnge (100mM). Spectra were recorded at 1 hour intervals for 16 hours. Further monitoring of the spectrum resulted in the lines becoming too close together to be resolved and these lines are not shown for clarity. Eventually, however, a peak at 540nm was observed and no further changes in the spectrum occurred.

The similarity of the intermediate and final spectra to those of ethanol solutions of $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2$ containing cnge, suggested that a sequence of reactions was being observed in which ethanolysis of cnge occurred in the presence of $CuCl_2$ giving first mono- and then bis-aOeu-copper(II) complexes in ethanol solution.

Hence, after the success of these preliminary experiments it was decided to attempt to quantify the

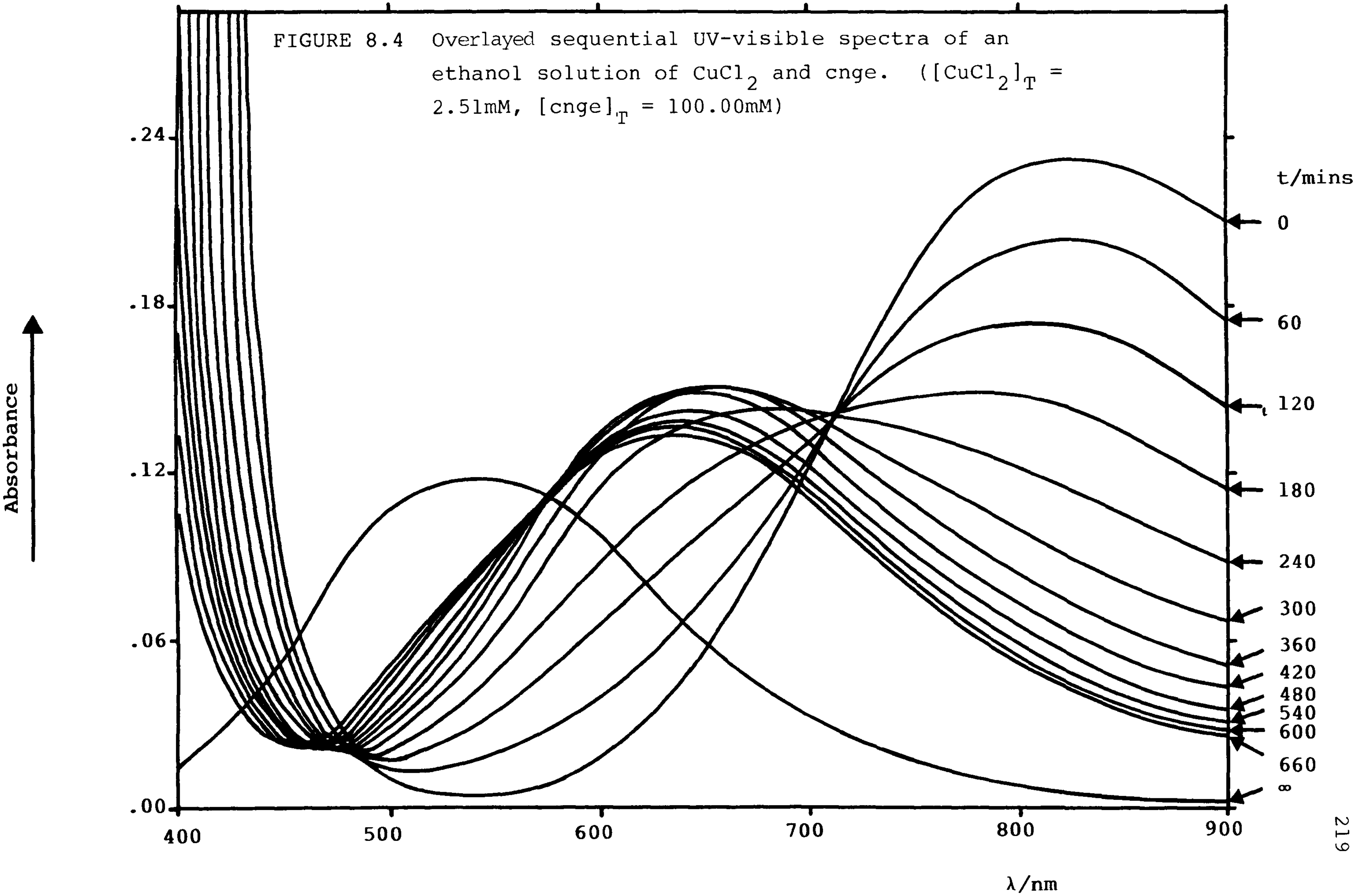


FIGURE 8.4 Overlayed sequential UV-visible spectra of an ethanol solution of $CuCl_2$ and cnge. ($[CuCl_2]_T$ = 2.51mM, $[cnge]_T$ = 100.00mM)

equilibria and reactions observed using visible spectroscopy. The study has been divided into three sections. The first two sections describe the investigation of the initial equilibrium on addition of cnge to $CuCl_2$ in ethanol, whilst the third section examines the kinetics and mechanism of the subsequent ethanolysis reactions.

8.2 The Initial Equilibria Present in the $CuCl_2$-cnge-EtOH System: The Stoichiometry of the Solution Species

8.2.1 The molar ratio method[67]

The simplest approach to examine the nature of the species using UV-visible spectroscopy is the Molar Ratio Method. The absorbance (A), at a suitable wavelength, of a series of solutions of constant metal concentration ($[M]_T$) containing varying concentrations of ligand ($[L]_T$) is measured and a plot of A against $[L]_T/[M]_T$ constructed. Ideally, two intersecting straight lines should be obtained with the point of intersection on interpolation to the $[L]_T/[M]_T$ axis giving the stoichiometric ratio of ligand to metal occurring in the complex (Figure 8.5). However, this method is valid only if the metal and ligand form only one complex and the stability constant for this complex is sufficiently large so as to produce a clear-cut point of intersection.

Figure 8.6 shows the molar ratio plot obtained for various ethanol solutions of $CuCl_2$ and cnge. The

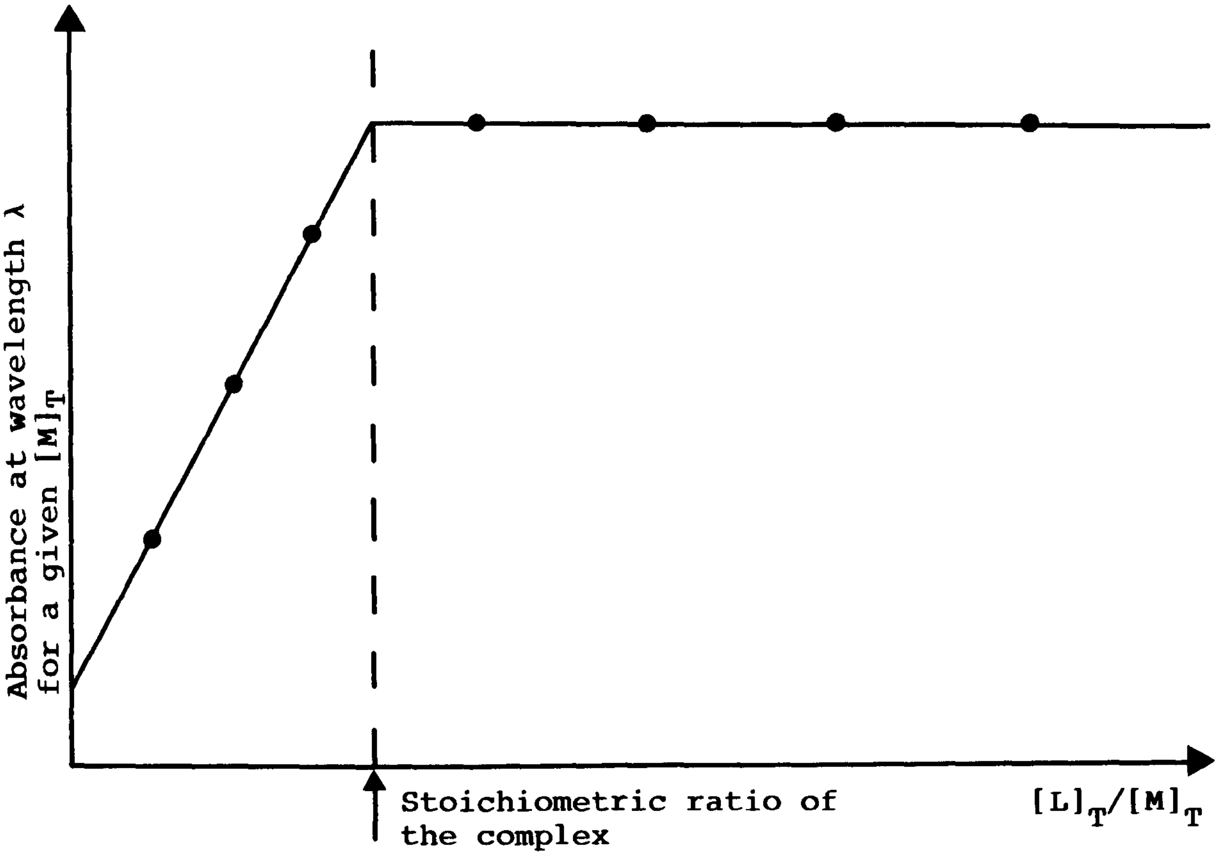


FIGURE 8.5 Idealised molar ratio plot

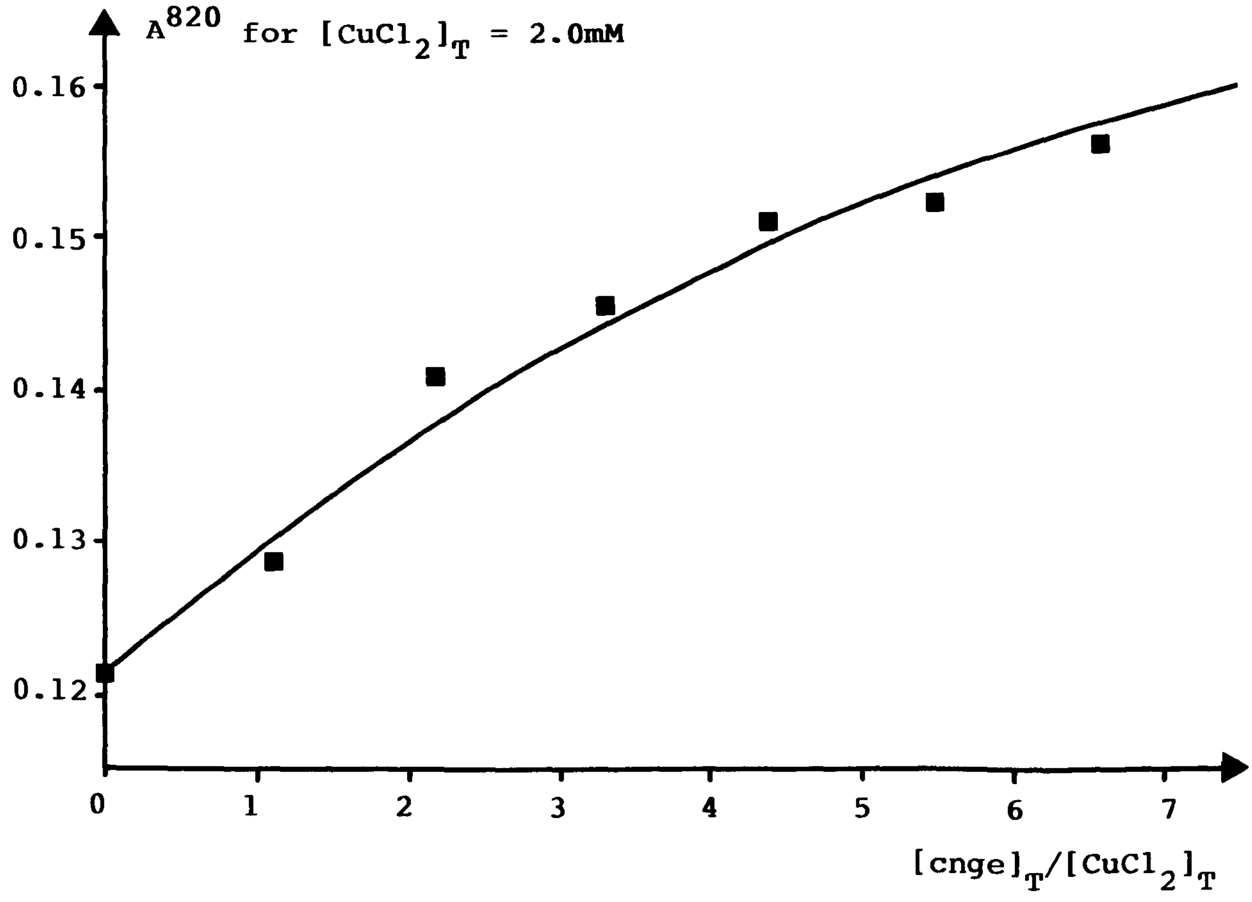


FIGURE 8.6 Molar ratio plot for the $CuCl_2$-cnge-EtOH system

absorbance values at 820nm are taken from experiment 8.5 (see Section 8.3). A curve is obtained for the plot rather than two intersecting lines, which suggests that the conditions for the molar ratio method are not satisfied by this system. Hence the results imply the formation of one or more complexes with low values for their stability constants. This work verifies the observations in the preliminary experiments that only large values of $[\text{cnge}]_T/[\text{CuCl}_2]_T$ gave the lowest λ_{max} value (820nm) and the greatest increase in absorbance for a particular $[\text{CuCl}_2]_T$.

Although the molar ratio method has been shown to be unsuitable for this system, it has been possible to demonstrate that only one or more weak complexes formed in solution. Further investigation of the initial equilibrium has been accomplished using a more suitable technique, the Method of Continuous Variation more commonly known as Job's Method.

8.2.2 Job's Method[67]

Consider the formation of complex ML_n from metal M and n moles of ligand L with overall stability constant β_n

$$M + nL \xrightarrow{\beta_n} ML_n$$

A series of solutions can be prepared such that the sum of total metal and total ligand concentrations ($[M]_T$ and $[L]_T$ respectively) is constant (C). Hence

$$[M]_T + [L_T] = C \qquad (1)$$

Three mass balance equations may now be written.

$$[M] = C(1-x) - [ML_n] \qquad (2)$$

$$[L] = C_x - n[ML_n] \qquad (3)$$

$$[ML_n] = \beta_n[M][L]^n \qquad (4)$$

where x is the mole fraction of the ligand.

Taking first differentials of equations 3 and 4, followed by elimination of [M] [L] and $[ML_n]$, yields a value for x, x_{max}, which is dependent only on n

i.e.
$$n = \frac{x_{max}}{1-x_{max}} \qquad (5)$$

Now at a given wavelength λ for the reaction

$$A_{obs} = \varepsilon_M[M] + \varepsilon_L[L] + \varepsilon_{ML_n}[ML_n] \qquad (6)$$

where A_{obs} is the observed absorbance per unit path length

ε_M, ε_L, ε_{ML_n} are the molar absorptivities of the metal, ligand and complex respectively.

The theoretical absorbance due to the ligand and metal alone if there were no reaction between them can be written as A_{theo} and therefore,

$$A_{theo} = \varepsilon_M[M] + \varepsilon_L[L] \qquad (7)$$

Using equations 2 and 3 the following is obtained

$$A_{obs} = \varepsilon_M C(1-x)-\varepsilon_M C[ML_n]+\varepsilon_L Cx-\varepsilon_L n[ML_n]+\varepsilon_{ML_n}[ML_n] \qquad (8)$$

$$A_{theo} = \varepsilon_M C(1-x)+\varepsilon_L Cx \qquad (9)$$

Hence, a corrected absorbance function Y_{calc}, can be defined as the difference between A_{obs} and A_{theo}. Subtracting equation 9 from equation 8

$$Y_{calc} = A_{obs}-A_{theo} = \varepsilon_{ML}[ML_n]-\varepsilon_M[ML_n]-n\varepsilon_L[ML_n] \qquad (10)$$

Thus, Y_{calc} is independent of C and a function of $[ML_n]$ only.

If the ligand does not absorb in the region of interest, as has been found for cnge, equation 10 becomes

$$Y_{calc} = \varepsilon_{ML}[ML_n]-\varepsilon_M[ML_n] \qquad (11)$$

Hence, if $\varepsilon_{ML}>\varepsilon_M$ then when $[ML_n]$ is a maximum Y_{calc} will be at a maximum.

Thus, if the Y_{calc} values of a set of solutions with $[M_T]+[L_T]=C$ at a given wavelength are plotted against mole fraction of ligand, x, a plot such as Figure 8.7 will result. Interpolation of the maximum Y_{calc} value onto the x-axis will give a value x_{max}. If x_{max} was 0.5 or 0.67 or 0.75 then, from equation 5, these values would correspond to values of n of 1 or 2 or 3 respectively and hence complex stoichiometries of 1:1, 1:2 or 1:3 respectively.

Experimentally A_{obs} is measured and A_{theo} obtained from $A_{theo} = \varepsilon_M C(1-x)$ (from equation 9 for non-absorbing L) where $\varepsilon_M C$ is readily available since when x = 0

$$A_{obs} = \varepsilon_M C$$

and hence $A_{theo} = A_{obs}^{x=0}(1-x)$

However, there are a number of inherent assumptions made in Job's Method. These are that:

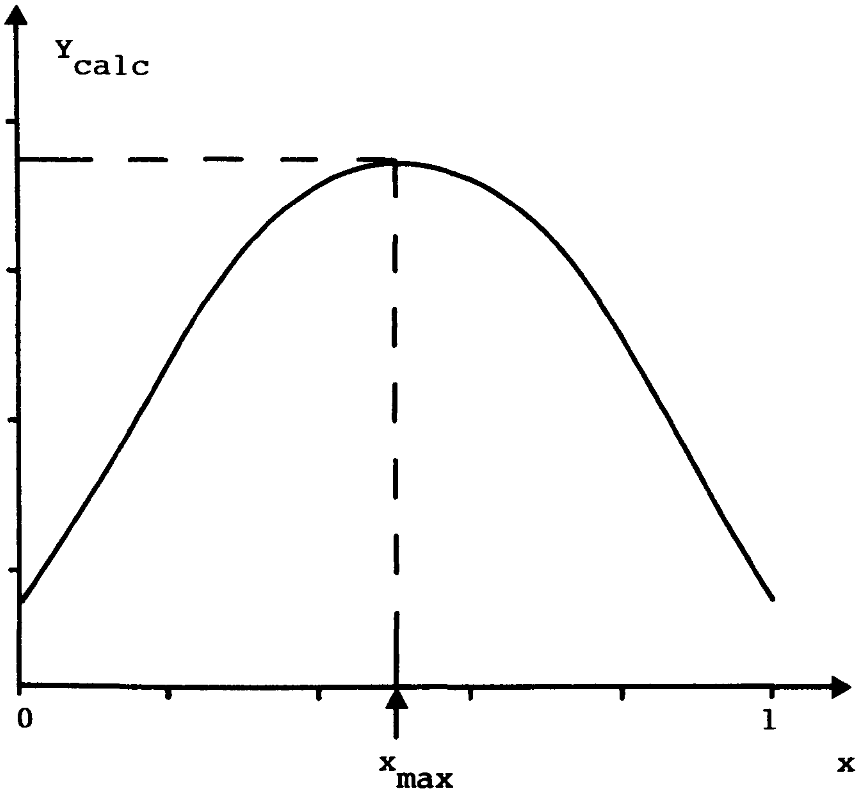


FIGURE 8.7 Idealised Job's plot

(a) The reactants do not participate in other equilibria in addition to the reaction specified.

(b) The activity coefficients are effectively constant.

(c) There is only one complex formed.

For the system studied, the first two conditions are assumed to be satisfied, but it seems unlikely that the latter is obeyed in the light of the molar ratio plot. However, if data are obtained at several wavelengths and a Job's plot constructed at each wavelength, then x_{max} may be found to be wavelength dependent. If so, then these x_{max} values would give the stoichiometries of the different complexes in solution.

8.2.3 Experimental

(i) Chemicals and Apparatus

Analar grade ethanol and copper(II) chloride (predried overnight at 110°C) and twice recrystallised cnge were used. Stock solutions of $CuCl_2$ and cnge were prepared several days prior to the experiments to allow for complete dissolution. This was particularly necessary for the cnge solutions. During solution make up and prior to an experiment all solutions were thermostatted to 20°C ±0.1°C. Aliquots of solutions were measured using grade A burettes (10ml volume, accuracy 0.02ml). All spectrophotometric measurements were made in stoppered quartz solution cells (10mm path length) using a Perkin Elmer Lambda 5 spectrometer fitted with a custom made sample and reference cell holder that was thermostatted to 20°C ±0.1°C. The cell holder (Figure 8.8) was manufactured from a copper block, milled to allow accurate location of, and the passage of the light beams through, the solution cells. The block was drilled to allow for internal circulation of the coolant (water/antifreeze 1:1) throughout the holder. This system ensured identical constant temperatures for both sample and reference cells.

(ii) Procedure

Sample and reference cells were filled with ethanol and placed in the thermostatted cell holder of the spectrometer. The cells were allowed to equilibrate to

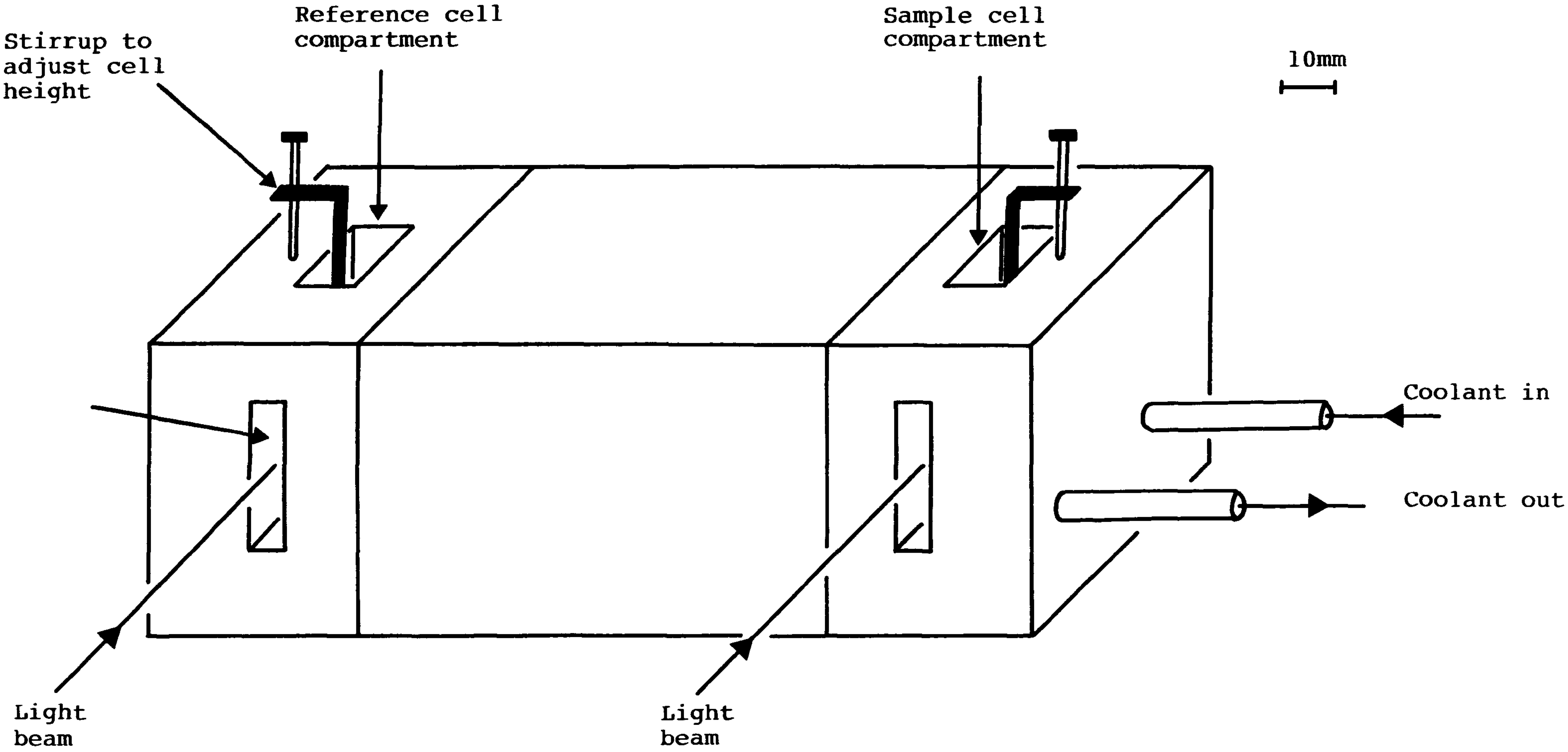


FIGURE 8.8 The thermostatted sample and reference cell holder

constant temperature and then the spectrometer was background corrected in the range 800-900nm. The sample cell was emptied and dried in a stream of nitrogen gas. Aliquots of equimolar $CuCl_2$ and cnge ethanol solutions (A and Bml respectively) were mixed and the resulting solution transferred to the sample cell in the spectrometer. Spectra were recorded every two minutes in the range 800-900nm until a constant spectrum was obtained. The sample cell was then rinsed with ethanol and dried with nitrogen as before. The procedure was then repeated using values of A and B until the range mole fraction cnge (x_{cnge}) 0.0 to 1.0 was completed. The complete experiment was performed four times. Experiments 8.1 and 8.2 used stock solutions with $[CuCl_2]_T$=$[cnge]_T$= 12.05mM. Experiments 8.3 and 8.4 used stock solutions with $[CuCl_2]_T$=$[cnge]_T$ = 12.05mM and 25.00mM respectively, however, values of A and B in these experiments were concentrated on the region x_{cnge} 0.5-0.75. Values of A and B for all the experiments are given in Appendix A. For each experiment, tables of data were collated from the spectra to give absorbance values at 800, 820, 840, 860 and 880nm which correlated with x_{cnge} values. Values of Y_{calc} were then calculated and plotted against x_{cnge} values.

8.2.4 Results and Discussion

Absorbance data and the corresponding Y_{calc} values at all wavelengths and x_{cnge} studied are collated for all experiments in Appendix A.

The Job plots at all the wavelengths studied in Experiment 8.1 are shown in Figure 8.9. The plots for Experiment 8.2 are shown in part in Figure 8.10a.

The curves for Experiments 8.1 and 8.2 all follow the same pattern with the maximum value of Y_{calc} at a particular x_{cnge} decreasing with increasing wavelength. This is in line with Figure 8.2 since the greatest difference in absorbance between the spectra of ethanol solutions of $CuCl_2$ and $CuCl_2$ with excess cnge occurs close to 800nm. All the curves pass through their maximum value of Y_{calc} at values of x_{cnge} between 0.5 and 0.7 and hence x_{max} lies in this range. This implies the formation of complexes with a 1:1 or 1:2 Cu:cnge ratio. However, it is not possible to distinguish between these two stoichiometries at different wavelengths. To try to resolve this problem experiments 8.3 and 8.4 were performed, concentrating on the x_{cnge} region 0.5 to 0.7. The Job plots at the maximum and minimum wavelengths studied for these experiments are shown in Figures 8.10b and c. The other plots are omitted for clarity. Although there is slight scatter in the data, all the curves follow the same pattern as before and maximise Y_{calc} at between 0.5 and 0.7 cnge.

Unfortunately, it has not been possible to observe different x_{max} values at different wavelengths and hence determine unequivocally the number and stoichiometry of the complexes in solution. This is presumably a consequence of very small stability constant(s) for the

FIGURE 8.9 Jobs plots for Experiment 8.1

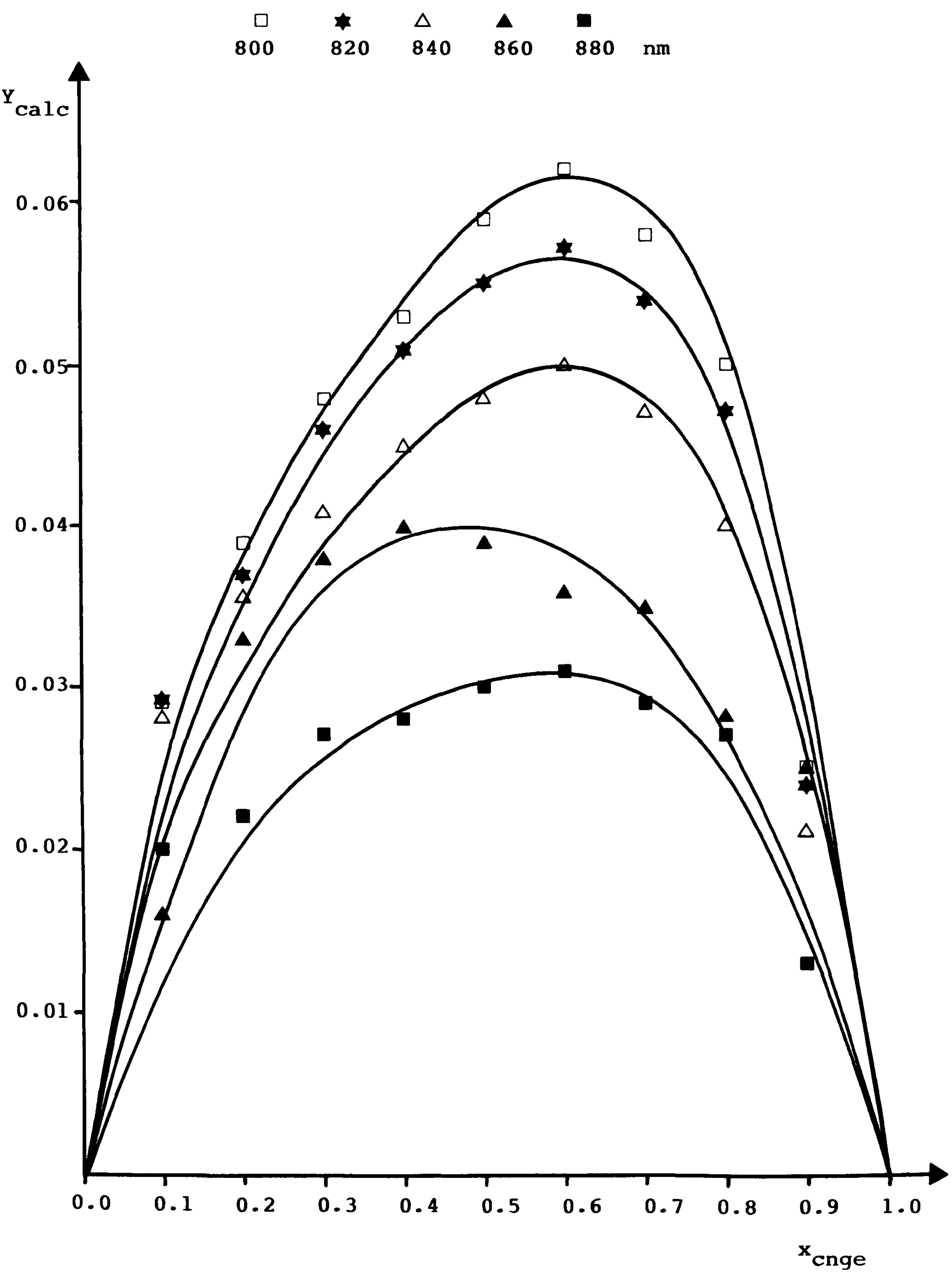


FIGURE 8.10a Jobs plots for Experiment 8.2

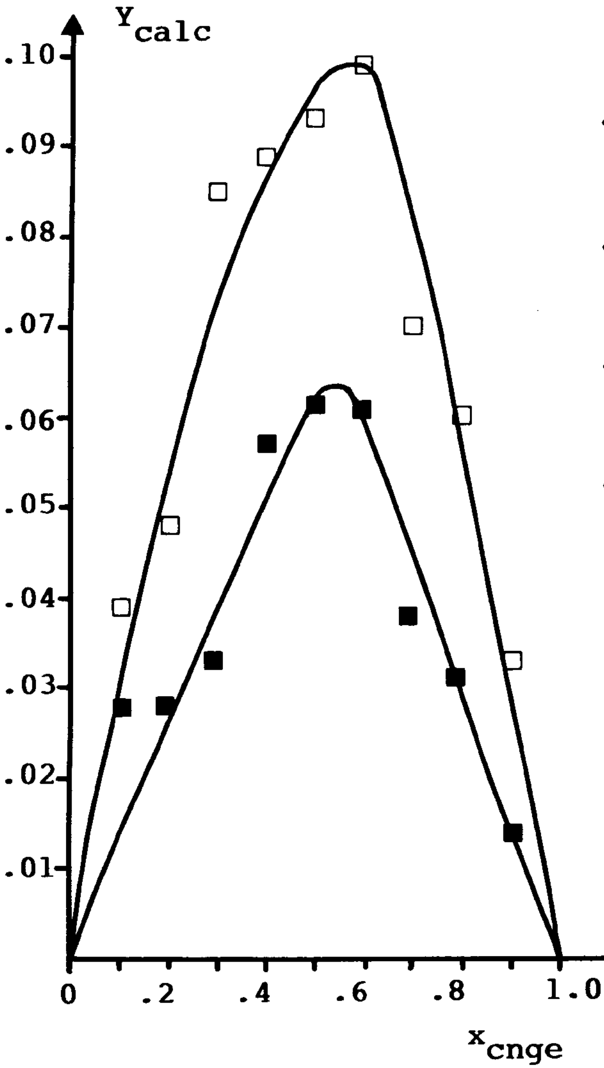


FIGURE 8.10b Jobs plots for Experiment 8.3

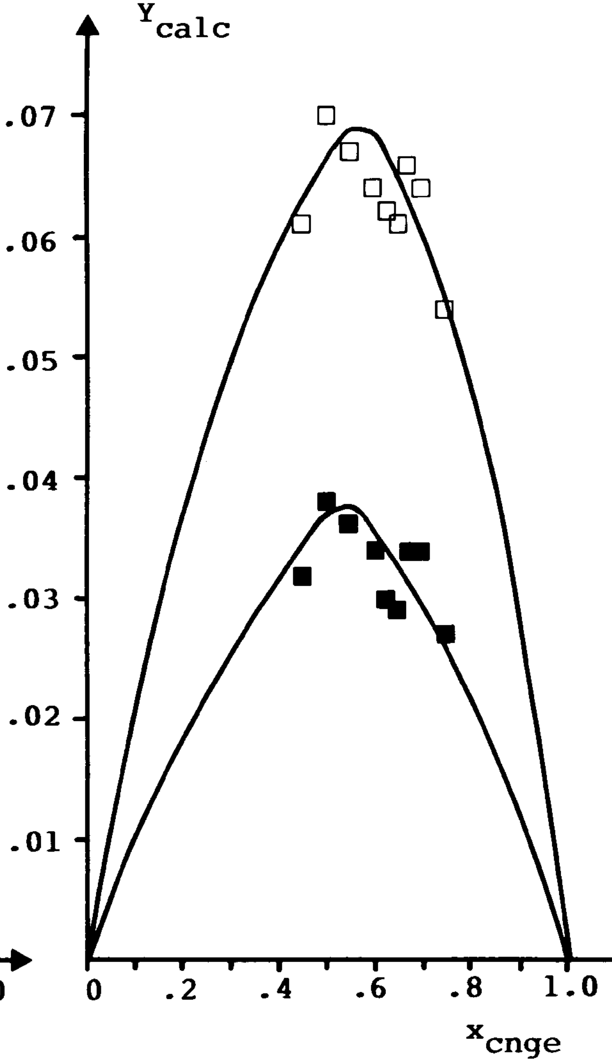
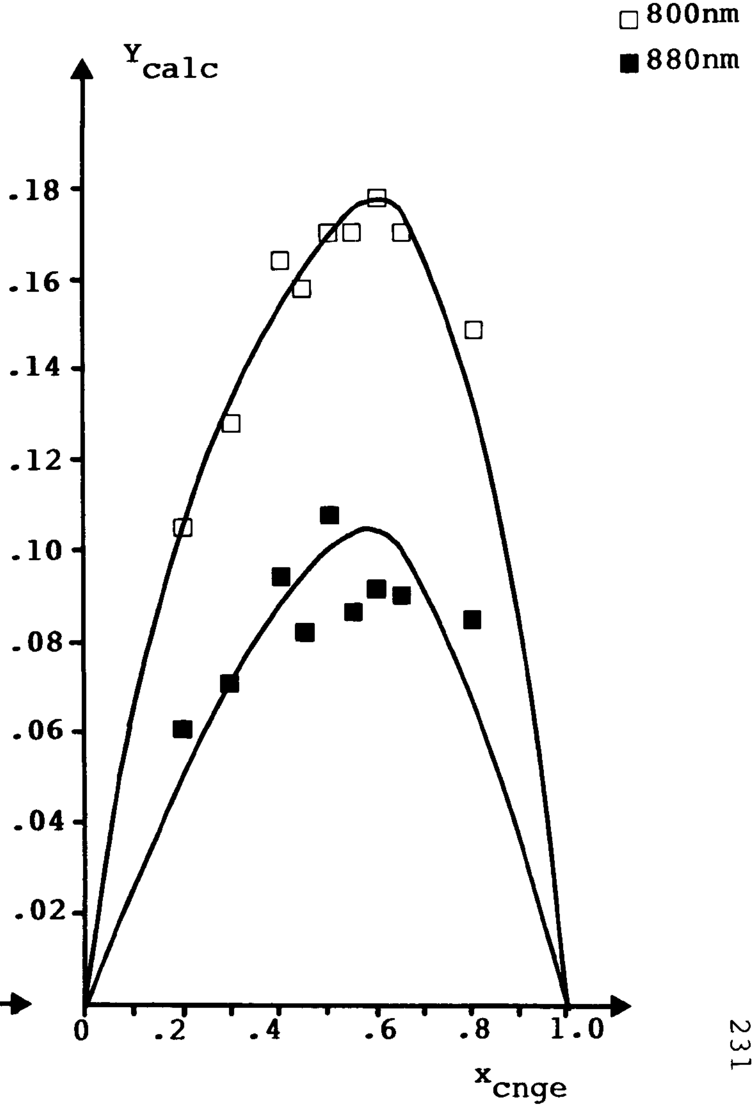


FIGURE 8.10c Jobs plots for Experiment 8.4



complex(es) and the broad overlapping bands for both the metal and the complex(es) in solution. Both will give rise to only relatively small differences between the spectra of the metal and the complex(es) in solution over a limited range of wavelengths even at x_{max} when the difference should be greatest. However, this work has demonstrated the presence of either one or both of the complexes with Cu:cnge ratios of 1:1 or 1:2. The presence of a 1:2 type complex is also consistent with the copper(II)-cnge complexes that have been studied structurally (Chapter Two). Apart from one complex in which the copper(II) atom was coordinated by 1-(2-aminoethyl) biguanide and cnge, all the complexes have shown two trans coordinated cnge ligands. However, it must be noted that none of these complexes were isolated from ethanol solutions.

Having demonstrated the presence of a mono- and/or bis-cnge-copper(II) complex in solution, it was then attempted to further quantify the equilibria by assuming the stepwise formation of these complexes and then calculating their stability constants.

8.3 The Initial Equilibria Present in the $CuCl_2$-cnge-EtOH System: the Stability of the Species in Solution

8.3.1 Introduction

In this work the stability constants have been evaluated using the Method of Corresponding Solutions.[67]

This method relies upon the relationship between the stability constants and a secondary concentration variable the complex formation function ($\bar{n}$; defined below). In the following sub-sections, firstly $\bar{n}$ is related to the stability constants, then it is shown how $\bar{n}$ can be calculated from spectrophotometric data and finally the experimental data is given.

8.3.2 The Relationship Between the Stability Constants and the Complex Formation Function

Consider the metal ion M and the ligand L interacting in solution. The equilibria present are

$$M + L \xrightleftharpoons{K_1} ML$$

$$ML + L \xrightleftharpoons{K_2} ML_2$$

$$ML_{n-1} + L \xrightleftharpoons{K_n} ML_n$$

and where

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (12)$$

and

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \qquad (13)$$

The maximum value of n (N) will be a function of both the maximum coordination number of the metal ion and the multidentism of the ligand. Writing mass balance equations for the total metal and ligand concentrations ($[M]_T$ and $[L]_T$ respectively):-

$$[M]_T = [M]+[ML]+[ML_2]+ \dots [ML_n] \tag{14}$$

$$[L]_T = [L]+[ML]+2[ML_2]+ \dots n[ML_n] \tag{15}$$

A function, $\bar{n}$, defined as the average number of ligands, L, attached to the metal M may be written

$$\bar{n} = \frac{\text{total bound ligand}}{\text{total metal}} = \frac{[L]_T-[L]}{[M]_T} \tag{16}$$

Substituting equations 14 and 15 in 16 gives

$$\bar{n} = \frac{[ML]+2[ML_2]+ \dots n[ML_n]}{[M]+[ML]+[ML_2]+ \dots [ML_n]} \tag{17}$$

Now substituting equation 12 in 17 gives

$$\bar{n} = \frac{K_1[M][L]+2K_1K_2[M][L]^2+\dots+nK_1K_2\dots K_n[M][L]^n}{[M]+K_1[M][L]+K_1K_2[M][L]^2+\dots+K_1K_2\dots K_n[M][L]^n} \tag{18}$$

Dividing through by [M] gives

$$\bar{n} = \frac{K_1[L]+2K_1K_2[L]^2+\dots+nK_1K_2\dots K_n[L]^n}{1+K_1[L]+K_1\ K_2[L]^2+\dots+K_1K_2\dots K_n[L]^n} \tag{19}$$

Returning to equation 16 and rearranging gives

$$[L_T] = \bar{n}[M]_T+[L] \tag{20}$$

so that if a series of solutions could be prepared in which $\bar{n}$ and [L] were constant although unknown, a plot of $[L_T]$ against $[M]_T$ would be a staight line of slope $\bar{n}$ and intercept [L]. Such a series of solutions are known as 'Corresponding Solutions'. Since $\bar{n}$ is shown in equation 19 to be a function of [L] only it is apparent that if it could be established that [L] was constant, albeit unknown, for a set of solutions $\bar{n}$ would also necessarily be constant. Thus, if a series of solutions of different $[M]_T$ and $[L]_T$ were prepared, a parameter measured (e.g. absorbance of a suitable wavelength) then the total metal and total ligand concentrations of strictly corresponding solutions could be determined by interpolation and plots of $[L]_T$ against $[M]_T$ would give $\bar{n}$ and [L] values. These values could be used to determine stability constants when N=1 or 2 by rearranging equation19.

Consider the case when N=1 then equation 19 becomes

$$\bar{n} = \frac{K_1[L]}{1+K_1[L]} \qquad (21)$$

which can be rearranged to give

$$\frac{\bar{n}}{(1-\bar{n})} = K_1[L] \qquad (22)$$

Thus, a plot of $\bar{n}/(1-\bar{n})$ with [L] will give a linear plot of gradient K_1.

Now, if N=2 then equation 19 can be rearranged to give

$$\bar{n} = (1-\bar{n})[L]K_1+(2-\bar{n})[L]K_1K_2 \qquad (23)$$

which, on division by $\bar{n}$ and further rearrangement, gives

$$\frac{(1-\bar{n})}{(2-\bar{n})[L]} = \frac{\bar{n}}{(2-\bar{n})[L]^2} \quad \frac{1}{K_1} - K_2 \qquad (24)$$

Thus, if the left hand side of equation 24 was plotted against $\bar{n}/(2-\bar{n})[L]^2$ then a straight line of gradient $1/K_1$ and ordinate intercept $-K_2$ is obtained. Hence, the relationship between $\bar{n}$, [L] and the stability constants is clearly demonstrated.

8.2.3 The Calculation of $\bar{n}$ using the Method of Corresponding Solutions

For the general equilibria defined earlier ε_{obs} can be defined such that

$$\varepsilon_{obs} = \frac{A_{obs} - \varepsilon_L[L]_T}{[M]_T} \qquad (25)$$

The absorbance at a specific wavelength A_{obs} is given by

$$A_{obs} = \varepsilon_M[M] + \left\{\sum_{i=1}^{i=n} (\varepsilon_i[ML_i])\right\} + \varepsilon_L[L] \qquad (26)$$

where ε_i is the molar absorptivity of ML_i at a specific wavelength. Substituting equation 26 in 25 gives

$$\varepsilon_{obs} = \frac{\varepsilon_M[M] + \left\{\sum_{i=1}^{i=n} (\varepsilon_i[ML_i])\right\} - \varepsilon_L([L]_T - [L])}{[M]_T} \qquad (27)$$

and hence from equation 15

$$\varepsilon_{obs} = \frac{\varepsilon_M[M] + \sum_{i=1}^{i=n} (\varepsilon_i[ML_i]) - \sum_{i=1}^{i=n} (\varepsilon_L i([ML_i]^i)}{[M]_T} \qquad (28)$$

Expanding using equation 13 and combining terms

$$\varepsilon_{obs} = \frac{\varepsilon_M[M] + \sum_{i=1}^{i=n}(\varepsilon_i\beta_i[M][L]^i - \varepsilon_L\beta_i[M][L]^i)}{[M]_T} \qquad (29)$$

Dividing through by [M] gives

$$\varepsilon_{obs} = \frac{\varepsilon_M + \sum_{i=1}^{i=n}(\varepsilon_i-\varepsilon_L)\beta_i[L]^i}{[M]_T/[M]} \qquad (30)$$

and from equations 14 and 13 this finally becomes

$$\varepsilon_{obs} = \frac{\varepsilon_M + \sum_{i=1}^{i=n}(\varepsilon_i-\varepsilon_L)\beta_i[L]^i}{1+\sum_{i=1}^{i=n}\beta_i[L]^i} \qquad (31)$$

Hence ε_{obs} is a function of [L] only, an analogous situation to $\bar{n}$ described earlier. If ε_{obs} is calculated from the absorbance of solutions of different $[L]_T$ and $[M]_T$ values using equation 25, it follows that solutions having the same ε_{obs} value must have the same [L] and $\bar{n}$ values. Thus, the solutions are said to be 'Corresponding Solutions'.

Thus, in practice A_{obs} is measured for a series of solutions of constant $[M]_T$ and increasing $[L]_T$. ε_{obs} is calculated. The experiment is then repeated at different $[M]_T$ values. A series of graphs of ε_{obs} against $[L]_T$ are plotted as illustrated in Figure 8.11. Sets of values of

FIGURE 8.11 Corresponding solutions: Plots of ε_{obs} against $[L]_T$ at various $[M]_T$ values

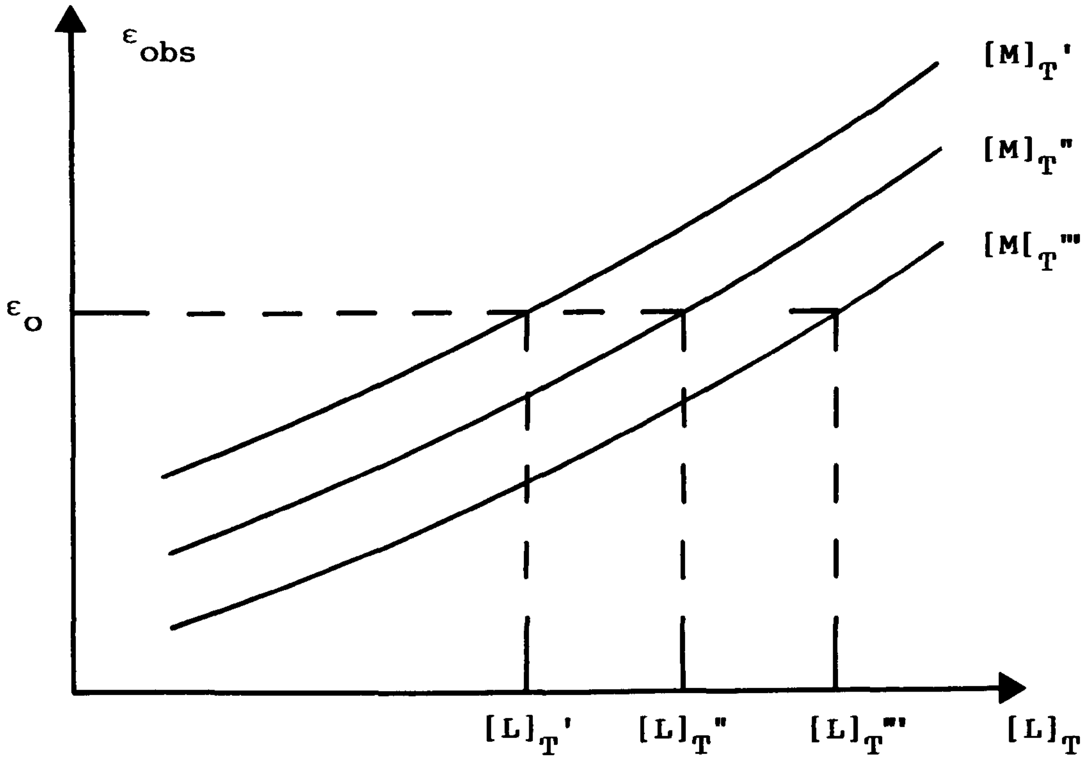
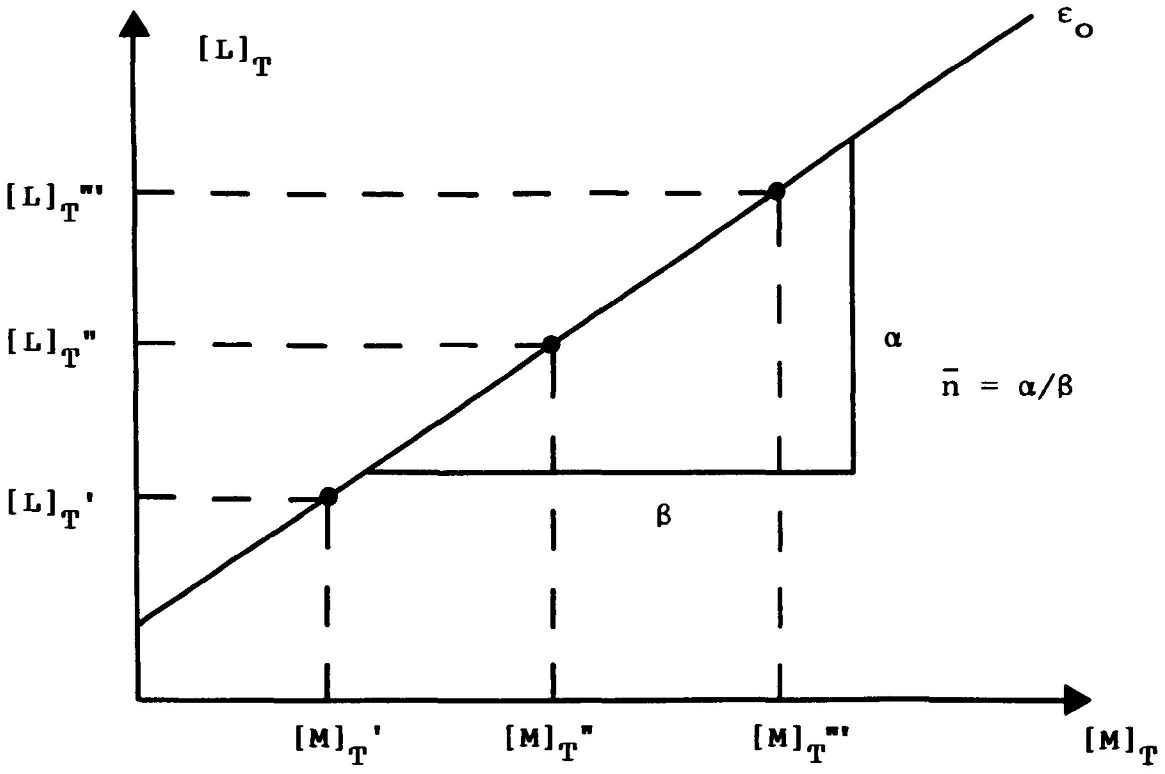


FIGURE 8.12 Corresponding solutions: Plot of $[L]_T$ against $[M]_T$ a series of solutions having the same value of ε_{obs} (ε_o from Figure 8.11)



$[M]_T$ and the corresponding $[L]_T$ are then determined for a series of ε_{obs} values. Linear plots at each ε_{obs} using equation 20, illustrated in Figure 8.12, then gives a series of $\bar{n}$ and [L] values from which stability constants can be calculated from a linear plot using equation 22 or 24 as appropriate.

8.3.4 Experimental

(i) Chemicals and Apparatus

These are described in Section 8.2.3(i).

(ii) Procedure

This is similar to that described in Section 8.2.3(ii), however, for this experiment (experiment 8.5) it was necessary to prepare solutions at several concentrations of $CuCl_2$ ($[CuCl_2]_T$) containing a range of cnge concentrations ($[cnge]_T$) for each $[CuCl_2]_T$. Thus it was necessary to mix aliquots of $CuCl_2$ and cnge solutions (A and Bml respectively) with one of ethanol (Cml) to obtain a sufficiently large range of concentrations. (Values of A, B and C are given in Appendix A.) The concentrations of the stock solutions of $CuCl_2$ and cnge were 36.03mM and 39.64mM respectively.

In practice solutions with a fixed $[cnge]_T$ containing various $[CuCl_2]_T$ were prepared and their absorbance at 820nm measured. The value of $[cnge]_T$ was then changed and the set of measurements repeated. For each set of measurements the spectrum of a solution of

$CuCl_2$ alone (9.01mM) was measured to act as internal standard. The range of concentrations studied was $[cnge]_T$ at 0.00, 2.20, 4.40, 6.61, 8.81, 11.01 and 13.21mM with $[CuCl_2]_T$ at 2.00, 4.00, 6.01, 9.01, 12.01 and 16.01mM for each $[cnge]_T$.

A further experiment (experiment 8.6) was also performed in which the stock $CuCl_2$ solution was diluted with ethanol to give several solutions of varying $[CuCl_2]_T$ in the range 2 to 20mM and their absorbancies at 820 and 880nm measured using the procedure described earlier.

8.3.5 Results and Discussion

The raw absorbance data at 820nm are collated together with the calculated ε_{obs} values in Appendix A. The data shows marginal scatter but are self consistent within sets of measurement at each $[cnge]_T$. The scatter is most pronounced for the data at $[cnge]_T$ = 2.20 and 6.61mM.

Over the concentration range employed the $CuCl_2$ solutions were shown to obey the Beer Lambert law

i.e. $A = cl\varepsilon$

where c = concentration

l = path length

A and ε as defined earlier.

This is illustrated in Figure 8.13 (data from experiment 8.6; collated in Appendix A). Hence the data at $[cnge]_T$ = 2.20 and 6.61mM have been normalised to the data for the other $[cnge]_T$ values.

FIGURE 8.13 Graphs of the absorbance at 880 and 820nm against the concentration of $CuCl_2$ in ethanol solution ($[CuCl_2]_T$)

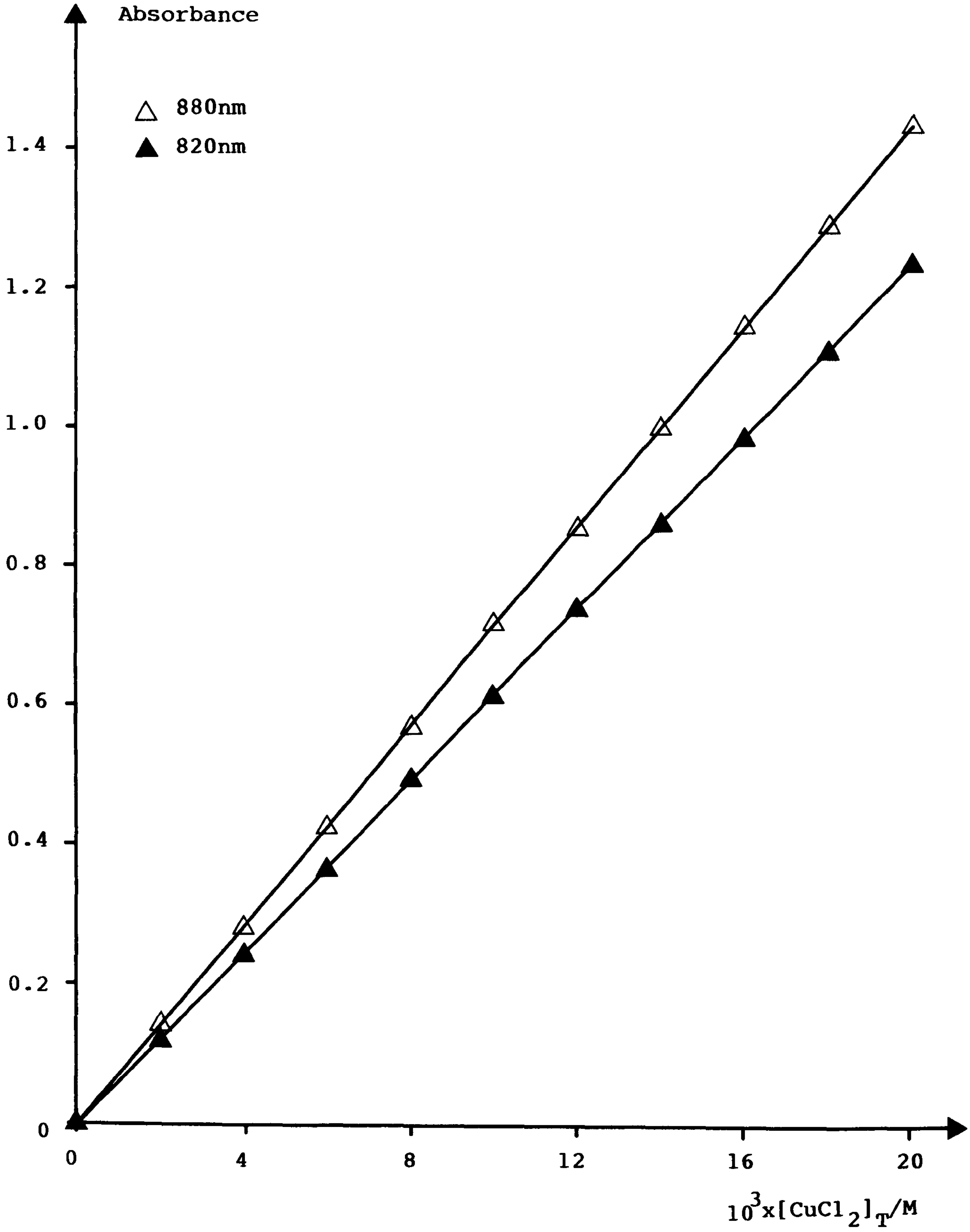


Figure 8.14 illustrates the plot of ε_{obs} at 820nm against $[cnge]_T$ for various $[CuCl_2]_T$. Curves have been visually fitted to the data. Sets of values of $[CuCl_2]_T$ and $[cnge]_T$ have been determined for ε_{obs} at the values 66, 67, 68, 69 and 70 $lmol^{-1}cm^{-1}$ (data in Appendix A). The plots of $[cnge]_T$ against $[CuCl_2]_T$ are illustrated in Figure 8.15. In agreement with equation 20 they are linear (corr.coeff's in the range 0.996 to 0.999), the intercepts on the $[cnge]_T$ axis and the gradients of the lines giving values of $\bar{n}$ and [cnge] (data in Appendix A).

Using these values of $\bar{n}$ and [cnge] the stability constants for the two cases when N=1 and N=2 have been determined; in Figure 8.16 $\bar{n}(1-n)^{-1}$ is plotted against [cnge], whilst in Figure 8.17 $(1-\bar{n})(2-\bar{n})^{-1}[cnge]^{-1}$ is plotted against $\bar{n}(2-\bar{n})^{-1}[cnge]^{-2}$.

For both analyses the points generated for ε_{obs} equal to 66 and 69 $lmol^{-1}cm^{-1}$ appear to fall on straight lines but those for ε_{obs} = 70 $lmol^{-1}cm^{-1}$ show considerable deviation from these lines implying that the data may not be linearly related. The validity of the points at ε_{obs} = 70$lmol^{-1}cm^{-1}$ could not be established since there was insufficient experimental data to extend the analysis to ε_{obs} greater than 70 $lmol^{-1}cm^{-1}$. Ignoring the points for ε_{obs} equal to 70 $lmol^{-1}cm^{-1}$, the plots of $\bar{n}(1-n)^{-1}$ against [cnge] gives a best straight line of gradient 795 (corr.coeff. 0.995) which, according to equation 22, is equal to K_1 (units $lmol^{-1}$). Similarly, the plot of $(1-\bar{n})(2-\bar{n})^{-1}[cnge]^{-1}$ against

FIGURE 8.14 Corresponding solutions: Plots of ε_{obs} at 820nm against $[cnge]_T$ at various $[CuCl_2]_T$

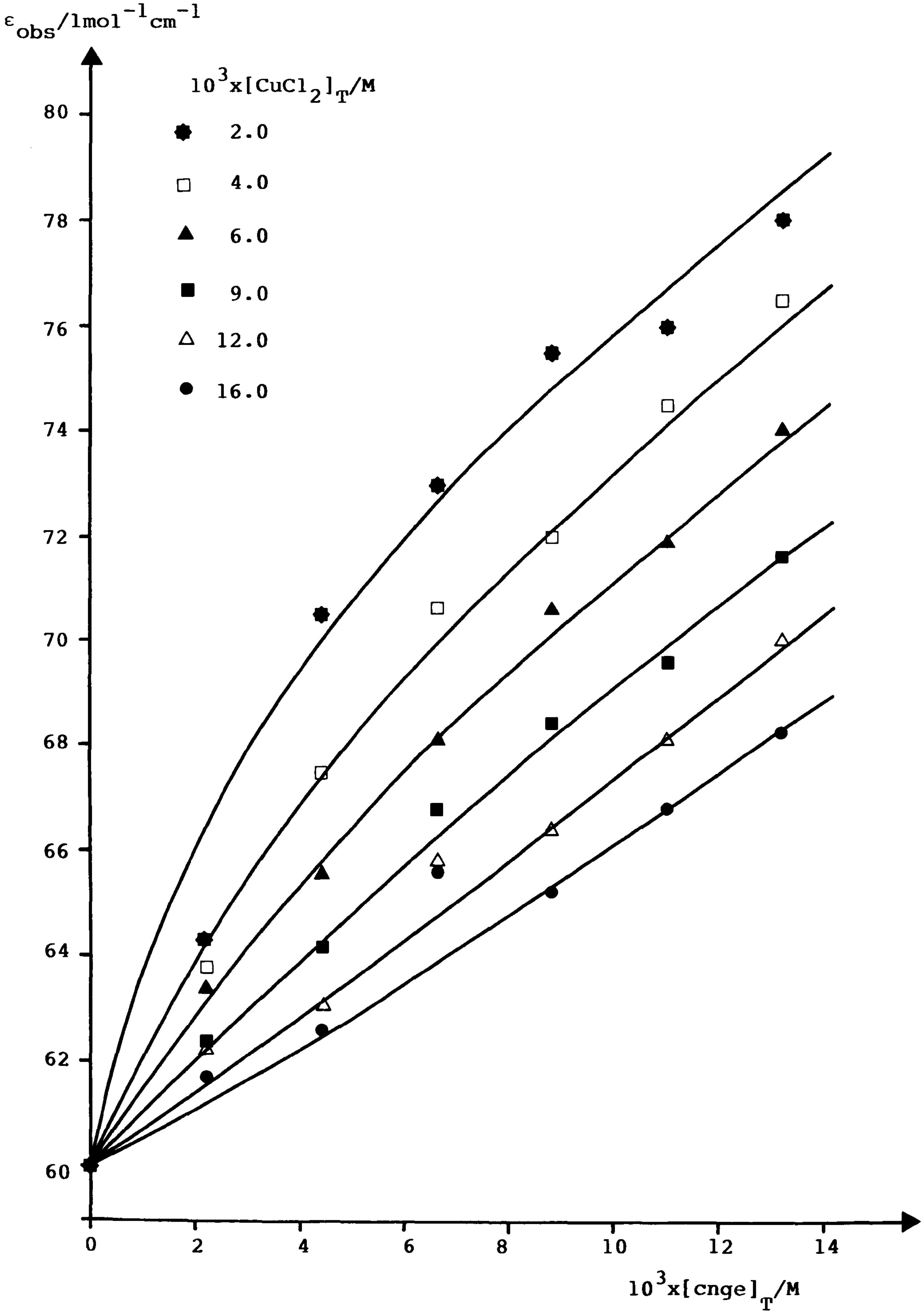


FIGURE 8.15 Corresponding solutions: Plots of $[\text{cnge}]_T$ against $[\text{CuCl}_2]_T$

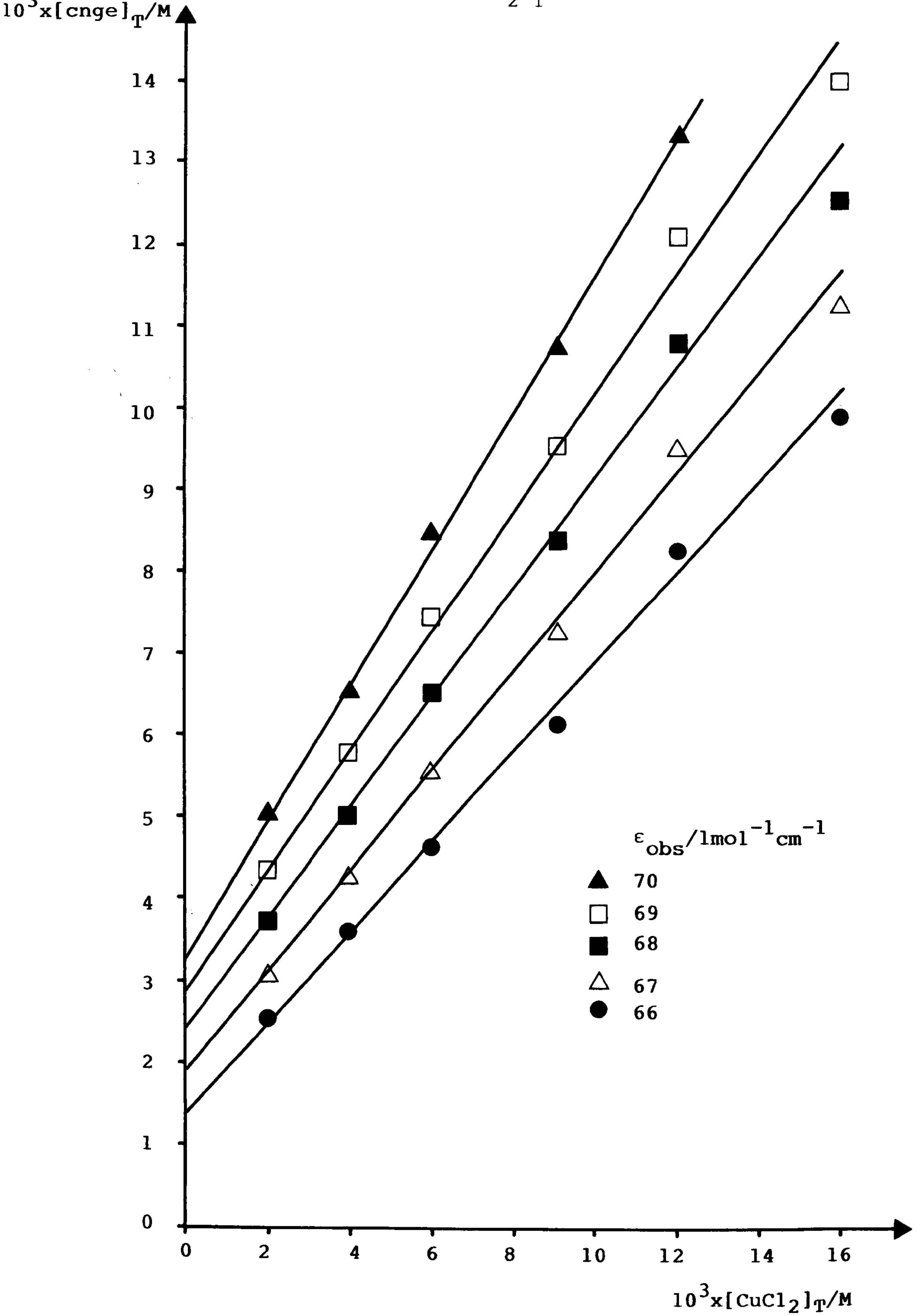


FIGURE 8.16 Corresponding solutions: plot of $\bar{n}(1-\bar{n})^{-1}$ against [cnge]

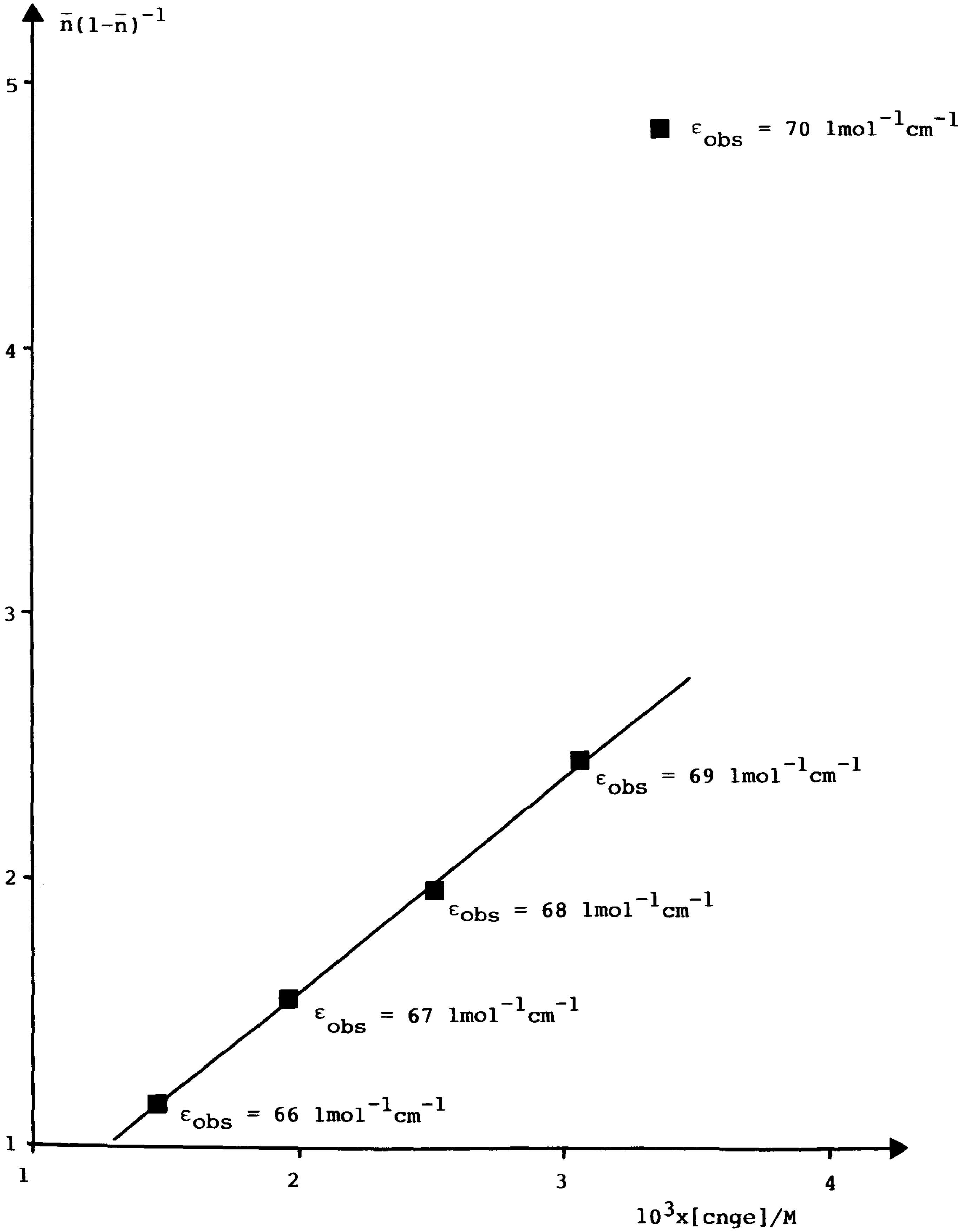
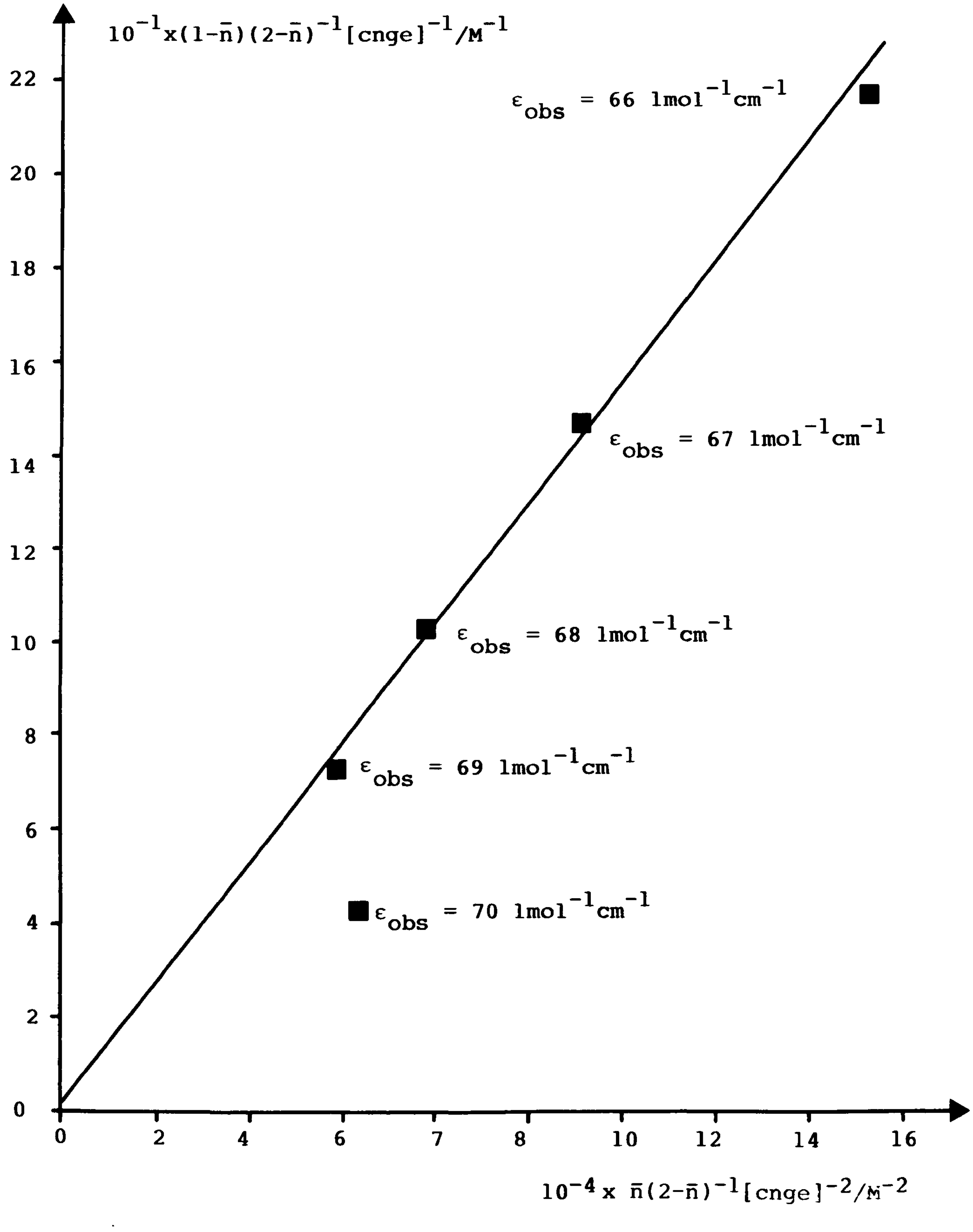


FIGURE 8.17 Corresponding solutions: plot of $(1-\bar{n})(2-\bar{n})^{-1}[\text{cnge}]^{-1}$ against $\bar{n}(2-\bar{n})^{-1}[\text{cnge}]^{-2}$



$\bar{n}(2-\bar{n})^{-1}[\text{cnge}]^{-2}$ (Figure 8.17) gives a best staight line (corr.coeff. 0.998) of gradient $1.24\text{x}10^{-3}$ and of ordinate intercept 4.7. Using equation 24 K_1 and K_2 are calculated to be 806 and -4.7 lmol^{-1} respectively.

The similar values of K_1 obtained from the two analyses and the small magnitude of K_2 suggest the sole formation of a mono cnge-copper(II) complex. However, if the data for ε_{obs} equal to 70 $\text{lmol}^{-1}\text{cm}^{-1}$ are included in the analysis, the plot of $(1-\bar{n})(2-\bar{n})^{-1}[\text{cnge}]^{-1}$ against $\bar{n}(2-\bar{n})^{-1}[\text{cnge}]^{-2}$ would give an increased gradient and a negative ordinate intercept which in turn imply a smaller K_1 value and a positive K_2 value. Hence, both mono and bis cnge-copper(II) complexes may be present in solution. The fact that the data for ε_{obs} equal to 70 $\text{lmol}^{-1}\text{cm}^{-1}$ differ considerably from the plot of $\bar{n}(1-\bar{n})^{-1}$ against [cnge] may provide additional evidence for the presence of the bis complex.

The inconclusive nature of the results may be attributable to the difficulties associated with the accurate measurement of the small absorbance changes which occur in these systems. Consideration of Figure 8.14 shows that the ε_{obs} values differ by no more than 10 $\text{lmol}^{-1}\text{cm}^{-1}$ at a given $[\text{cnge}]_T$ and by no more than 20 $\text{lmol}^{-1}\text{cn}^{-1}$ at a given $[\text{CuCl}_2]_T$. It is possible that the concentration ranges studed ($[\text{cnge}]_T$ from 2.21 to 13.21mM, $[\text{CuCl}_2]_T$ from 2.00 to 16.01mM and $[\text{cnge}]_T/[\text{CuCl}_2]_T$ from 0.14 to 6.6) are too restricted and more consistent data might be obtained from an extended study. Unfortunately time constraints did not permit such an extension.

During the course of the study of the $CuCl_2$-cnge-EtOH system, an investigation of the equilibrium constants for the formation of mono and bis(aOeu)-copper(II) complexes was envisaged using the techniques applied to the cnge-copper(II) system. The literature revealed that a similar study had been attempted by Dutta[68] in aqueous solutions. (In this reference the ligands are incorrectly termed alkylguanylureas.) Dutta's work demonstrated spectrophotometrically the formation of mono and bis aOeu copper(II) complexes by varying the pH of aqueous solutions containing $CuCl_2$ and [aOeuH]Cl. Formation of the blue mono aOeu complex was complete at pH 4.0, whilst formation of the red-violet bis aOeu complex was complete when the pH was increased to pH 6.8. Since the conditions employed in this investigation do not reflect those encountered in the system considered in this chapter, the study of the interaction of uncoordinated aOeu with copper(II) ions in ethanol was contemplated. Unfortunately, uncoordinated aOeu could not be synthesised (as noted in Chapter Six) and hence the study could not be pursued.

8.4 The Kinetics and Mechanism of the Ethanolysis Reactions Occurring in the $CuCl_2$-cnge-EtOH System

8.4.1 Introduction

The preliminary experiments revealed that by monitoring the UV-visible spectrum of an ethanol solution containing $CuCl_2$ and cnge, it was possible to follow the reactions occurring in solution (as illustrated in Figure 8.4). Extraction of viable kinetic data from the experimental data available did, however, prove to be more difficult than first envisaged.

The concurrence of the three λ_{max} values observed in Figure 8.4 with those found for $CuCl_2$, $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2$ in the presence of cnge (Table 8.1) implied the consecutive formation of these complexes. By monitoring, as a function of time, the changes in absorbance at these λ_{max} values, it was thought possible to evaluate the rate of decay or formation of the species giving rise to the absorptions and hence to evaluate reaction rates.

8.4.2 Experimental

(i) Chemicals and Apparatus

Stock ethanol solutions of $CuCl_2$ (29.98 and 60.57mM) and cnge (119.86 and 119.98mM) were prepared; the experimental apparatus was as described in Section 8.2.3(i).

(ii) Procedure

A background correction was performed (Section 8.2.3.(ii)) in the range 900-400nm. Aliquots of a $CuCl_2$ solution, a cnge solution and ethanol (Aml, Bml and Cml respectively) were mixed and the resulting solution transferred to the sample cell in the spectrometer. Absorbance measurements were made at 820, 715, 640 and

540nm every 10 minutes for at least 400 mins. The interval between measurements was then increased to 60 minutes and the measurements continued for at least a further 720 minutes. The contents of the sample cell were then transferred to a stoppered bottle and maintained at 20°C for several days. The absorbancies of this solution were then measured at the four specified wavelengths. The sample cell was washed and dried. The whole experiment was repeated several times using different aliquots of the reagents to obtain measurements for the range of $[CuCl_2]_T$:$[cnge]_T$ values shown below:

Experiment	$[CuCl_2]_T$/mM:$[cnge]_T$/mM	Experiment	$[CuCl_2]_T$/mM:$[cnge]_T$/mM
8.7	2:40	8.11	4:40
8.8	2:60	8.12	4:60
8.9	2:80	8.13	4:80
8.10	2:100	8.14	4:100

8.4.3 Results and Discussion

Changes in the absorptions at 820, 715, 640 and 540nm for experiments 8.10 and 8.14 are shown in Figures 8.18 and 8.19 respectively. The other six experiments exhibited near identical behaviour. All absorbance data are given in Appendix A. The Figures show the decay of the absorption at 820nm, the growth and then decay of the absorption at 640nm and the growth of the absorption at 540nm. The absorption at 715nm remains relatively constant until ~200 mins. when it starts to decrease.

FIGURE 8.18 Changes in the absorptions at 820, 715, 640 and 540nm for experiment 8.10

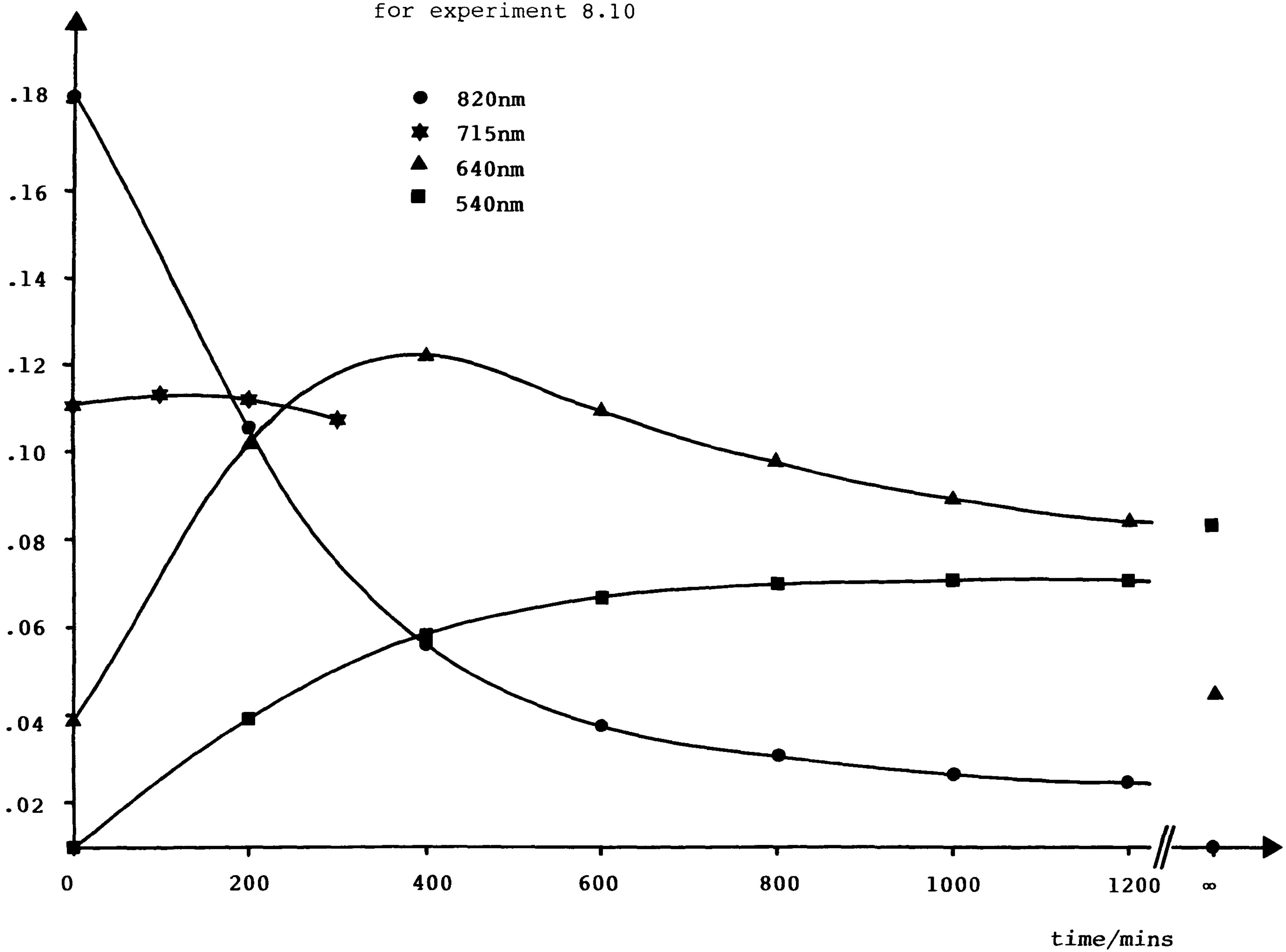
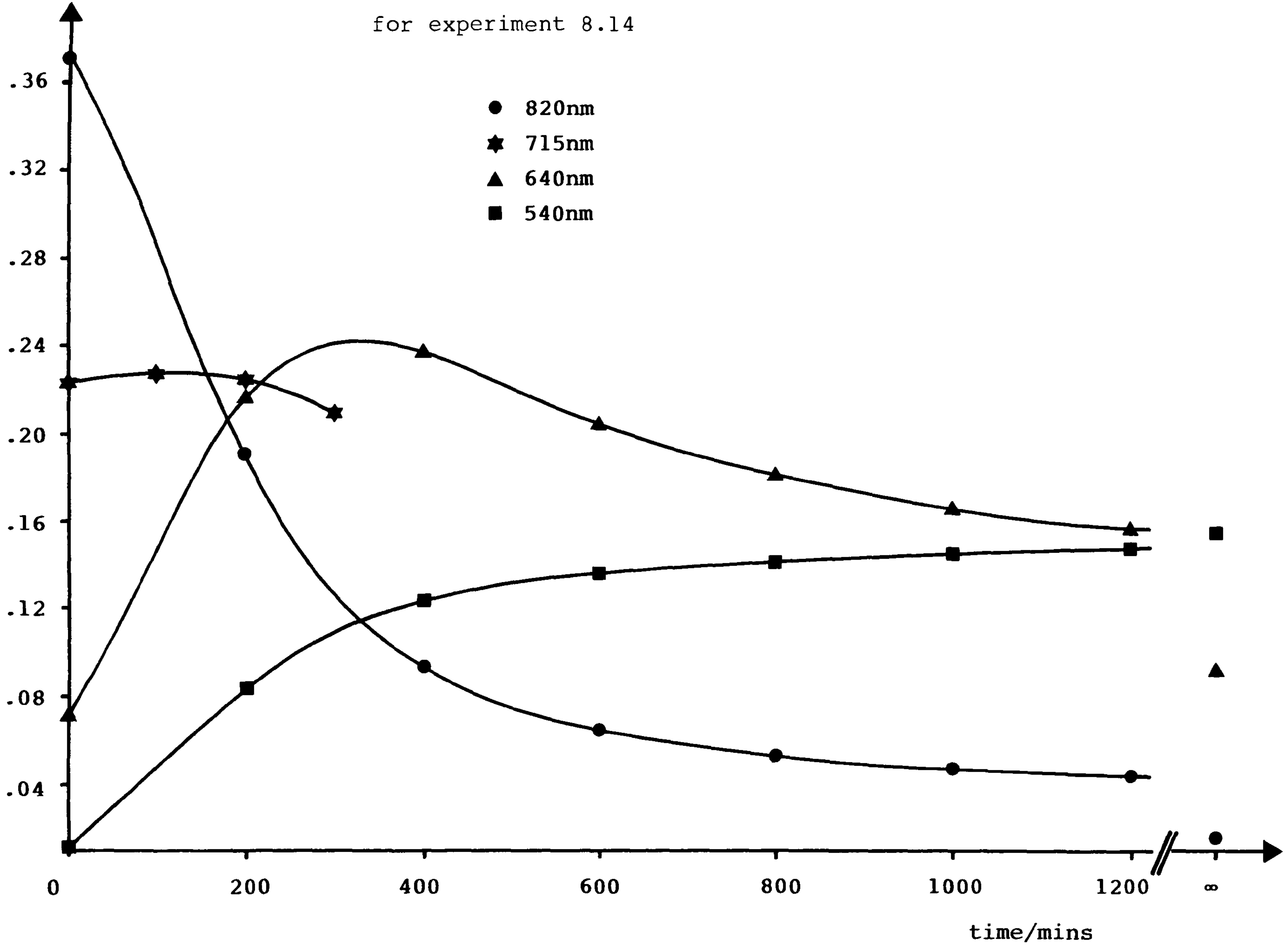


FIGURE 8.19 Changes in the absorptions at 820, 715, 640 and 640nm for experiment 8.14



Examination of the data at 820nm for all the experiments indicates that the times taken for the absorbancies to reach 50% of their initial values (defined as the half life) were very similar (Table 8.2) and gave an average of 234 minutes.

TABLE 8.2 Half lives of the absorption at 820nm

Experiment	$[CuCl_2]_T$/mM: $[cnge]_T$/mM	Initial Absorbance	50% of Initial Absorbance	Half Life /mins
8.7	2:40	0.174	0.087	245
8.8	2:60	0.184	0.092	250
8.9	2:80	0.180	0.090	235
8.10	2:100	0.182	0.091	235
8.11	4:40	0.353	0.177	225
8.12	4:60	0.354	0.177	250
8.13	4:80	0.374	0.187	225
8.14	4:100	0.371	0.186	210

Thus, at each $[CuCl_2]_T$ the half life and hence the reaction rate, is independent of $[cnge]_T$. The similarity in the half lives for the two sets of experiments at $[CuCl_2]_T$ = 2.0 and 4.0mM indicates that the rate is proportional to $[CuCl_2]_T$. It may be surmised that the reacting species is a copper(II)-cnge complex since under the conditions of the experiments (a vast excess of cnge) the concentration of such a complex will be virtually independent of $[cnge]_T$.

For a quantitative kinetic analysis, the adsorption data must be converted into concentration data. For this system the existence of two equilibria involving coordination of $CuCl_2$ and $[Cu(aOeu)Cl_2]$ by cnge as well as the formation of the intermediate and final products of the ethanolysis, complicates the situation such that a rigorous analysis cannot readily be undertaken. Consequently, simplification of the analysis was considered. Figure 8.4 clearly shows the presence of isosbestic points at 715 and 555nm. Since the presence of an isosbestic point generally indicates that the presence in solution of only two species with differing absorptions, it was assumed that the point at 715nm exists whilst the starting material and intermediate predominates (i.e. the concentration of the final product could be assumed to be negligible) and the point at 555nm exists whilst the intermediate and final product predominates (i.e. the concentration of the starting material could be assumed to be negligible).

Figures 8.18 and 8.19 illustrate that the isosbestic point at 715nm is maintained for ~200 mins. Thus for this section of the reaction the absorptions arising from the $[Cu(aOeu)_2]Cl_2$ in solution can be ignored and only the reaction of the copper(II)-cnge complex to form the mono-(aOeu)-copper(II) complex considered.

Figures 8.20 and 8.21 show the decay of the absorption at 820nm for all experiments up to 200

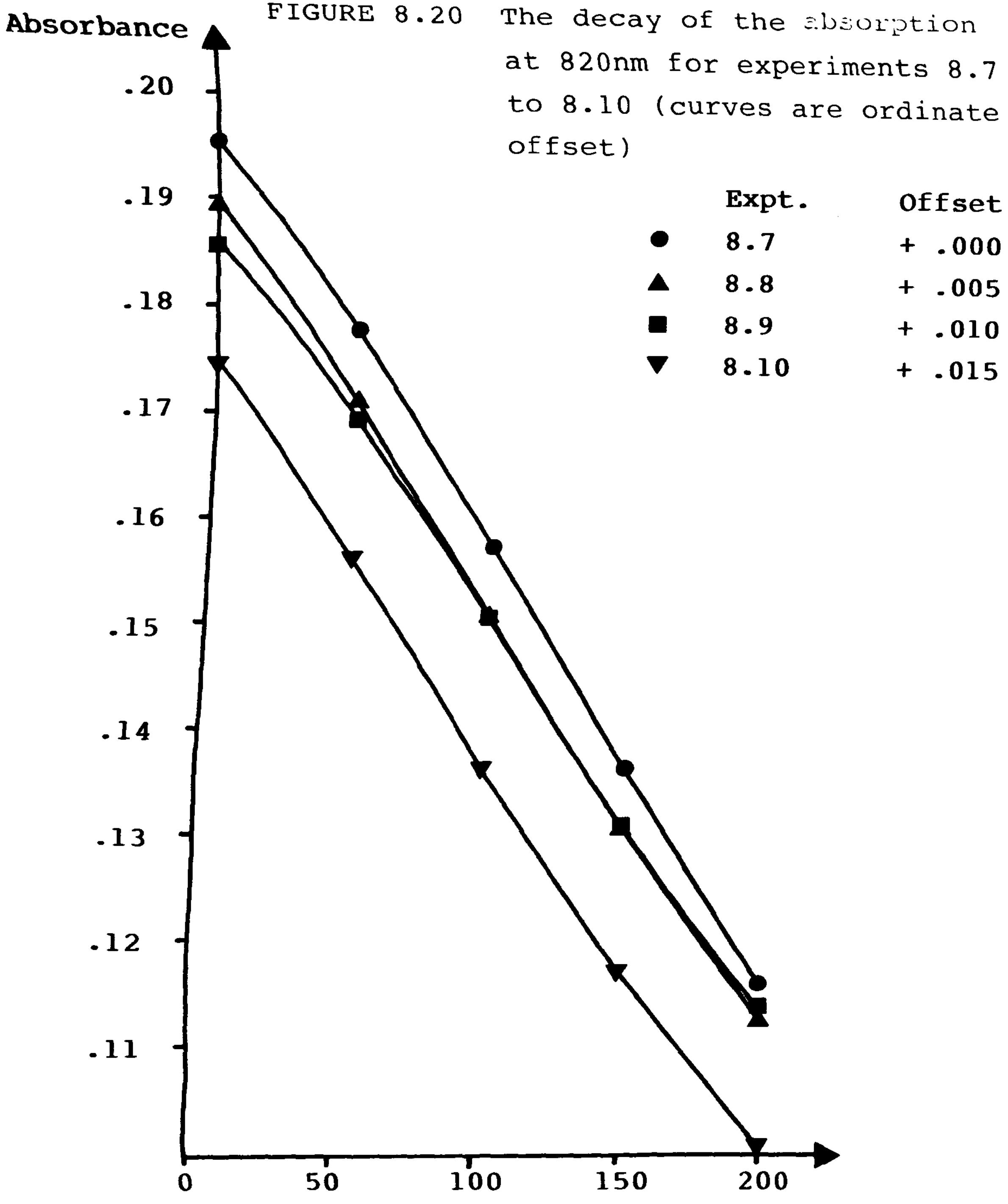


FIGURE 8.20 The decay of the absorption at 820nm for experiments 8.7 to 8.10 (curves are ordinate offset)

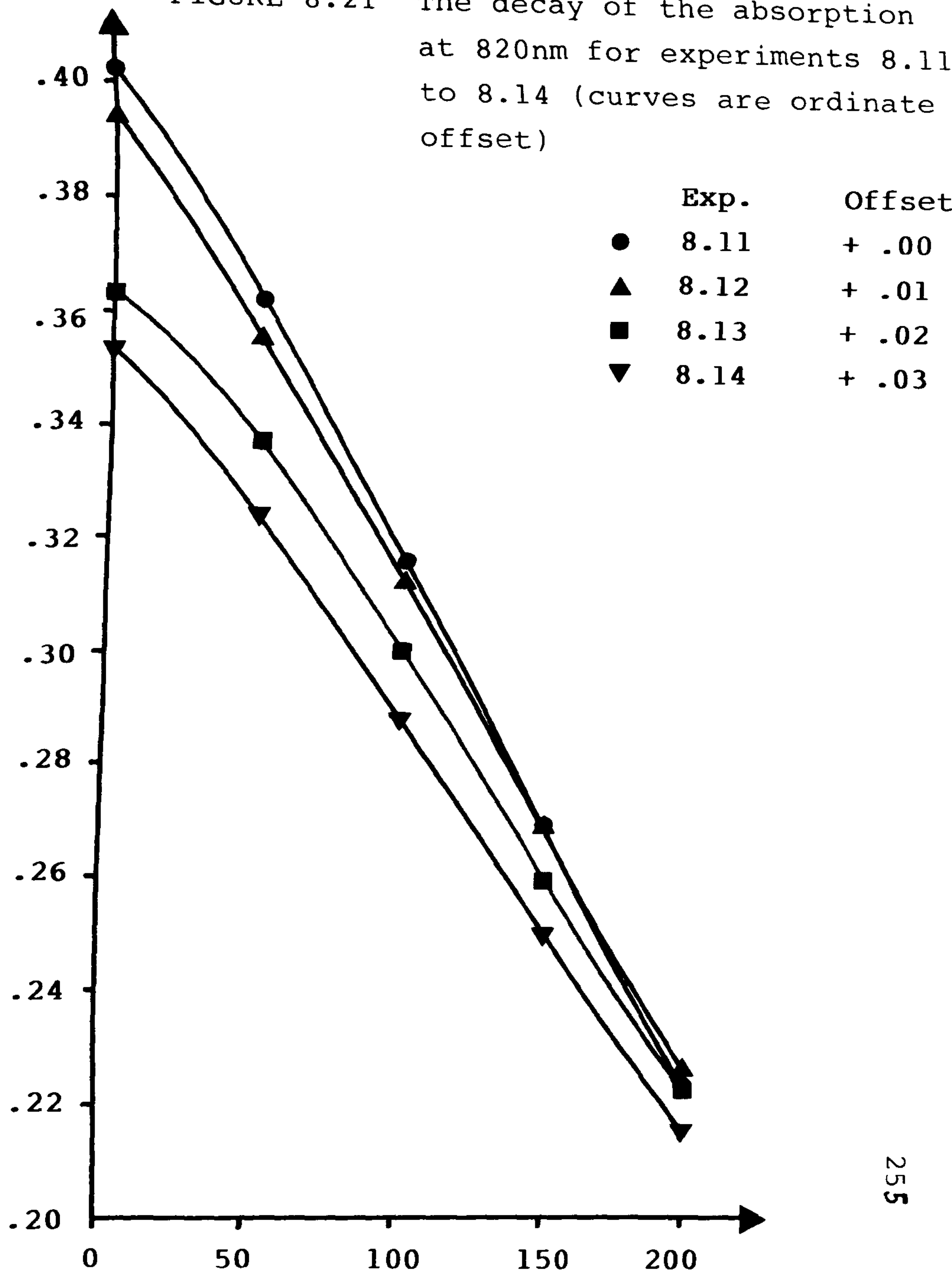


FIGURE 8.21 The decay of the absorption at 820nm for experiments 8.11 to 8.14 (curves are ordinate offset)

minutes. Surprisingly the decay is seen first to accelerate and then to slow down. This behaviour is not typical of a simple reaction (i.e. either first, second or third order) but it has been observed for series first order reactions exemplified by certain hydrolysis.[69]

Initially it was thought the two reactions may arise from the formation and decay of the copper(II) mono-(aOeu) intermediate complex and that the existence of the isosbestic point at 715nm was accidental. An attempted analysis of the data in Figures 8.20 and 8.21 on this basis (i.e. the three absorbing species have ε values close to those for ethanol solutions of $CuCl_2$, $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2Cl_2]$ in the presence of cnge) was, however, quite unsuccessful. They could only be rationalised by assuming two of the absorbing species to have ε values close to that of ethanol solutions of $CuCl_2$ + cnge and the third to have an ε value close to that of ethanol solutions of $[Cu(aOeu)Cl_2]_2$ + cnge. This implies that the formation of the copper(II) mono-(aOeu) complex from the copper(II)-cnge complex proceeds via an intermediate which has the same absorption properties as the initial copper(II)-cnge complex, thus generating the isosbestic point. It follows that the initial reaction must occur at a site remote from the copper(II) chromophore.

A curve fitting exercise was performed on the decay at 820nm for experiment 8.10 assuming series first order kinetics in an attempt to quantify the rate constants. This experiment was chosen for analysis since it has the greatest $[CuCl_2]_T$:$[cnge]_T$ ratio (i.e. 2:100). It is for this experiment the assumptions that $[cnge]_T$ remains constant and that the formation of the copper(II)-cnge complex is favourable, are most valid.

Time dependent values of absorbance for different rate constants were computed as follows. Concentrations of the copper(II)-cnge complex, the intermediate complex and the copper(II)-mono-aOeu complex {[Cu(cnge)], [I] and [Cu(aOeu)] respectively} were calculated (see below) and then the absorbance values for the complexes, derived using their ε values at 820nm, summed at regular time intervals.

The relationship used to calculate the concentrations of the different complexes are derived thus:

Consider the case

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

The differential equations are

$$\frac{d[A]}{dt} = -k_1[A] \qquad (32)$$

$$\frac{d[B]}{dt} = k_1[A]-k_2[B] \qquad (33)$$

$$\frac{d[C]}{dt} = k_2[B] \qquad (34)$$

Equation 32 integrates to give

$$[A] = [A]_o e^{-k_1 t} \tag{35}$$

Substituting equation 35 into 33 gives

$$\frac{d[B]}{dt} = k_1[A]_o e^{-k_1 t} - k_2[B] \tag{36}$$

Equation 36 intergrates to give

$$[B] = \frac{[A]_o\ k_1\ (e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1} \tag{37}$$

Also

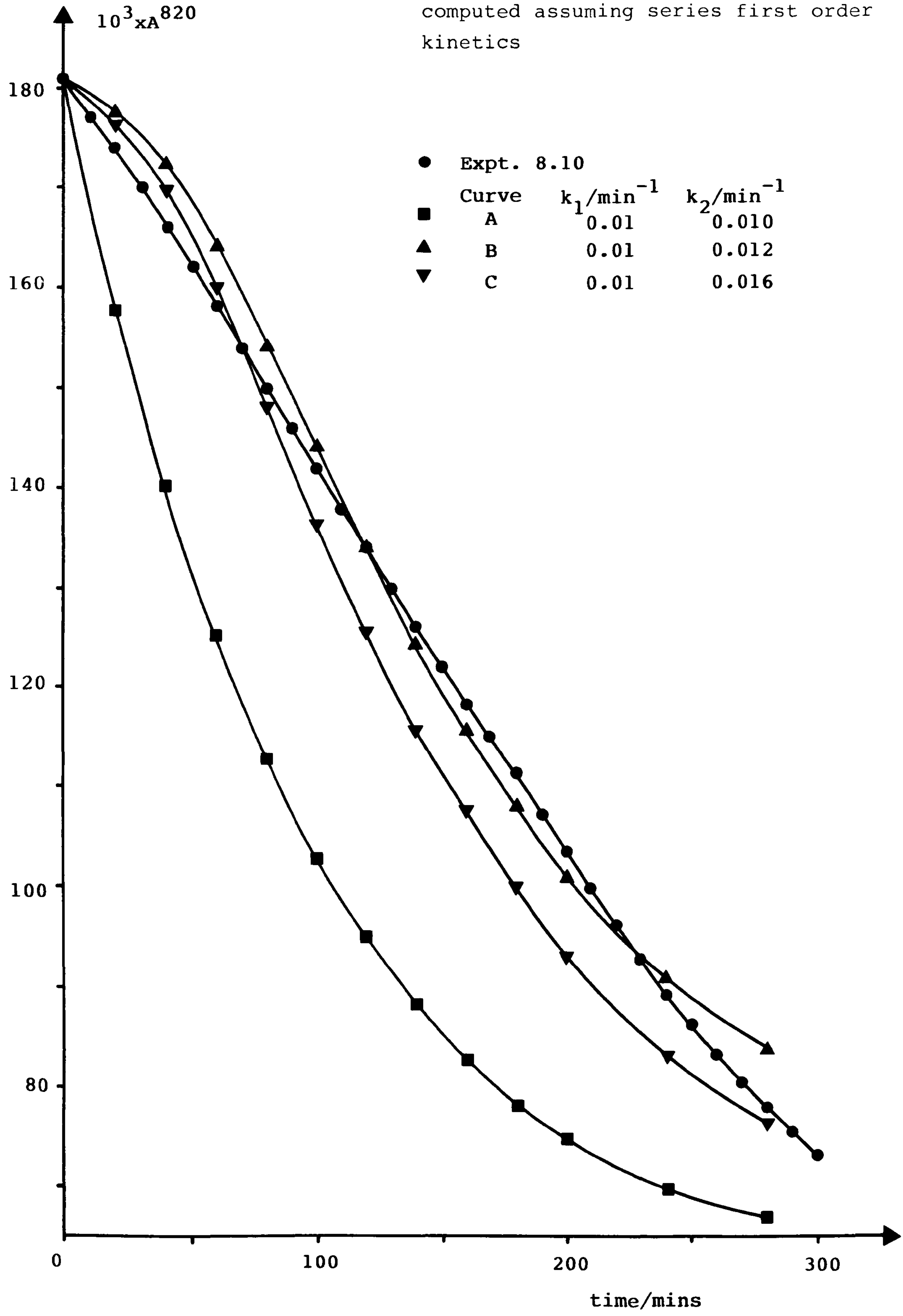
$$[A]+[B]+[C] = [A]_o \tag{38}$$

Rearranging $$[C] = [A]_o - [A] - [B] \tag{39}$$

thus, [A],[B],[C] can be calculated for various k_1 and k_2 values at various t values provided that $[A]_o$ (the initial concentration of A) is known. In the system under study [A] = [Cu(cnge)], [B]=[I] and [C]=[Cu(aOeu)].

Figure 8.22 shows the decay of the 820nm absorption for experiment 8.10 and several computed curves (A,B and C) in the 0 to 300 minute period. Values of k_1 and k_2 close to 0.01 min^{-1} gave curves which were most similar to the experimental data. For completeness the curve for $k_1=k_2=0.01$ (A) is given. As expected, it is exponential in form and shows considerable deviation from the experimental data. The best overall fit to the experimental data was found for $k_1=0.01$ and $k_2=0.012$ min^{-1} (curve B). A better fit in the 0-100 minute period

FIGURE 8.22 The decay of the absorption at 820nm for experiment 8.10 and curves computed assuming series first order kinetics



was achieved using k_1=0.01 and k_2=0.016 min^{-1} (curve C), however, this curve then deviated from the experimental data in the 100-200 minute region.

Both curves B and C after 200 minutes tend to absorbance values greater than the experimental data. This is in line with the formation of the bis(aOeu)-copper(II) complex at the expense of the mono-(aOeu)-copper(II) complex since the molar absorptivity of the bis complex is considerably lower than that of the mono complex at 820nm.

Clearly an ideal fit to the experimental data was not possible, implying that unambiguous values for the rate constant cannot be readily obtained. Nonetheless, the analysis is of value as it indicates that the ethanolysis reaction proceeds by series first order kinetics with values of k_1 and k_2 close to 0.01 min^{-1}. This conclusion introduces a further complication to the $CuCl_2$-cnge-EtOH system by increasing the number of species involved in the formation of the mono(aOeu) complex. Furthermore, it is not unreasonable to expect that the conversion of the mono(aOeu) complex to the bis(aOeu) follows a similar mechanism.

Unfortunately, this could not be confirmed as careful inspection of the spectral data associated with the isosbestic point at 555nm (Figure 8.4) indicated that detailed analysis was not possible as the rate of change of the absorption was too slow to be accurately monitored using the equipment available.

8.5 The $CuCl_2$-cnge-EtOH System: General Conclusions

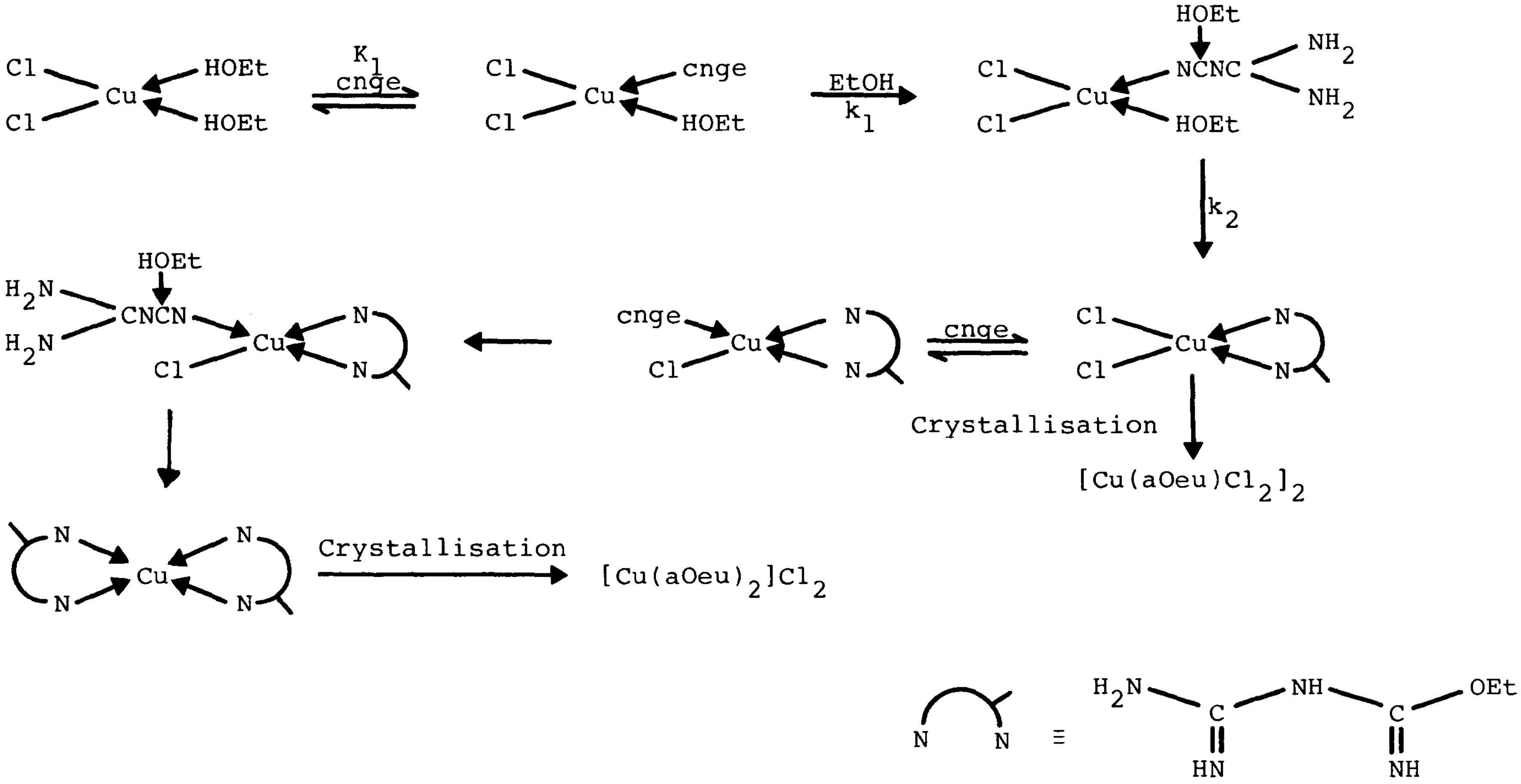
The structural and infrared studies described in Chapters Six and Seven allied with the UV-visible studies discussed in the present chapter, have gone some way to unravelling the processes that occur in ethanol solutions containing copper(II) chloride and cnge.

A mechanism consistent with the available data is presented in Scheme 8.1. The dissolution of anhydrous copper(II) chloride in ethanol results in the formation of a solvated copper(II) species. Chloride anions may be ligands (as shown) or may themselves be solvated. Addition of cnge to the solution displaces a solvent molecule and gives a mono(cnge)-copper(II) species. This process may be repeated to give a bis(cnge)-copper(II) species (not shown), however, the thermodynamic study (Section 8.3) implies that the mono(cnge) species will predominate. Ethanolysis then occurs in a two step process: nucleophilic attack by the ethanol on the nitrile carbon followed by proton transfer and rearrangement to produce a mono(aOeu)-copper(II) species.

Crystallisation from solution at this stage affords $[Cu(aOeu)Cl_2]_2$.

The ethanolysis process is then repeated by the addition of ethanol to cnge coordinated to a mono-(aOeu)-copper(II) species followed by rearrangement to give the bis(aOeu)-copper(II) complex. Cnge does not coordinate the bis complex since only axial sites on the copper(II) ion are available and hence the reaction

SCHEME 8.1 Reactions Occurring in the $CuCl_2$-cnge-EtOH System



ceases when all the copper(II) ions are converted to bis(aOeu) complexes.

Crystallisation at this stage affords $[Cu(aOeu)_2]Cl_2$.

The preliminary studies have simply revealed the complexity of the ethanolysis process; they seem to have revealed more questions than they have answered. Clearly, many more studies must be effected if true understanding and quantitative interpretation of the reaction are to be achieved.

APPENDIX A

NON-STRUCTURAL DATA

'OBEY' Computer Program for use with PE680 Software as described in Chapter Seven

```
SET FILID SP001

&L2 SET WAIT OFF

SCAN X,2300,1500,1.0

SAVE X,*

DIFF X Y

SAVE X,*

DO PAUSE,3000

DO PAUSE,600

&GOTO L2
```

Aliquot Data for Experiments 8.1, 8.2, 8.3 and 8.4

Experiments 8.1 and 8.2

$CuCl_2$ A/ml	10	9.0	8.0	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.0
cnge B/ml	0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
x_{cnge}	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0

Experiment 8.3

$CuCl_2$ A/ml	10.0	5.5	5.0	4.5	4.0	3.7	3.5	3.3	3.0	2.5
cnge B/ml	0.0	4.5	5.0	5.5	6.0	6.3	6.5	6.7	7.0	7.5
x_{cnge}	0.0	0.45	0.50	0.55	0.60	0.63	0.65	0.67	0.70	0.75

Experiment 8.4

$CuCl_2$ A/ml	10.0	8.0	7.0	6.0	5.5	5.0	4.5	4.0	3.5	3.0	2.0
cnge B/ml	0.0	2.0	3.0	4.0	4.5	5.0	5.5	6.0	6.5	7.0	8.0
x_{cnge}	0.0	0.20	0.30	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.80

Absorbance and Corrected Absorbance Data for Experiment 8.1

	λ/nm					
	800	820	840	860	880	x_{cnge}
A	0.608	0.676	0.730	0.773	0.798	0.0
	0.575	0.638	0.685	0.720	0.738	0.1
	0.525	0.578	0.618	0.646	0.660	0.2
	0.474	0.519	0.552	0.575	0.585	0.3
	0.418	0.456	0.483	0.499	0.507	0.4
	0.363	0.393	0.413	0.425	0.429	0.5
	0.305	0.328	0.342	0.349	0.350	0.6
	0.240	0.257	0.266	0.270	0.269	0.7
	0.172	0.182	0.186	0.188	0.186	0.8
	0.086	0.092	0.094	0.094	0.093	0.9
	0	0	0	0	0	1.0
Y_{calc}	0	0	0	0	0	0.0
	0.028	0.029	0.028	0.016	0.020	0.1
	0.039	0.037	0.034	0.033	0.022	0.2
	0.048	0.046	0.041	0.038	0.027	0.3
	0.053	0.051	0.045	0.040	0.028	0.4
	0.059	0.055	0.048	0.039	0.030	0.5
	0.062	0.057	0.050	0.036	0.031	0.6
	0.058	0.054	0.047	0.035	0.029	0.7
	0.050	0.047	0.040	0.028	0.027	0.8
	0.025	0.024	0.021	0.025	0.013	0.9
	0	0	0	0	0	1.0

Absorbance and Corrected Absorbance Data for Experiment 8.2

	λ/nm					
	800	820	840	860	880	x_{cnge}
	0.650	0.723	0.778	0.813	0.847	0.0
	0.624	0.688	0.734	0.771	0.790	0.1
	0.568	0.622	0.663	0.692	0.706	0.2
	0.540	0.585	0.616	0.640	0.650	0.3
	0.479	0.517	0.542	0.559	0.565	0.4
A	0.418	0.449	0.468	0.480	0.484	0.5
	0.359	0.382	0.393	0.401	0.400	0.6
	0.265	0.281	0.289	0.293	0.292	0.7
	0.090	0.199	0.203	0.203	0.200	0.8
	0.098	0.101	0.103	0.101	0.099	0.9
	0	0	0	0	0	1.0
	0	0	0	0	0	0.0
	0.039	0.037	0.034	0.039	0.028	0.1
	0.048	0.041	0.042	0.028	0.028	0.2
	0.085	0.079	0.071	0.071	0.033	0.3
	0.089	0.083	0.075	0.071	0.057	0.4
Y_{calc}	0.093	0.088	0.079	0.074	0.061	0.5
	0.099	0.093	0.082	0.076	0.061	0.6
	0.070	0.064	0.056	0.049	0.038	0.7
	0.060	0.054	0.047	0.040	0.031	0.8
	0.033	0.029	0.025	0.020	0.014	0.9
	0	0	0	0	0	1.0

Absorbance and Corrected Absorbance Data

for Experiment 8.3

	λ/nm					
	800	820	840	860	880	x_{cnge}
A	0.626	0.695	0.748	0.790	0.814	0.00
	0.405	0.439	0.461	0.475	0.480	0.45
	0.388	0.412	0.431	0.442	0.445	0.50
	0.349	0.375	0.391	0.400	0.402	0.55
	0.314	0.336	0.350	0.357	0.357	0.60
	0.294	0.314	0.325	0.332	0.331	0.63
	0.280	0.299	0.310	0.315	0.314	0.65
	0.273	0.290	0.300	0.304	0.303	0.67
	0.252	0.267	0.276	0.279	0.278	0.70
	0.210	0.223	0.229	0.231	0.230	0.75
	0	0	0	0	0	1.00
Y_{calc}	0	0	0	0	0	0.00
	0.061	0.057	0.050	0.041	0.032	0.45
	0.070	0.065	0.057	0.041	0.038	0.50
	0.067	0.062	0.054	0.045	0.036	0.55
	0.064	0.058	0.051	0.041	0.034	0.60
	0.062	0.057	0.048	0.040	0.030	0.63
	0.061	0.056	0.048	0.039	0.029	0.65
	0.066	0.061	0.053	0.043	0.034	0.67
	0.064	0.059	0.052	0.042	0.034	0.70
	0.054	0.049	0.042	0.034	0.027	0.75
	0	0	0	0	0	1.00

Absorbance and Corrected Absorbance Data for Experiment 8.4

	λ/nm					
	800	820	840	860	880	x_{cnge}
	1.342	1.488	1.608	1.708	1.764	0.00
	1.178	1.296	1.382	1.442	1.472	0.20
	1.068	1.168	1.238	1.286	1.306	0.30
	0.969	1.050	1.104	1.138	1.151	0.40
	0.897	0.970	1.016	1.045	1.052	0.45
A	0.841	0.904	0.944	0.966	1.070	0.50
	0.775	0.830	0.864	0.880	0.881	0.55
	0.715	0.782	0.790	0.801	0.798	0.60
	0.641	0.681	0.703	0.711	0.707	0.65
	0.616	0.652	0.672	0.679	0.673	0.70
	0.417	0.438	0.446	0.445	0.438	0.80
	0	0	0	0	0	1.00
	0	0	0	0	0	0.00
	0.104	0.106	0.096	0.076	0.061	0.20
	0.129	0.126	0.112	0.090	0.071	0.30
	0.164	0.157	0.139	0.113	0.093	0.40
	0.159	0.152	0.132	0.106	0.082	0.45
Y_{calc}	0.170	0.160	0.140	0.112	0.108	0.50
	0.171	0.160	0.140	0.111	0.087	0.55
	0.178	0.187	0.147	0.118	0.092	0.60
	0.171	0.160	0.140	0.113	0.090	0.65
	0.213	0.206	0.190	0.167	0.144	0.70
	1.149	0.140	0.124	0.103	0.085	0.80
	0	0	0	0	0	1.00

Aliquot Data for Experiment 8.5

Concentrations of stock solution of $CuCl_2$ = 36.06mM and of cnge = 39.64mM

A/ml	C/ml	$[CuCl_2]_T$/mM	A/ml	C/ml	$[CuCl_2]_T$/mM
B/ml=0.0, $[cnge]_T$/mM=0.00			B/ml=1.0, $[cnge]_T$/mM=2.21		
1.0	17.0	2.00	1.0	16.0	2.00
2.0	16.0	4.00	2.0	15.0	4.00
3.0	15.0	6.01	3.0	14.0	6.01
2.0	6.0	9.01	4.5	12.5	9.01
3.0	6.0	12.01	6.0	11.0	12.01
4.0	5.0	16.01	8.0	9.0	16.01
B/ml=2.0, $[cnge]_T$/mM=4.41			B/ml=3.0, $[cnge]_T$/mM=6.61		
1.0	15.0	2.00	1.0	14.0	2.00
2.0	14.0	4.00	2.0	13.0	4.00
3.0	13.0	6.01	3.0	12.0	6.01
4.5	11.5	9.01	4.5	10.5	9.01
6.0	10.0	12.01	6.0	9.0	12.01
8.0	8.0	16.01	8.0	7.0	16.01
B/ml=4.0, $[cnge]_T$/mM=8.81			B/ml=5.0, $[cnge]_T$/mM=11.01		
1.0	13.0	2.00	1.0	12.0	2.00
2.0	12.0	4.00	2.0	11.0	4.00
3.0	11.0	6.01	3.0	10.0	6.01
4.5	9.5	9.01	4.5	8.5	9.01
6.0	8.0	12.01	6.0	7.0	12.01
8.0	6.0	16.01	8.0	5.0	16.01
B/ml=6.0, $[cnge]_T$/mM=13.21					
1.0	11.0	2.00			
2.0	10.0	4.00			
3.0	9.0	6.01			
4.5	7.5	9.01			
6.0	6.0	12.01			
8.0	4.0	16.01			

Absorbance Data for Experiment 8.5

$[\mathrm{CuCl}_2]_T/\mathrm{mM}$	2.00	4.00	6.01	9.01	12.01	16.01	9.01 std
$[\mathrm{cnge}]_T/\mathrm{mM}=0.00$							
A^{820}	0.122	0.237	0.360	0.551	0.726	0.961	0.549
$\varepsilon^{820}_{obs}/\mathrm{lmol^{-1}cm^{-1}}$	61.0	59.0	60.0	61.0	60.5	60.0	60.9
$\mathrm{cnge}]_T/\mathrm{mM}=2.20$							
A^{820}	0.119	0.236	0.352	0.521	0.693	0.915	0.500
$\varepsilon^{820}_{obs}/\mathrm{lmol^{-1}cm^{-1}}$	59.5	59.0	58.7	57.8	57.7	57.1	55.5
$\mathrm{cnge}]_T/\mathrm{mM}=4.40$							
A^{820}	0.141	0.270	0.394	0.578	0.758	1.002	0.543
$\varepsilon^{820}_{obs}/\mathrm{lmol^{-1}cm^{-1}}$	70.5	67.5	65.6	64.2	63.1	62.6	60.2
$\mathrm{cnge}]_T/\mathrm{mM}=6.61$							
A^{820}	0.135	0.262	0.379	0.558	0.733	0.972	0.505
$\varepsilon^{820}_{obs}/\mathrm{lmol^{-1}cm^{-1}}$	67.5	65.5	63.1	61.9	61.0	60.7	56.0
$\mathrm{cnge}]_T/\mathrm{mM}=8.81$							
A^{820}	0.151	0.288	0.425	0.616	0.797	1.044	0.535
$\varepsilon^{820}_{obs}/\mathrm{lmol^{-1}cm^{-1}}$	75.5	72.0	70.7	68.4	66.4	65.2	59.4
$\mathrm{cnge}]_T/\mathrm{mM}=11.01$							
A^{820}	0.152	0.298	0.432	0.627	0.818	1.089	0.540
$\varepsilon^{820}_{obs}/\mathrm{lmol^{-1}cm^{-1}}$	76.0	74.5	71.9	69.6	68.1	66.8	59.9
$\mathrm{cnge}]_T/\mathrm{mM}=13.21$							
A^{820}	0.156	0.306	0.445	0.645	0.841	1.092	0.542
$\varepsilon^{820}_{obs}/\mathrm{lmol^{-1}cm^{-1}}$	78.0	76.5	74.0	71.6	70.0	68.2	60.2

Corresponding $[CuCl_2]_T$ and $[cnge]_T$ Values for Experiment 8.5

	ε_{obs}^{820}=66 $lmol^{-1}cm^{-1}$	ε_{obs}^{820}=67 $lmol^{-1}cm^{-1}$	ε_{obs}^{820}=68 $lmol^{-1}cm^{-1}$	ε_{obs}^{820}= 69 $lmol^{-1}cm^{-1}$	ε_{obs}^{820}=70 $lmol^{-1}cm^{-1}$
$[CuCl_2]_T$/mM	$[cnge]_T$/mM	$[cnge]_T$/mM	$[cnge]_T$/mM	$[cnge]_T$/mM	$[cnge]_T$/mM
2.00	2.55	3.10	3.70	4.35	5.05
4.00	3.60	4.30	5.00	5.75	6.55
6.01	4.65	5.55	6.50	7.45	8.50
9.01	6.10	7.25	8.40	9.55	10.75
12.01	8.25	9.50	10.80	12.10	13.35
16.01	9.90	11.25	12.60	14.00	-

Corresponding [cnge] and $\bar{n}$ Values for Experiment 8.5

ε_{obs}^{820}	[cnge]	$\bar{n}$
66	1.46	0.537
67	1.96	0.596
68	2.50	0.653
69	3.07	0.710
70	3.35	0.831

Aliquot and Absorbance Data for Experiment 8.6

Concentration of stock solution of $CuCL_2$ = 36.06mM

A/ml	C/ml	$[CuCl_2]_T$	A^{880nm}	A^{820nm}
1.0	17.0	2.01	0.144	0.123
2.0	16.0	4.01	0.286	0.246
3.0	15.0	6.01	0.429	0.370
2.0	7.0	8.01	0.572	0.494
2.5	6.5	10.02	0.716	0.617
3.0	6.0	12.02	0.858	0.740
3.5	5.5	14.02	1.001	0.862
4.0	5.0	16.02	1.145	0.985
4.5	4.5	18.02	1.288	1.109
5.0	4.0	20.03	1.432	1.233

Aliquot Data for Experiments 8.7 to 8.14

$[CuCl_2]$ stock soln. = 29.98mM, [cnge] stock soln. = 119.86mM

Experiment Number	A	B	C	$[CuCl_2]_T$/mM	$[cnge]_T$/mM
8.7	1.3	6.7	12.0	1.95	40.15
8.8	1.3	10.0	8.7	1.95	59.93
8.9	1.3	13.3	5.0	1.95	79.71
8.10	1.3	16.7	2.0	1.95	100.08

$[CuCl_2]$ stock soln. = 60.57mM, [cnge] stock soln. = 119.98mM

Experiment Number	A	B	C	$[CuCl_2]_T$/mM	$[cnge]_T$/mM
8.11	1.3	6.7	12.0	3.93	40.19
8.12	1.3	10.0	8.7	3.93	59.99
8.13	1.3	13.3	5.4	3.93	79.78
8.14	1.3	16.7	2.0	3.93	100.20

Absorbance Data For Experiment 8.7 $[CuCl_2]_T$:$[cnge]_T$ 2:40mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.174	.033	.011	.101
10	.171	.037	.013	.102
20	.168	.041	.014	.102
30	.164	.045	.016	.103
40	.160	.048	.018	.104
50	.156	.052	.019	.105
60	.152	.056	.021	.106
70	.149	.060	.023	.106
80	.145	.064	.024	.107
90	.141	.067	.026	.107
100	.137	.071	.027	.108
110	.133	.074	.029	.108
120	.129	.078	.031	.109
130	.125	.081	.032	.110
140	.122	.085	.034	.110
150	.118	.088	.035	.111
160	.114	.091	.037	.111
170	.111	.094	.038	.111
180	.107	.097	.040	.112
190	.104	.100	.041	.112
200	.100	.103	.043	.112
210	.097	.105	.044	.112
220	.094	.108	.045	.112
230	.091	.110	.047	.112
240	.088	.112	.048	.112
250	.085	.114	.049	.112
260	.082	.115	.050	.112
270	.080	.117	.051	.111
280	.077	.118	.052	.111
290	.075	.119	.053	.110
300	.073	.120	.055	.110
310	.071	.120	.055	.109
320	.069	.121	.056	.108
330	.067	.121	.057	.108
340	.065	.121	.058	.107
350	.063	.121	.059	.106
360	.062	.121	.059	.105
370	.060	.121	.060	.104
380	.059	.121	.061	.103
390	.058	.120	.062	.102
450	.051	.117	.065	.096
510	.047	.113	.067	.091
570	.043	.109	.069	.086
630	.040	.105	.071	.082
690	.038	.102	.072	.078
750	.036	.099	.072	.075
810	.034	.096	.073	.072
870	.033	.094	.074	.069
930	.032	.091	.074	.067
990	.031	.090	.075	.065
1050	.030	.088	.075	.063
1110	.029	.086	.076	.062
1170	.028	.085	.076	.060
Final	.009	.047	.081	.023

Absorbance Data For Experiment 8.8 $[CuCl_2]_T:[cnge]_T$ 2:60mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.182	.037	.013	.108
10	.179	.040	.015	.109
20	.175	.044	.017	.109
30	.171	.047	.018	.110
40	.168	.051	.020	.110
50	.164	.054	.021	.111
60	.160	.058	.023	.111
70	.157	.061	.024	.112
80	.153	.065	.026	.112
90	.149	.068	.027	.113
100	.145	.072	.029	.113
110	.141	.075	.030	.113
120	.137	.079	.032	.114
130	.133	.082	.033	.114
140	.130	.085	.035	.114
150	.126	.088	.036	.115
160	.122	.092	.038	.115
170	.118	.095	.039	.115
180	.115	.098	.041	.115
190	.111	.100	.042	.115
200	.108	.103	.044	.115
210	.104	.106	.045	.115
220	.101	.108	.046	.115
230	.098	.111	.048	.115
240	.095	.113	.049	.115
250	.092	.115	.050	.115
260	.089	.117	.051	.115
270	.086	.118	.053	.114
280	.083	.120	.054	.114
290	.080	.121	.055	.114
300	.078	.122	.056	.113
310	.076	.123	.057	.112
320	.074	.124	.058	.112
330	.071	.125	.059	.111
340	.070	.125	.060	.110
350	.068	.125	.061	.109
360	.066	.126	.061	.109
370	.064	.125	.062	.108
380	.063	.125	.063	.107
390	.061	.125	.064	.106
400	.060	.125	.064	.105
460	.053	.122	.067	.099
796	.036	.102	.076	.076
856	.035	.100	.077	.073
916	.033	.097	.078	.071
976	.032	.095	.078	.069
1036	.031	.093	.079	.067
1096	.030	.092	.079	.065
1156	.030	.090	.080	.064
1216	.029	.089	.080	.062
Final	.007	.043	.081	.020

Absorbance Data For Experiment 8.9 $[CuCl_2]_T:[cnge]_T$ 2:80mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.180	.036	.010	.109
10	.177	.040	.012	.109
20	.173	.043	.013	.110
30	.169	.047	.015	.110
40	.165	.050	.016	.110
50	.161	.054	.018	.110
60	.157	.057	.019	.111
70	.153	.061	.021	.111
80	.149	.064	.022	.111
90	.145	.068	.024	.111
100	.141	.071	.025	.112
110	.137	.075	.027	.112
120	.133	.078	.029	.112
130	.129	.082	.030	.112
140	.125	.085	.032	.112
150	.121	.088	.033	.112
160	.117	.091	.035	.113
170	.113	.094	.036	.113
180	.109	.097	.038	.113
190	.105	.100	.039	.113
200	.102	.103	.040	.112
210	.098	.105	.042	.112
220	.095	.107	.043	.112
230	.091	.110	.044	.112
240	.088	.112	.046	.112
250	.085	.114	.047	.111
260	.082	.115	.048	.111
270	.079	.117	.049	.110
280	.077	.118	.050	.110
290	.074	.119	.052	.109
300	.072	.120	.052	.108
310	.070	.121	.053	.108
320	.068	.121	.054	.107
330	.066	.122	.055	.106
340	.063	.122	.056	.105
350	.062	.122	.057	.104
360	.060	.122	.057	.103
370	.058	.122	.058	.102
380	.057	.122	.059	.101
390	.056	.121	.059	.100
400	.054	.121	.060	.099
460	.048	.117	.063	.093
520	.043	.113	.065	.088
580	.040	.109	.067	.083
640	.037	.106	.068	.079
700	.035	.102	.069	.075
760	.033	.099	.070	.072
820	.031	.097	.071	.070
880	.030	.094	.072	.067
940	.029	.092	.072	.065
1000	.028	.090	.073	.063
1060	.027	.088	.073	.061
1120	.026	.086	.074	.059
1180	.025	.085	.074	.058
Final	.008	.047	.084	.023

Absorbance Data For Experiment 8.10 $[CuCl_2]_T$:$[cnge]_T$ 2:100mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.181	.038	.010	.111
10	.177	.041	.011	.111
20	.174	.044	.013	.111
30	.170	.047	.014	.112
40	.166	.050	.016	.112
50	.162	.054	.017	.112
60	.158	.057	.019	.112
70	.154	.060	.020	.112
80	.150	.064	.021	.112
90	.146	.067	.023	.112
100	.142	.070	.025	.113
110	.138	.074	.026	.113
120	.134	.077	.028	.113
130	.130	.080	.029	.113
140	.126	.083	.031	.113
150	.122	.087	.032	.113
160	.118	.090	.034	.113
170	.115	.093	.035	.113
180	.111	.096	.036	.113
190	.107	.098	.038	.112
200	.103	.101	.039	.112
210	.100	.104	.041	.112
220	.096	.106	.042	.112
230	.093	.108	.043	.112
240	.090	.110	.045	.111
250	.087	.112	.046	.111
260	.084	.114	.047	.110
270	.081	.116	.048	.110
280	.078	.117	.049	.109
290	.076	.118	.050	.109
300	.073	.119	.051	.108
310	.071	.120	.052	.107
320	.069	.121	.053	.107
330	.067	.121	.054	.106
340	.065	.122	.055	.105
350	.063	.122	.055	.104
360	.061	.122	.056	.103
370	.059	.122	.057	.102
380	.058	.122	.057	.101
390	.056	.122	.058	.100
450	.049	.119	.061	.094
510	.044	.115	.064	.089
570	.041	.111	.066	.084
630	.038	.108	.067	.080
690	.035	.104	.069	.077
750	.033	.101	.070	.073
810	.032	.098	.070	.070
870	.030	.095	.070	.067
930	.028	.093	.070	.065
990	.027	.090	.071	.063
1050	.026	.088	.071	.061
1110	.025	.087	.071	.061
1170	.025	.085	.072	.059
Final	.008	.047	.084	.023

Absorbance Data For Experiment 8.11 $[CuCl_2]_T$:$[cnge]_T$ 4:40mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.353	.060	.012	.198
10	.349	.064	.014	.198
20	.344	.070	.016	.199
30	.338	.076	.019	.202
40	.332	.081	.022	.202
50	.325	.087	.024	.203
60	.319	.094	.026	.204
70	.312	.100	.029	.205
80	.305	.107	.032	.207
90	.298	.113	.035	.208
100	.290	.120	.038	.209
110	.283	.127	.040	.210
120	.275	.134	.043	.212
130	.268	.141	.046	.212
140	.260	.147	.049	.214
150	.253	.154	.052	.215
160	.245	.161	.055	.216
170	.237	.167	.058	.216
180	.230	.174	.061	.218
190	.223	.179	.064	.218
200	.215	.186	.067	.219
210	.208	.191	.070	.219
220	.201	.196	.072	.220
230	.194	.202	.075	.220
240	.187	.206	.078	.220
250	.181	.211	.080	.220
260	.174	.215	.083	.220
270	.168	.218	.085	.219
280	.163	.222	.088	.219
290	.157	.225	.090	.217
300	.152	.227	.092	.217
310	.147	.229	.094	.215
320	.142	.230	.097	.214
330	.137	.231	.098	.213
340	.133	.234	.100	.211
350	.129	.233	.103	.209
360	.125	.233	.104	.207
370	.121	.232	.106	.205
380	.118	.232	.108	.203
390	.115	.231	.109	.200
400	.112	.230	.110	.198
445	.101	.225	.115	.188
505	.089	.216	.121	.175
565	.081	.206	.126	.164
625	.074	.198	.129	.154
685	.069	.190	.132	.146
745	.064	.184	.134	.138
805	.061	.178	.136	.132
865	.058	.174	.138	.127
925	.055	.168	.139	.122
985	.052	.165	.141	.117
1045	.050	.160	.142	.113
1105	.049	.157	.143	.110
1165	.047	.154	.144	.107
Final	.016	.094	.153	.047

Absorbance Data For Experiment 8.12 $[CuCl_2]_T:[cnge]_T$ 4:60mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.354	.059	.007	.201
10	.351	.063	.009	.203
20	.346	.067	.010	.204
30	.340	.072	.012	.204
40	.335	.078	.015	.205
50	.328	.084	.017	.206
60	.321	.090	.020	.207
70	.314	.096	.023	.207
80	.307	.103	.025	.208
90	.299	.109	.028	.209
100	.292	.116	.031	.210
110	.284	.123	.034	.211
120	.276	.129	.037	.211
130	.268	.136	.040	.212
140	.260	.143	.043	.213
150	.252	.149	.046	.213
160	.244	.156	.049	.214
170	.236	.163	.052	.214
180	.228	.169	.055	.215
190	.220	.175	.058	.215
200	.213	.181	.061	.215
210	.205	.187	.063	.215
220	.198	.192	.066	.215
230	.191	.197	.069	.215
240	.183	.202	.072	.215
250	.177	.207	.075	.215
260	.170	.211	.077	.214
270	.164	.215	.080	.213
280	.158	.218	.082	.212
290	.152	.221	.085	.211
300	.146	.223	.087	.210
310	.141	.225	.089	.209
320	.136	.226	.091	.207
330	.131	.227	.093	.205
340	.127	.228	.095	.204
350	.123	.228	.097	.202
360	.119	.229	.098	.200
370	.115	.228	.100	.197
380	.112	.228	.101	.195
390	.109	.227	.103	.193
400	.106	.226	.104	.191
460	.091	.218	.111	.177
520	.081	.209	.116	.165
580	.073	.200	.120	.154
640	.067	.192	.123	.145
700	.062	.185	.126	.137
760	.058	.178	.128	.131
820	.055	.172	.130	.124
880	.052	.167	.131	.119
940	.049	.163	.132	.115
1000	.047	.158	.133	.110
1060	.045	.155	.134	.106
Final	.014	.088	.161	.041

Absorbance Data For Experiment 8.13 $[CuCl_2]_T:[cnge]_T$ 4:80mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.374	.070	.015	.219
10	.366	.076	.018	.221
20	.360	.081	.021	.221
30	.353	.088	.024	.222
40	.345	.094	.026	.222
50	.337	.101	.030	.223
60	.328	.109	.032	.223
70	.320	.116	.036	.224
80	.311	.124	.039	.225
90	.302	.131	.043	.225
100	.293	.139	.046	.226
110	.285	.147	.049	.226
120	.275	.154	.053	.227
130	.266	.162	.056	.227
140	.257	.169	.060	.228
150	.248	.177	.063	.228
160	.238	.184	.067	.228
170	.230	.191	.070	.228
180	.221	.197	.074	.228
190	.213	.204	.077	.228
200	.204	.209	.080	.228
210	.196	.215	.083	.227
220	.188	.220	.087	.227
230	.181	.225	.089	.226
240	.173	.229	.092	.225
250	.166	.232	.095	.224
260	.160	.235	.097	.222
270	.154	.237	.100	.221
280	.148	.240	.102	.219
290	.142	.241	.104	.217
300	.137	.242	.106	.215
310	.132	.243	.108	.213
320	.128	.243	.110	.211
330	.123	.243	.112	.208
340	.120	.242	.113	.206
350	.116	.242	.115	.203
360	.113	.240	.116	.201
370	.109	.240	.117	.198
380	.106	.238	.119	.196
390	.104	.236	.120	.193
400	.101	.235	.121	.190
450	.090	.226	.126	.178
510	.081	.216	.130	.166
570	.074	.206	.133	.155
630	.068	.198	.136	.147
690	.064	.191	.138	.139
750	.060	.185	.140	.133
810	.057	.179	.141	.127
870	.054	.174	.143	.122
930	.052	.169	.144	.117
990	.050	.165	.145	.113
1050	.048	.162	.146	.110
1110	.046	.158	.146	.107
1170	.045	.155	.147	.104
Final	.012	.087	.156	.039

Absorbance Data For Experiment 8.14 $[CuCl_2]_T:[cnge]_T$ 4:100mM

Time/mins	Absorbance			
	820nm	640nm	540nm	715nm
0	.371	.070	.013	.222
10	.365	.076	.016	.223
20	.358	.083	.019	.224
30	.350	.089	.022	.224
40	.341	.097	.025	.224
50	.333	.104	.028	.225
60	.324	.111	.032	.225
70	.315	.119	.035	.226
80	.305	.127	.039	.226
90	.296	.135	.042	.226
100	.286	.144	.046	.227
110	.276	.151	.050	.227
120	.266	.159	.053	.227
130	.257	.167	.057	.227
140	.247	.175	.061	.228
150	.238	.182	.064	.227
160	.228	.190	.068	.227
170	.219	.196	.072	.227
180	.210	.203	.075	.227
190	.201	.209	.078	.226
200	.193	.215	.082	.226
210	.185	.220	.085	.225
220	.177	.225	.088	.224
230	.169	.229	.091	.223
240	.162	.233	.094	.221
250	.155	.236	.096	.220
260	.149	.238	.099	.218
270	.143	.240	.101	.216
280	.137	.242	.104	.214
290	.132	.243	.106	.212
300	.127	.243	.108	.210
310	.123	.243	.110	.207
320	.119	.243	.112	.205
330	.115	.243	.113	.202
340	.111	.242	.115	.200
350	.108	.240	.116	.197
360	.105	.239	.118	.195
370	.102	.238	.119	.192
380	.099	.236	.120	.189
390	.097	.235	.121	.187
400	.094	.233	.122	.184
440	.086	.226	.126	.175
500	.077	.216	.130	.163
560	.070	.206	.134	.153
620	.065	.198	.136	.144
680	.061	.191	.138	.137
740	.057	.185	.140	.130
800	.054	.179	.142	.125
860	.052	.174	.143	.120
920	.050	.170	.145	.116
980	.048	.166	.146	.112
1040	.046	.162	.146	.109
1100	.045	.159	.147	.106
1160	.043	.156	.148	.103
Final	.014	.092	.155	.043

Computed Values for the Decay of the 820nm Absorption

A^{820} values calculated using ε^{820} for Cu(cnge) and I = 90.5 $lmol^{-1}cm^{-1}$ and for Cu(aOeu) = 29.0 $lmol^{-1}cm^{-1}$

t/mins	0	20	40	60	80	100	120	140	160	180	200	240	280
$k_1=k_2$ = 0.01 min^{-1}													
[Cu(cnge)]/mM	2.0	1.64	1.34	1.10	0.90	0.74	0.60	0.49	0.40	0.33	0.27	0.18	0.15
[I]/mM	0	0	0	0	0	0	0	0	0	0	0	0	0
[Cu(aOeu)]/mM	0	0.34	0.66	0.90	1.10	1.26	1.40	1.51	1.60	1.67	1.73	1.82	1.85
$10^3 x A^{820}$	181	158	141	126	113	104	95	88	83	78	75	69	67
k_1 = 0.01, k_2 = 0.012													
[Cu(cnge)]/mM	2.0	1.64	1.34	1.10	0.40	0.74	0.60	0.49	0.40	0.33	0.27	0.18	0.15
[I]/mM	0	0.32	0.51	0.62	0.66	0.67	0.64	0.61	0.55	0.50	0.44	0.35	0.27
[Cu(aOeu)]/mM	0	0.04	0.15	0.28	0.44	0.59	0.76	0.90	1.05	1.17	1.29	1.47	1.58
$10^3 x A^{820}$	181	178	172	164	154	144	134	125	116	108	101	91	84
k_1 = 0.01, k_2 0.016													
[Cu(cnge)]/mM	2.0	1.64	1.34	1.10	0.90	0.74	0.60	0.49	0.40	0.33	0.27	0.18	0.12
[I]/mM	0	0.31	0.48	0.55	0.57	0.55	0.51	0.47	0.42	0.36	0.31	0.23	0.17
[Cu(aOeu)]/mM	0	0.05	0.18	0.35	0.53	0.71	0.89	1.04	1.18	1.31	1.42	1.59	1.71
$10^3 x A^{820}$	181	178	170	160	148	137	126	117	108	100	94	83	76

APPENDIX B

OBSERVED AND CALCULATED STRUCTURE FACTORS

Observed and calculated structure factors for

$[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$

```
     H  /FO/  /FC/  PHI

** K=   0   L=   0 **

     1   274   297    0
     2   303   277    0

** K=   1   L=   0 **

    -1   160   204    0
     0   245   241    0
     2   144   119    0

** K=   2   L=   0 **

    -2   199   238    0
    -1  1218  1228    0
     0   321   337    0
     1   514   420    0
     2   159   143    0

** K=   3   L=   0 **

    -2   157   169    0
    -1   238   234    0
     0   192   187    0
     1   127   113    0

** K=   4   L=   0 **

    -3   133   133    0
    -2   336   363    0
    -1   334   316    0
     0   282   283    0
     1   300   272    0

** K=   5   L=   0 **

    -3   123   123    0
    -2   158   153    0
    -1   304   305    0
     1    89    98    0
     3   159   126    0

** K=   6   L=   0 **

    -3   107   115    0
    -2   163   172    0
    -1   127   134    0
     0   236   247    0
     1   105   107  180
```

```
     H  /FO/  /FC/  PHI

** K=   7   L=   0 **

    -2   188   188    0
    -1    75    80    0
     0   183   210    0
     2   210   189    0

** K=   8   L=   0 **

    -2    99    97    0
    -1   135   119    0
     0   115   110  180

** K=   9   L=   0 **

    -2   109    96    0
    -1   139   131    0
     1   179   169    0

** K=  11   L=   0 **

    -1    94    99    0

** K=-11   L=   1 **

     2   100    90    0

** K=-10   L=   1 **

     1   150   160    0

** K=  -9   L=   1 **

     0    99   119    0
     1   219   209    0
     2   107   118    0

** K=  -8   L=   1 **

     0   158   181    0
     1   131   112    0
     2   143   127    0

** K=  -7   L=   1 **

    -1   124   121    0
     0   351   370    0
     1   200   189    0
     2   175   177    0
```

```
     H  /FO/  /FC/  PHI

** K=  -6   L=   1 **

    -1   136   152    0
     0   243   256    0
     1   198   203    0
     2   211   199    0

** K=  -5   L=   1 **

    -2   139   145    0
    -1   362   341    0
     0   248   245    0
     1   322   349    0
     2   194   202    0

** K=  -4   L=   1 **

    -2   151   132    0
    -1   332   308    0
     0   400   396    0
     1   441   420    0
     2   114   116  180

** K=  -3   L=   1 **

    -3   140   137    0
    -2   134   132    0
     0   555   560    0
     1   372   394    0

** K=  -2   L=   1 **

    -3   119   107    0
    -2   196   183    0
     0   469   450    0
     1   136   136  180
     2   136   159    0

** K=  -1   L=   1 **

    -2   322   279    0
    -1   633   546    0
     0   352   351    0

** K=   0   L=   1 **

    -2   486   395    0
    -1   224   284    0
     0   252   168    0
     1   264   299    0
```

```
   H  /FO/  /FC/  PHI

** K=   1    L=   1 **

  -3   119   137    0
  -2   333   353    0
  -1   102   108    0
   1   142   132  180
   2   139   116    0

** K=   2    L=   1 **

  -3   149   165    0
  -2   219   242    0
  -1   358   282    0
   0   391   413    0
   1    97    88    0
   3   138   125    0

** K=   3    L=   1 **

  -3   171   188    0
  -1   106   108    0
   1   205   181    0
   3   147   136    0

** K=   4    L=   1 **

  -3   160   170    0
  -2   111   111    0
  -1   393   366    0
   1   111   109    0
   2   206   193    0
   3   139   110    0

** K=   5    L=   1 **

  -2    85    92    0
  -1   173   157    0
   2   154   143    0

** K=   6    L=   1 **

  -2   208   207    0
   0   106   122    0
   1   257   261    0
   2    94    81    0

** K=   7    L=   1 **

  -2   125   133    0
   0   154   156    0
```

```
   H  /FO/  /FC/  PHI

   1   117   121    0
   2   112   105    0

** K=   8    L=   1 **

   0   209   229    0

** K=   9    L=   1 **

  -1   136   129    0
   0   109   119    0

** K= 10    L=   1 **

  -1   135   128    0
   1    91   103    0

** K=-12    L=   2 **

   1   127   119    0

** K=-11    L=   2 **

   1   139   118    0

** K=-10    L=   2 **

  -1   113   128    0
   0   158   189    0
   1   137   149    0

** K= -9    L=   2 **

  -1   138   138    0
   0   138   143    0

** K= -8    L=   2 **

  -2   114   120    0
  -1   254   255    0
   1   128   130    0

** K= -7    L=   2 **

  -2   178   167    0
  -1   113   125    0
   0   279   301    0
   1   211   205    0

** K= -6    L=   2 **
```

```
   H  /FO/  /FC/  PHI

  -2   252   252    0
   0   261   262    0

** K= -5    L=   2 **

  -3   128   122    0
  -2   150   126    0
  -1   498   466    0
   0   382   364    0
   1    95   102    0
   2    87    89    0
   3   113   107    0

** K= -4    L=   2 **

  -3   186   170    0
  -1   350   312    0
   0   313   275  180

** K= -3    L=   2 **

  -3   138   117    0
  -2   394   340    0
  -1   417   371    0
   0   163   180    0
   1   315   329    0
   2   170   204    0
   3    95    95    0

** K= -2    L=   2 **

  -2   217   201    0
   0   179   173  180
   1    81    94  180

** K= -1    L=   2 **

  -3   202   164    0
  -2   232   226    0
  -1   274   276    0
   0   501   466    0
   1   357   431    0
   2   118   124    0

** K=   0    L=   2 **

  -2   172   182    0
  -1   274   308  180
   0   165   138    0
   1   139   124  180
```

```
   H  /FO/  /FC/  PHI

   2   196   221    0

** K=   1   L=   2 **

  -4   119    83    0
  -2   174   227    0
  -1   274   298    0
   0   595   537    0
   2   217   226    0

** K=   2   L=   2 **

  -3   116   113    0
  -2    93    84  180
  -1   434   355    0
   1   381   367    0
   2   182   176    0

** K=   3   L=   2 **

  -3   128   119    0
  -2   182   164    0
  -1   274   242    0
   0   210   193  180
   1   332   316    0

** K=   4   L=   2 **

  -2   255   222    0
  -1   150   150    0
   0   394   392    0
   1   283   271    0
   2    98    86    0
   3   122   111    0

** K=   5   L=   2 **

  -3   101   104    0
   0   186   183    0

** K=   6   L=   2 **

  -3   105   101    0
  -2   158   128    0
  -1   281   259    0
   0   237   240    0
   1   186   170    0
   2   179   180    0

** K=   7   L=   2 **
```

```
   H  /FO/  /FC/  PHI

  -2    98   117    0

** K=   8   L=   2 **

  -2   154   137    0
  -1   166   148    0
   0   181   199    0
   1   165   162    0

** K=  10   L=   2 **

  -1   125   115    0
   0   106   105    0

** K=-11   L=   3 **

   0    85    91    0

** K=-10   L=   3 **

   1   117   122    0

** K= -9   L=   3 **

  -1   146   150    0
   0    95   108    0

** K= -8   L=   3 **

   0   180   192    0
   2   108    87    0

** K= -7   L=   3 **

  -2   180   175    0
   2   117   108    0

** K= -6   L=   3 **

  -2   142   130    0
  -1   149   154    0
   2   117   121    0

** K= -5   L=   3 **

  -3   112   109    0
  -2    95    92    0
  -1   129   125    0
   0   255   235    0
   2   145   147    0
```

```
   H  /FO/  /FC/  PHI

** K= -4   L=   3 **

  -3   108   119    0
  -2   131   115    0
  -1    79    75    0
   1   242   269    0

** K= -3   L=   3 **

  -3   109   100    0
  -2   115   110    0
  -1   422   344    0
   1   284   330    0
   3   168   162    0

** K= -2   L=   3 **

  -3   115   117    0
  -1   155   148    0
   0   439   393    0
   2    95   108    0

** K= -1   L=   3 **

  -2   218   226    0
   0   369   330    0
   1   120   153    0
   2   265   290    0

** K=   0   L=   3 **

  -2   236   273    0
  -1   230   272    0
   1   174   173    0
   2   107   114    0

** K=   1   L=   3 **

  -2   119   157    0
  -1   105   119    0
   0   488   448    0
   1   212   224    0
   2    88    84    0

** K=   2   L=   3 **

  -3   138   159    0
  -2   139   154    0
   0   351   317    0
   1    86   101    0
```

```
   H  /FO/  /FC/  PHI

   2   123   123    0

** K=  3   L=  3 **

  -3   158   131    0
  -1   470   406    0
   1   126   125    0
   3   100   110    0

** K=  4   L=  3 **

  -3   125   110    0
  -1   369   313    0
   0    92    85    0
   1   238   229    0

** K=  5   L=  3 **

  -3    97    76    0
  -2   191   165    0
   1   117   104    0
   2   118   119    0

** K=  6   L=  3 **

  -2   181   181    0
  -1    81    90    0
   0   172   171    0
   1    97    91    0
   2   126   114    0

** K=  7   L=  3 **

   0   124   126    0

** K=  8   L=  3 **

   0   152   167    0

** K=  9   L=  3 **

  -1    89    91    0

** K= 10   L=  3 **

  -1   132   145    0

** K= -9   L=  4 **

   0   107   112    0
```

```
   H  /FO/  /FC/  PHI

** K= -8   L=  4 **

   0   144   156    0
   1   143   133    0
   2   133   120    0

** K= -7   L=  4 **

  -2   119   111    0
  -1   114   120    0
   2   111   109    0

** K= -6   L=  4 **

  -2   111   101    0
   0   321   323    0
   1   135   144    0

** K= -5   L=  4 **

  -3   120   109    0
  -2   116   104    0
   0   135   138    0
   1   118   120    0

** K= -4   L=  4 **

  -3   130   131    0
  -1   491   446    0
   1   223   249    0
   2   127   124    0
   3    91    97    0

** K= -3   L=  4 **

  -1   295   261    0
   1   147   168    0

** K= -2   L=  4 **

  -2   258   283    0
   0   367   338    0
   1   229   256    0
   2    91    92    0

** K= -1   L=  4 **

  -3    95    72    0
  -2   167   194    0
   0   206   171    0
```

```
   H  /FO/  /FC/  PHI

   2   151   168    0

** K=  0   L=  4 **

  -2    89   101    0
  -1   244   250    0
   0   271   260    0
   2   125   129    0

** K=  1   L=  4 **

  -2   136   161    0
   0   321   306    0
   1   277   287    0
   2   218   206    0

** K=  2   L=  4 **

  -2   126   125    0
  -1   142   130    0
   1   116   109    0
   2    95    87    0

** K=  3   L=  4 **

  -3   108   102    0
   0   255   262    0
   1   327   322    0
   2   136   130    0

** K=  4   L=  4 **

   1   178   166    0

** K=  5   L=  4 **

  -2   239   196    0
  -1   196   175    0
   0   271   279    0
   1   196   206    0
   2   119   112    0

** K=  6   L=  4 **

  -1   107   117    0
   0   132   147    0

** K=  7   L=  4 **

  -2   134   121    0
```

```
   H  /FO/  /FC/  PHI

  -1   144   146    0
   0   199   215    0
   1   130   130    0

** K=  8   L=  4 **

  -2   105   107    0

** K=  9   L=  4 **

  -1   153   145    0
   0    99   112    0

** K= 10   L=  4 **

  -1    91    82    0

** K=-10   L=  5 **

  -1   124   140    0

** K= -9   L=  5 **

   1   158   147    0

** K= -8   L=  5 **

  -2   141   156    0
   0   124   140    0
   2   115    94    0

** K= -7   L=  5 **

  -2   126   116    0
   0   217   213    0
   2    98   117    0

** K= -6   L=  5 **

  -1   109   102    0
   1   192   183    0

** K= -5   L=  5 **

  -3   122   114    0
  -2   127   123    0
  -1   166   153    0
   1   168   174    0
   2   135   140    0
```

```
   H  /FO/  /FC/  PHI

** K= -4   L=  5 **

  -1   146   143    0
   0   206   199    0
   2   125   126    0

** K= -3   L=  5 **

  -3   114   114    0
  -1   331   292    0
   0   134   134    0
   1   357   402    0

** K= -2   L=  5 **

  -2    96   105    0
  -1    80    91    0
   1   270   290    0
   2   115   109    0
   3   117    95    0

** K= -1   L=  5 **

  -2   246   263    0
  -1   119   129    0
   0   745   659    0
   2   155   182    0

** K=  0   L=  5 **

   0   433   391    0
   1   135   135    0
   2   150   155    0

** K=  1   L=  5 **

  -3    96   108    0
  -2   143   158    0
   0   203   186    0
   1   300   299    0
   2   134   126    0

** K=  2   L=  5 **

  -1   295   261    0
   0   224   220    0
   1    96    99    0

** K=  3   L=  5 **
```

```
   H  /FO/  /FC/  PHI

  -2   150   138    0
  -1   279   256    0
   0   320   312    0
   1   198   207    0

** K=  4   L=  5 **

  -3   125   124    0
  -1   268   258    0
   1   207   199    0

** K=  5   L=  5 **

  -2   158   156    0
  -1   242   206    0
   0   157   185    0

** K=  6   L=  5 **

  -2   174   165    0
   0   234   255    0

** K=  7   L=  5 **

  -2   117   117    0

** K=  8   L=  5 **

  -1   162   155    0

** K=  9   L=  5 **

   0   103   107    0

** K=-10   L=  6 **

   1   114   116    0

** K= -9   L=  6 **

   1   123   103    0

** K= -8   L=  6 **

  -2   110   120    0
  -1    90    92    0
   0   168   180    0

** K= -7   L=  6 **
```

```
   H  /FO/  /FC/  PHI


   0   226   233    0
   1   125   107    0
   2   135   129    0

** K= -6   L=   6  **

  -2    97   109    0
  -1   157   153    0
   0   118   123    0
   1   146   146    0
   2   107   135    0

** K= -5   L=   6  **

  -2   169   147    0
  -1   257   244    0
   0   155   159    0
   1   219   231    0

** K= -4   L=   6  **

  -3   127   107    0
  -1   197   181    0
   0   267   259    0
   1   245   249    0
   3    96    80    0

** K= -3   L=   6  **

  -3   126   151    0
  -2   129   125    0
  -1   282   270    0
   0   299   257    0
   1   151   170    0
   2   113   111    0

** K= -2   L=   6  **

  -2   145   176    0
  -1   347   308    0
   0   226   213    0
   2   111   116    0

** K= -1   L=   6  **

  -2   229   251    0
  -1   273   247    0
   0   345   315    0
   1   119   142    0
```

```
   H  /FO/  /FC/  PHI


** K=   0   L=   6  **

  -2   195   216    0
   0   242   246    0
   1   163   148    0
   2   157   145    0

** K=   1   L=   6  **

  -2   240   250    0
  -1   254   248    0
   0   159   152    0

** K=   2   L=   6  **

  -3   111   113    0
  -1   227   213    0
   0   250   244    0
   1   224   226    0

** K=   3   L=   6  **

  -3   164   166    0
  -1   173   162    0
   0    75    74    0
   1   128   129    0

** K=   4   L=   6  **

  -2   104   120    0
  -1   310   282    0
   0   141   159    0
   1   106   111    0
   2   124   113    0

** K=   5   L=   6  **

  -2   123   124    0
   0    98   116    0
   1   115   121    0

** K=   6   L=   6  **
  -2   173   173    0
  -1   100    93    0
   0   147   164    0
   1   140   145    0

** K=   7   L=   6  **
```

```
   H  /FO/  /FC/  PHI


  -2   109    99    0
  -1    88    82    0
   0   139   156    0

** K=   8   L=   6  **

  -2    94    87    0
  -1   142   139    0
   0   148   154    0

** K=   9   L=   6  **

  -1   129   122    0

** K=-11   L=   7  **

   0    93   107    0

** K=-10   L=   7  **

   0   124   122    0

** K= -9   L=   7  **

  -1   169   165    0

** K= -8   L=   7  **

  -2   111   132    0
  -1   158   168    0
   0   168   177    0
   1   159   150    0

** K= -7   L=   7  **

  -2   166   163    0
   0   200   193    0

** K= -6   L=   7  **

  -2   179   188    0
  -1   249   245    0
   0   245   259    0
   1    93    84    0
   2    91    93    0

** K= -5   L=   7  **

  -3   113   104    0
  -1   256   239    0
```

```
   H  /FO/  /FC/  PHI

** K= -4   L=   7 **

  -3   156   146    0
  -2   195   204    0
  -1   316   276    0
   0   195   198    0
   1   205   218    0
   2   102    95    0

** K= -3   L=   7 **

  -2   142   168    0
   1    96   113    0

** K= -2   L=   7 **

  -2   176   175    0
  -1   331   321    0
   0   254   238    0
   1   227   230    0

** K= -1   L=   7 **

   0   287   252    0
   1   128   124    0

** K=  0   L=   7 **

  -2   220   245    0
  -1   145   121    0
   0   378   365    0
   2   147   151    0

** K=  1   L=   7 **

  -1   387   354    0
   0   221   211    0
   1   114   125    0

** K=  2   L=   7 **

  -1   275   265    0
   1   208   219    0

** K=  3   L=   7 **

  -2   271   266    0
  -1   222   210    0
   0   173   172    0
   1   156   173    0
```

```
   H  /FO/  /FC/  PHI

** K=  4   L=   7 **

  -3    92    81    0
  -1   170   146    0
   0   153   174    0

** K=  5   L=   7 **

  -3   172   140    0
  -2   126   132    0
  -1   237   213    0
   0   169   188    0

** K=  6   L=   7 **

  -2   162   159    0
  -1   107   103    0

** K=  7   L=   7 **

  -2   186   168    0
  -1   148   145    0
   0   102   107    0

** K=-11   L=   8 **

   1   138   106    0

** K= -9   L=   8 **

   0   156   149    0

** K= -8   L=   8 **

   0   137   142    0
   2    90    88    0

** K= -7   L=   8 **

  -2   119   118    0
   2    91    88    0

** K= -6   L=   8 **

  -2   101   113    0
  -1   191   186    0
   0   172   182    0
   1   113   110    0
   2    95   107    0
```

```
   H  /FO/  /FC/  PHI

** K= -5   L=   8 **

   0    86   103    0
   1   153   169    0

** K= -4   L=   8 **

  -3   128   128    0
  -2   160   169    0
  -1   251   237    0
   0   150   147    0
   1   256   252    0

** K= -3   L=   8 **

  -1   182   182    0
   0   255   236    0

** K= -2   L=   8 **

  -3   103   102    0
  -2   154   162    0
  -1   294   268    0
   0   373   336    0
   1    83    82    0
   2    99   110    0

** K= -1   L=   8 **

  -2   206   220    0
  -1   246   228    0
   1   142   141    0

** K=  0   L=   8 **

  -2   303   296    0
  -1   271   254    0
   0   198   193    0
   1   108    94    0

** K=  1   L=   8 **

  -3   124   146    0
  -2   187   191    0
  -1    88    90    0
   0   313   302    0

** K=  2   L=   8 **

  -3   170   186    0
```

```
   H  /FO/  /FC/  PHI


  -2   163   166    0
  -1   211   196    0

** K=  3   L=  8 **

  -3   126   147    0
  -2   114   115    0
  -1   376   335    0

** K=  4   L=  8 **

  -3   117   112    0
  -2   122   111    0
  -1    93    88    0

** K=  5   L=  8 **

  -3   119    94    0
  -2   246   225    0

** K=  6   L=  8 **

  -2   107   102    0

** K=  7   L=  8 **

   0   109   108    0

** K= -9   L=  9 **

  -1   125   113    0
   0   160   154    0
   1   110   127    0

** K= -8   L=  9 **

   1    91    97    0

** K= -7   L=  9 **

  -2   196   177    0
  -1   174   164    0
   0   262   251    0
   1   111    98    0

** K= -6   L=  9 **

   0   235   227    0

** K= -5   L=  9 **
```

```
   H  /FO/  /FC/  PHI


  -3   143   154    0
  -2   127   118    0
  -1   364   329    0
   0   127   131    0
   1   104    89    0

** K= -4   L=  9 **

  -2   127   113    0
  -1   351   337    0

** K= -3   L=  9 **

  -2   283   266    0
  -1   153   148    0
   0   117   119    0
   1    96   100    0

** K= -2   L=  9 **

  -3   135   149    0
  -2   268   275    0
   0   155   144    0
   1    86    94    0

** K= -1   L=  9 **

  -3   149   163    0
  -2   146   149    0
  -1   142   120    0
   1    89    85  180

** K=  0   L=  9 **

  -3   130   151    0
  -2   146   176    0
  -1   147   146    0
   0   214   212    0
   2    97   114    0

** K=  1   L=  9 **

   0    79    84  180
   2   100    89    0

** K=  2   L=  9 **

  -2   134   130    0
  -1   249   237    0
   1   150   154    0
```

```
   H  /FO/  /FC/  PHI


** K=  3   L=  9 **

   1   107   120    0

** K=  4   L=  9 **

  -2   104   123    0
   0   150   154    0
   1   135   146    0

** K=  6   L=  9 **

  -1   104   113    0
   0   133   136    0

** K= -9   L= 10 **

  -1    92    95    0
   0   156   150    0

** K= -8   L= 10 **

   0   109   101    0

** K= -7   L= 10 **

  -2   147   143    0
  -1   223   218    0
   0    96    88    0

** K= -5   L= 10 **

  -2   219   224    0
  -1   100   104    0
   0    97   102    0

** K= -4   L= 10 **

  -3   119   135    0

** K= -3   L= 10 **

  -3   161   185    0
  -1   112   121    0
   1   101   107    0

** K= -2   L= 10 **

   2   154   152    0
```

```
   H  /FO/  /FC/  PHI

** K= -1   L= 10  **

  -2    98   107    0
   0   104   100    0
   2   112   113    0

** K=  0   L= 10  **

   0   124   114    0
   1   232   238    0

** K=  1   L= 10  **

   0   112   122    0
   1    94    97    0

** K=  2   L= 10  **

  -1   185   168    0
   0   280   290    0
   1   100   111    0

** K=  3   L= 10  **

  -1   162   152    0
   1   127   121    0

** K=  4   L= 10  **

  -2   112   131    0
  -1   263   237    0
   0    88    93    0

** K=  5   L= 10  **

  -2   130   117    0
   0   121   140    0

** K=  6   L= 10  **

  -2   158   138    0

** K= -7   L= 11  **

   0   108    91    0

** K= -5   L= 11  **

  -1   150   144    0
   0    98   111    0
```

```
   H  /FO/  /FC/  PHI

   1   133   127    0

** K= -4   L= 11  **

  -1   105    95    0
   1   126   130    0

** K= -3   L= 11  **

  -2   148   148    0
  -1   152   143    0
   0   159   144    0
   1   195   203    0

** K= -2   L= 11  **

  -2   108    96    0
   0   174   160    0

** K= -1   L= 11  **

  -1   148   156    0
   0   336   309    0
   1   118   117    0

** K=  0   L= 11  **

  -1   121   135    0
   0   142   117    0

** K=  1   L= 11  **

  -2   161   162    0
  -1   295   267    0
   0   147   146    0
   1   102   108    0

** K=  2   L= 11  **

  -2    88    91    0
  -1   100   118    0
   1   116   119    0

** K=  3   L= 11  **

  -2   153   149    0
  -1   139   138    0
   0   116   109    0

** K=  4   L= 11  **
```

```
   H  /FO/  /FC/  PHI

  -1   125   114    0
   0   116   120    0

** K=  5   L= 11  **

  -1    97    97    0

** K= -8   L= 12  **

   0   173   161    0

** K= -6   L= 12  **

  -1   186   181    0
   0   104    85    0
   1   136   118    0

** K= -5   L= 12  **

  -1   111   116    0
   0   158   157    0
   1   130   122    0

** K= -4   L= 12  **

  -2   126   122    0
  -1    96    99    0
   0   140   138    0

** K= -3   L= 12  **

  -1   274   260    0
   0   124   125    0

** K= -2   L= 12  **

  -2   114    98    0
  -1   121   130    0

** K= -1   L= 12  **

  -2   238   241    0
   0   189   177    0

** K=  0   L= 12  **

  -2   116   121    0

** K=  1   L= 12  **
```

```
   H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI


  -1   180   186    0       -1   126   136    0
   0   136   138    0

** K=   3   L= 12  **

  -2   127   120    0
  -1   174   173    0

** K=   4   L= 12  **

  -1   134   121    0

** K=  -6   L= 13  **

  -1   138   137    0
   0   139   129    0

** K=  -5   L= 13  **

  -1   101   115    0

** K=  -4   L= 13  **

  -1   184   159    0

** K=  -2   L= 13  **

  -2   133   141    0
  -1   110   108    0
   0   120   123    0

** K=  -1   L= 13  **

  -2   129   124    0

** K=   0   L= 13  **

  -2    99   116    0
  -1   130   134    0
   0   144   143    0

** K=   2   L= 13  **

  -1   146   141    0

** K=  -4   L= 14  **

  -1   115   141    0

** K=  -2   L= 14  **
```

Observed and calculated structure factors for clge.EtOH

```
   H  /FO/  /FC/  PHI

** K=    0   L=    0 **

   2   397   424   90
   4    20    20    0
   6   340   345    0
   8    23    23  180

** K=    1   L=    0 **

   1   159   155   90
   2    45    45  180
   3   111   111   90
   4    53    49  180
   5    37    34   90
   6    63    64  180
   8    72    73  180

** K=    2   L=    0 **

   0   469   463  180
   1    90    84   90
   2   267   256  180
   3   361   352   90
   4   182   174  180
   5    63    70   90
   6    38    36  180
   7    63    61   90
   8   104   101    0

** K=    3   L=    0 **

   1   116   104  270
   2   474   462    0
   4   137   132  180
   7   123   123  270
   8    74    70    0

** K=    4   L=    0 **

   0    79    70    0
   1    63    65  270
   2    93    91    0
   3   128   128  270
   4    67    64  180
   5    39    37   90
   6    40    41  180
   7    35    35   90

** K=    5   L=    0 **
```

```
   H  /FO/  /FC/  PHI

   1    21    20  270
   2    84    85    0
   3    48    51   90
   5    30    33   90
   6    92    87  180

** K=    6   L=    0 **

   0   110   106    0
   1   186   182   90
   2    65    65  180
   3    33    27   90
   5   129   135   90
   6    59    63    0

** K=    7   L=    0 **

   1    84    77   90
   2    18    14    0
   4    45    43    0
   5    38    45  270
   6    58    54  180

** K=    8   L=    0 **

   0   144   144  180
   1    66    62  270
   2    46    45  180
   3    40    41   90

** K=    9   L=    0 **

   1    28    27   90
   2   120   119    0
   4    85    84  180

** K=   10   L=    0 **

   0    23    26  180
   1    61    61  270
   2    28    33  180

** K=    0   L=    1 **

   1   193   209   90
   2   324   361  270
   3   192   201  270
   4    25    29  270
   5    29    30   90
   6    20    20  270
```

```
   H  /FO/  /FC/  PHI

   7   179   179   90
   8    71    72  270

** K=    1   L=    1 **

   0   309   311  270
   1   113   108  237
   2   357   383   84
   3   256   245  157
   4   163   148  152
   5    61    64   69
   6   174   177  284
   7    56    55  266
   8    44    42   64

** K=    2   L=    1 **

   0   464   468  180
   1   544   597   79
   2   221   218   93
   3    62    60  200
   4   130   113  207
   5    38    40  203
   6   164   156  168
   7    64    66   37
   8    45    45   87

** K=    3   L=    1 **

   0    30    37   90
   1   166   172   73
   2    92    82  227
   3   199   190    5
   4    64    55  284
   5   131   128  263
   6    41    39   46
   7    42    40  285
   8    24    26   15

** K=    4   L=    1 **

   0    24    28  180
   1    67    68  293
   2   134   136  236
   3   270   255  271
   4   138   121  113
   5    32    36  160
   6    26    23  223
   7    41    39  124
```

```
   H /FO/ /FC/ PHI          H /FO/ /FC/ PHI          H /FO/ /FC/ PHI


** K=   5  L=  1 **         2   78   79 327          0  294  307 180
                                                     1  132  133 143
   0  178  162  90      ** K=   0  L=  2 **          2   91   98 172
   1  244  235 189                                   3   65   53 294
   2  111  108 208         0  403  422 180           4   31   27 319
   3  107   94  90         1  399  448   0           5   64   61 295
   4   50   52 347         2  284  294 180           6   35   37 261
   5   68   70 239         3   70   72 180           7   41   43 205
   6   49   51  89         4   34   31 180
   7   52   53  85         5  125  123 180       ** K=   5  L=  2 **
                           7  137  137   0
** K=   6  L=  1 **        8   85   85 180           0  165  164 270
                                                     1  129  115 271
   0   46   47 270      ** K=   1  L=  2 **          2  158  149 221
   1   84   87 128                                   3   95   88 207
   2   49   44 254         0  274  267 270           4   79   80 329
   3   51   52  57         1  491  537 357           6   69   72 334
   4   36   37 182         2  140  134 189           7   38   39 217
   5   36   38 356         3  296  295 345
   6   54   55 201         4  289  288 339       ** K=   6  L=  2 **
                           5   68   65 353
** K=   7  L=  1 **        6  129  134 324           0  166  167   0
                           7   54   53  50           1   82   84 310
   0  110  102 270                                   2  115  117  60
   1   56   57 109      ** K=   2  L=  2 **          3   31   31 278
   2   22   20 312                                   4  109  105 282
   3   68   59 177         0  509  516 180           5   52   60 267
   4   36   38 189         1  352  389 261           6   40   46  29
   5   78   76 290         2  232  225 353           7   44   48 329
   6   49   51 293         3   43   37 284
                           4  239  223  37       ** K=   7  L=  2 **
** K=   8  L=  1 **        5  125  119 278
                           6  137  136 133           1   75   73   3
   0   40   37 180         7   75   69 224           2  154  154 158
   1  137  142 271         8   48   50 153           3   20   18  56
   2  109  107 112                                   4   65   61  19
   4   86   84 234      ** K=   3  L=  2 **          5   79   78  24
   5   67   71 263                                   6   27   24 340
                           0  498  519  90
** K=   9  L=  1 **        1  189  187 167       ** K=   8  L=  2 **
                           2  167  174 177
   0   52   53  90         3  138  125 354           0   25   19   0
   1   55   54  43         4  103  102 161           1   26   26 118
   3   51   50  36         5   59   60 193           2   60   58 339
   4   33   31 348         6  129  132  86           3   24   25 199
                           7   53   56  82           4   62   57  56
** K=  10  L=  1 **        8   32   34 242           5   28   26 278

   0   81   80   0      ** K=   4  L=  2 **       ** K=   9  L=  2 **
   1   36   33 313
```

```
   H /FO/  /FC/ PHI        H /FO/  /FC/ PHI        H /FO/  /FC/ PHI


   1   53    49 187        5  134   139 106        0   39    38 180
   2   42    41  79        6   29    29 126        1   21    23 120
   3   37    41 348        7   73    73 147        2   35    29 212
   4   45    42 123        8   20    23 290        3   72    72  95
                                                   5   23    24 256
** K= 10  L=  2 **      ** K=  4  L=  3 **
                                                ** K=  9  L=  3 **
   0   81    8[illegible]   0        0  257   237   0
   1   39    44  85        1  166   162  38        0   26    22  90
   2   23    24 258        2   61    63  43        1   60    60 205
                           3   21    21  20        2   37    44 262
** K=  0  L=  3 **         4   96    97 328        3   55    55 200
                           5   77    78  91        4   39    40 237
   1  354   377 270        6  117   119   1
   2  139   140 270        7   71    70 329     ** K= 10  L=  3 **
   3  203   191  90
   4  100    92  90     ** K=  5  L=  3 **         0   54    51 180
   7   73    73 270                                1   51    51  81
                           0  190   191 270        2   21    15 275
** K=  1  L=  3 **         1   76    76 313
                           2   93    98 212     ** K=  0  L=  4 **
   0   29    32 270        3  129   131 235
   1  467   491 268        4   20    22 340        0  318   313   0
   2  190   184  51        5   50    51  11        2   76    75   0
   3  243   226 313        6   81    79 201        3  144   144 180
   4  127   119  92        7   46    44  46        4  117   116 180
   5   41    41 351                                5  133   131 180
   6   42    43 126     ** K=  6  L=  3 **         8   58    61   0
   7  143   143 279
   8   41    39 120        0   30    34   0     ** K=  1  L=  4 **
                           1   52    53 151
** K=  2  L=  3 **         2   53    53 279        0   18    15 270
                           3   31    31 138        1  170   163 255
   0  305   290 180        4   75    73  49        2  290   280 134
   1  501   530 234        5   53    50  49        3  190   172 145
   2  182   179  65        6   51    50  34        4  140   128  83
   3  128   121 114        7   38    37 120        5   57    58  97
   4   91    87 302                                6   66    67 192
   5   71    69 315     ** K=  7  L=  3 **         7   91    94 276
   6   35    32 196                                8   38    36 131
   7  113   113 221        0   21    25  90
   8   53    58  27        1   81    83 257     ** K=  2  L=  4 **
                           2  146   150  42
** K=  3  L=  3 **         3   55    49 333        0  271   274   0
                           4   75    84 127        1  161   172 229
   0  209   220  90        5   81    78 116        2   80    80 284
   1  172   143 245        6   28    27   1        3  112   107 312
   2   86    97  59                                4   50    46 130
   3   65    69  53     ** K=  8  L=  3 **         5  132   130  18
   4  102    93  22                                6   71    72 357
```

```
 H /FO/ /FC/ PHI


 7   26   27 270
 8   50   56 339

** K=  3  L=  4 **

 0   62   69 270
 1  299  286  80
 2  215  209 323
 3   27   28 319
 4   86   81 350
 5  129  127 245
 7   63   63 102
 8   31   33 323

** K=  4  L=  4 **

 0  264  241   0
 1  238  247 101
 2   67   65 242
 3   32   34 118
 4   75   74 114
 5  143  148  93
 6   74   69  20
 7   74   74 105

** K=  5  L=  4 **

 1   42   43 210
 2  138  132  14
 3   92   95 157
 4  161  160 173
 5   48   50  99
 6   68   67 190
 7   36   37 285

** K=  6  L=  4 **

 0  116  108 180
 1   84   89 300
 2   92   87 179
 3  144  137  84
 4   95   92 213
 5   45   39 217
 6   53   53 179

** K=  7  L=  4 **

 2   95   99 340
 3   83   77 189
 4   34   33 295
```

```
 H /FO/ /FC/ PHI


 5   48   48 271
 6   20   11  27

** K=  8  L=  4 **

 0   55   59 180
 1   28   28 278
 2   40   42 335
 3   57   57 281
 4   47   44  45
 5   22   22  93

** K=  9  L=  4 **

 0   35   37 270
 2   28   28 297
 3   61   56  18

** K= 10  L=  4 **

 0   40   36 180
 1   36   35  15

** K=  0  L=  5 **

 1   52   46 270
 2  111  108 270
 3  357  372 270
 4  234  234  90
 5   24   25 270
 6   52   49  90
 7   40   42  90
 8   20   17 270

** K=  1  L=  5 **

 0  153  142  90
 1  111  110  91
 2   74   75 232
 3  148  149 138
 4   22   27 338
 5   96   91 130
 6   64   62  24
 7   39   41  67
 8   51   52 297

** K=  2  L=  5 **

 0   47   37   0
 1  357  346 127
```

```
 H /FO/ /FC/ PHI


 2   97   94 267
 3   99   95  72
 4   69   66 254
 5   55   56  32
 6   61   54 295
 7  103  108 147
 8   24   25 280

** K=  3  L=  5 **

 0   45   46  90
 1   96   93 104
 2  174  169 241
 3   51   47 258
 4  137  128 220
 5  122  116 261
 6   22   26 122
 7   23   26 226

** K=  4  L=  5 **

 0  135  122 180
 1  228  241  14
 2  150  143 130
 3   51   52 355
 4  103   99 191
 5   82   83 192
 6  101  102 149
 7   93   94  19

** K=  5  L=  5 **

 0   36   41 270
 1  122  114  39
 3  141  139 148
 4   66   64 307
 5   78   79 339
 6   55   59 323
 7   28   27 335

** K=  6  L=  5 **

 1   62   62 252
 2   35   42 325
 3  107  108 255
 4   20   21 220
 5   43   42 248
 6   38   37 215

** K=  7  L=  5 **
```

```
   H /FO/ /FC/ PHI


   0   21   18 270
   1   39   44 123
   2   32   31 190
   3  133  132  11
   5   28   32 221
** K=   8  L=   5 **

   0   54   60   0
   1   34   32 314
   4   27   29 112

** K=   9  L=  5 **

   0   36   36  90
   1   47   53  78
   3   32   29  19

** K=   0  L=   6 **

   0  313  298 180
   1   19   17   0
   3  103  100   0
   4   48   40   0
   5   39   34   0
   6   38   36 180

** K=   1  L=  6 **

   0  217  210  90
   1  157  157 294
   2  111  103 228
   3   57   59 235
   4   95   93 303
   5   65   66  64
   6   54   54  80

** K=   2  L=   6 **

   0  156  142 180
   1   28   27 331
   2  115  118  84
   3   92   83 151
   4   64   66 324
   5   76   75 200
   6   46   51 153

** K=   3  L=   6 **

   0  229  229 270
```

```
   H /FO/ /FC/ PHI


   1  129  126  71
   2  123  131 202
   3   74   67 312
   4   69   71 285
   5   90   91 309
   6   75   77 267
   7   67   68  82

** K=   4  L=   6 **

   0   73   76 180
   1   99  104  18
   2   76   74 144
   3  173  168 286
   4   62   59 283
   5   44   46 322
   6   24   24 269
   7   57   56 357

** K=   5  L=   6 **

   0   48   55  90
   1  102   95 277
   2   49   55 116
   3  162  156 358
   4   30   31  49
   5   71   71  79
   6   66   64  34

** K=   6  L=   6 **

   0   75   80   0
   1   80   78 226
   2   69   74 359
   3   81   82 125
   4   73   71  43
   5   85   84 258
   6   31   30 339

** K=   7  L=   6 **

   0   68   62  90
   1   48   50 148
   2   68   72 151
   4   47   42 109
   5   23   24 214

** K=   8  L=   6 **

   1   66   71 127
```

```
   H /FO/ /FC/ PHI


   4   40   40 259

** K=   9  L=   6 **

   1   36   27 323
   2   35   38 174

** K=   0  L=   7 **

   2   42   42 270
   4  119  112 270
   5   46   43  90
   6   56   57 270
   7   43   43 270

** K=   1  L=   7 **

   0  239  224 270
   1   81   78  87
   2   99   93 291
   3   50   50 307
   4   52   55 323
   5   49   48 309
   6   61   63 227
   7   24   32  99

** K=   2  L=   7 **

   0   95   83   0
   1  163  161 245
   2  168  177 137
   3   30   32 349
   4   63   58 112
   5   88   90 359
   6   85   83  27
   7   25   25 268

** K=   3  L=   7 **

   0   47   44  90
   1   31   33 333
   2  107  110  76
   3  209  206 354
   4   78   78  94
   5   21   26  51
   6   22   26 143

** K=   4  L=   7 **

   0   31   25 180
```

```
     H  /FO/  /FC/ PHI

     1    17    12 357
     2   116   115 336
     3   150   150 110
     4   101   102 340
     5    52    56 201
     6    26    26 231

**  K=    5   L=    7  **

     0    41    41  90
     1    92    94 247
     2   108   107  37
     3   141   136 183
     4   101    90 127
     5    48    47 100
     6    36    38  81

**  K=    6   L=    7  **

     0    42    47 180
     1    69    75 189
     2    19    22 248
     5    79    80  15

**  K=    7   L=    7  **

     0    51    53 270
     1    52    57 233
     2    38    44 183
     3    23    23 252
     4    45    41   4

**  K=    8   L=    7  **

     1    30    34  66
     2    20    20 263
     3    29    29 247

**  K=    0   L=    8  **

     0   326   309   0
     1   154   147 180
     4    27    27 180
     5    25    24   0
     6    81    86   0
     7    53    51 180

**  K=    1   L=    8  **

     0    58    56  90
```

```
     H  /FO/  /FC/ PHI

     1    47    46 113
     2    24    25  86
     3    41    41 148
     4    60    56 107
     5    29    30 298
     6    29    27  86
     7    24    22 331

**  K=    2   L=    8  **

     0    57    57 180
     1    23    20  35
     2    50    53 233
     3   150   149  80
     4    51    49 137
     5    30    26 360
     6    35    32 118

**  K=    3   L=    8  **

     0   103   109 270
     1    64    63  33
     2   110   100  56
     3   108    99 153
     4    97    93 123
     5    20    23 274
     6    40    42 259

**  K=    4   L=    8  **

     0    45    41   0
     2    50    46  10
     3    74    75 243
     4    48    46 239
     5    48    45 125
     6    26    20 173

**  K=    5   L=    8  **

     0    25    26  90
     1   109   115 204
     2    52    50 308
     3    87    85 173
     4    47    44 309
     5    66    68 157

**  K=    6   L=    8  **

     0    45    48   0
     1    22    24 343
```

```
     H  /FO/  /FC/ PHI

     2    85    88 256
     3    49    49  48
     4    64    68 104
     5    30    31  80

**  K=    7   L=    8  **

     0    43    47 270
     1    54    60  47
     2    50    47 289
     3    30    28 351
     4    30    33 276

**  K=    8   L=    8  **

     0    32    27 180
     2    25    22 156

**  K=    0   L=    9  **

     1    51    54  90
     2    18    14 270
     3    22    23  90
     4    60    60  90
     6    43    48  90

**  K=    1   L=    9  **

     0    29    28 270
     1    45    46  15
     2   112   115 107
     3   103   105 195
     4    53    55 125
     5    28    30 283
     6    58    65 292

**  K=    2   L=    9  **

     1    85    81  29
     2    76    79 184
     3    60    64 262
     4    91    90 210
     5    31    29 211

**  K=    3   L=    9  **

     0    87    83 270
     1   102    99 173
     2   133   132 240
     3    26    30 137
```

```
    H  /FO/  /FC/ PHI

    4  104   102 304
    5   54    57 176
    6   32    28 350

** K=   4   L=   9 **

    0   23    26   0
    1   36    37 349
    2   79    79 333
    3   32    31 306
    4   58    59  67
    5   33    32 224

** K=   5   L=   9 **

    0   87    85  90
    1   68    74  30
    2   48    50 309
    3   47    44  31
    4   78    74 219
    5   20    18 316

** K=   6   L=   9 **

    0   57    61   0
    1   47    46 120
    2   27    26 156
    4   44    44 185

** K=   7   L=   9 **

    1   23    22  51

** K=   8   L=   9 **

    0   24    23 180

** K=   0   L=  10 **

    0   32    33   0
    1   65    70   0
    2  108   105 180
    4   42    43 180
    6   39    42   0

** K=   1   L=  10 **

    0   18    19 270
    1   86    83 355
    2   74    70 234
```

```
    H  /FO/  /FC/ PHI

    3  105   104 333
    4   75    73 303

** K=   2   L=  10 **

    0   73    71 180
    1   20    20 307
    2   56    62 329
    4   72    70  35
    5   45    46 243

** K=   3   L=  10 **

    0   30    27  90
    1   50    48 221
    2   30    35  13
    3   33    34  19
    4   49    50 186
    5   43    43  66

** K=   4   L=  10 **

    1   57    56 119
    2   72    74  58
    4   73    70 300
    5   23    24   2

** K=   5   L=  10 **

    0   35    32  90
    1   38    38 333
    2   34    40 221
    3   44    45 341
    4   23    20 306

** K=   6   L=  10 **

    2   41    43 164
    3   43    42 250

** K=   0   L=  11 **

    1   67    64 270
    2   32    34 270
    4   35    31  90
    5   22    21 270

** K=   1   L=  11 **

    0   98    94 270
```

```
    H  /FO/  /FC/ PHI

    1   56    57 310
    2   70    72  35
    3   71    70   7
    4   56    56 119
    5   40    40  42

** K=   2   L=  11 **

    0   20    18 180
    1   26    27  98
    2   70    74  60
    3   57    54  95
    4   50    48 303
    5   22    21  76

** K=   3   L=  11 **

    0   63    64  90
    1   39    35 201
    2   45    44 114
    4   36    41  33

** K=   4   L=  11 **

    0   74    75 180
    1   26    25 217
    2   38    40 228

** K=   5   L=  11 **

    1   32    26 131
    3   25    26 309

** K=   6   L=  11 **

    1   25    26 239

** K=   0   L=  12 **

    1   29    31   0
    2   55    52 180
    3   35    34 180
    4   42    43 180

** K=   1   L=  12 **

    1   49    49 165
    2   84    82 135
    3   60    65 164
    4   58    60  46
```

```
 H /FO/ /FC/ PHI       H /FO/ /FC/ PHI       H /FO/ /FC/ PHI

** K=  2  L= 12 **

   1   25    28 202
   2   47    50 305
   3   28    26 347

** K=  3  L= 12 **

   0   23    25 270
   1   32    26 120
   2   32    35 312

** K=  4  L= 12 **

   0   33    36   0
   1   31    36 227
   2   23    19 172

** K=  0  L= 13 **

   2   40    40 270

** K=  1  L= 13 **

   0   41    34 270
   1   41    45 241
   2   33    33 229

** K=  2  L= 13 **

   0   32    29   0
   1   24    26 229
   2   24    27   8

** K=  3  L= 13 **

   0   20    17  90
```

Observed and calculated structure factors for $[Cu(clge)_2(NO_3)_2]$

```
  H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

** K=  0   L=  0 **       ** K=  6   L=  0 **        -7   170   157    0
                                                     -6   269   254    0
  2   655   476  180        0   240   252    0        -4   184   189    0
  4   564   432  180        4   176   163    0        -2   436   453    0
  6   669   651    0                                 -1   101    97  180
  8   350   365    0      ** K=  0   L=  1 **         0   369   397    0
                                                      2   304   276    0
** K=  1   L=  0 **        -7   344   317    0        6   337   318    0
                           -3  1010   955    0        8   168   180    0
  1   728   704    0       -1   314   342    0
  3   328   340  180        1   167   202    0      ** K=  4   L=  1 **
  4   176   148    0        3   599   608    0
  5   134   155  180        5   198   220    0       -9   192   175    0
  6   211   196  180        7   369   372    0       -5   285   295    0
  7   353   343    0                                 -4   241   247    0
  9   202   217    0      ** K=  1   L=  1 **        -3   256   281    0
 10   110   110    0                                 -2   391   431  180
                           -8   337   353    0        1   321   316    0
** K=  2   L=  0 **        -6   259   257    0        2   292   273    0
                           -4   301   309    0        3   296   294    0
  0   281   277  180       -2   391   419    0        4   183   157  180
  2   721   695    0        0   605   652    0        5   232   207    0
  3   223   169    0        2   471   474    0        9   126   128    0
  4   465   441    0        3   145   140  180
  5   505   460  180        4   454   451    0      ** K=  5   L=  1 **
  6   173   162    0        5   264   254    0
  8   181   182    0        6   193   199    0       -6   181   175    0
                            8   172   185    0       -4   158   187    0
** K=  3   L=  0 **        10   151   153    0       -2   183   165    0
                                                      0   157   139    0
  1   473   447    0      ** K=  2   L=  1 **         2   174   156    0
  2   247   232    0                                  4   245   224    0
  3   179   168    0       -9   147   119    0        6   117   121    0
  5   379   352    0       -7   376   380    0
  6   120   113  180       -6   176   154    0      ** K=  6   L=  1 **
  7   207   189  180       -5   314   305    0
                           -4   234   219  180       -3   291   294    0
** K=  4   L=  0 **        -3   186   127  180        3   208   213    0
                           -2   121   129    0
  0   197   172  180       -1   901   974    0      ** K=  7   L=  1 **
  1   393   358  180        0   196   201    0
  2   468   428    0        1   645   658    0       -4   125   148    0
  3   104    67    0        5   389   377    0
  4   336   323    0        6   109   122  180      ** K=  0   L=  2 **
  6   174   165    0        7   224   226    0
                            9   116   111    0       -8   267   288    0
** K=  5   L=  0 **                                  -6   551   567    0
                          ** K=  3   L=  1 **        -4   217   230    0
  3   255   262    0                                  0  1154  1062    0
  5   182   180    0      -10   181   168    0        2   180   229    0
```

```
   H /FO/ /FC/ PHI         H /FO/ /FC/ PHI         H /FO/ /FC/ PHI

   4  446  430   0         8  148  137 180         3  186  156   0
   6  392  409   0                                 4  450  451   0
  10  164  164   0      ** K=  4  L=  2 **         6  214  197   0
                                                   8  127  132   0
** K=  1  L=  2 **        -8  140  118   0        10  145  141   0
                          -4  155  152   0
  -9  229  232   0        -2  543  557   0      ** K=  2  L=  3 **
  -7  288  278   0         1  149  118 180
  -5  258  262   0         2  194  174   0        -9  182  195   0
  -3  378  378   0         4  279  254   0        -6  121  122   0
  -2  218  182 180         6  117  101   0        -5  301  306   0
  -1  456  500   0         8  199  184   0        -3  494  497   0
   0  132  126 180                                -1  309  366   0
   1  539  574   0      ** K=  5  L=  2 **         1  193  206   0
   2  311  271   0                                 3  379  394   0
   3  550  526   0        -3  204  192   0         5  336  329   0
   5  254  257   0        -1  211  211   0         7  191  180   0
   9  231  257   0         1  250  234   0
                           5  159  169   0      ** K=  3  L=  3 **
** K=  2  L=  2 **         7  141  150   0
                                                 -10  156  129   0
  -8  174  173   0      ** K=  6  L=  2 **        -8  165  158   0
  -6  241  235   0                                -6  231  233   0
  -5  232  227   0        -4  157  176   0        -4  213  237   0
  -4  376  371   0         0  191  191   0        -2  121  133   0
  -3  257  247   0         2  109  190   0        -1  227  232   0
  -2  408  440   0         6  138  127   0         0  553  570   0
  -1  544  566 180                                 1  143  122 180
   0  258  292   0      ** K=  0  L=  3 **         2  141  155   0
   1  231  206   0                                 4  349  347   0
   2  554  560   0        -7  418  442   0         6  119  131   0
   4  321  319   0        -5  332  339   0
   6  184  174   0        -3  213  249   0      ** K=  4  L=  3 **
   7  135  143   0        -1  412  425   0
   8  196  184   0         1  571  569   0        -5  215  209   0
   9  117  116 180         3  615  601   0        -3  244  241   0
  10  154  138   0         5  318  323   0        -1  205  226   0
                           9  216  235   0         1  250  276   0
** K=  3  L=  2 **                                 2  128  115 180
                        ** K=  1  L=  3 **         3  179  181   0
  -7  174  200   0                                 5  136  126   0
  -5  271  284   0       -10  125  109   0         7  205  192   0
  -3  343  347   0        -8  192  194   0
  -1  304  337   0        -6  172  170   0      ** K=  5  L=  3 **
   1  132  155   0        -5  175  154 180
   2  220  206 180        -4  533  505   0        -6  161  159   0
   3  378  357   0        -2  716  706   0        -4  127  113   0
   4  185  183   0        -1  512  517   0         0  246  232   0
   5  264  282   0         1  561  530 180         2  199  181   0
   7  239  226   0         2  637  608   0         6  157  149   0
```

```
   H /FO/ /FC/ PHI

** K=   6  L=   3 **

  -3  117  113   0
  -1  112  128   0
   1  158  156   0

** K=   7  L=   3 **

  -2  123  127   0

** K=   0  L=   4 **

 -10  253  253   0
  -6  323  325   0
  -4  679  630   0
  -2  345  365   0
   0  195  224   0
   2  506  498   0
   4  280  309   0
   6  430  427   0

** K=   1  L=   4 **

  -9  213  205   0
  -8  154  147   0
  -6  204  167 180
  -5  461  449   0
  -4  317  204 180
  -3  861  764   0
  -2  630  558   0
   0  161  129   0
   1  189  107   0
   5  494  471   0
   6  436  432   0
   8  209  214 180
   9  160  175   0

** K=   2  L=   4 **

  -9  164  175   0
  -8  195  188   0
  -7  186  197 180
  -6  240  246   0
  -4  337  347   0
  -3  191  169   0
  -2  302  340   0
  -1   99   86   0
   0  164  186   0
   1  187  142 180
   2  400  419   0
```

```
   H /FO/ /FC/ PHI

   4  435  425   0
   7  131  131   0
   8  133  146   0

** K=   3  L=   4 **

  -7  280  285   0
  -6  190  199 180
  -5  163  163   0
  -2  325  304   0
  -1  444  497   0
   0  231  208 180
   1  553  511   0
   2  153  153 180
   3  139  145   0
   7  402  402   0

** K=   4  L=   4 **

  -8  214  215   0
  -4  175  176   0
  -2  216  241   0
   0  283  295   0
   1  153  166 180
   2  169  160   0
   4  229  187   0
   5  196  189   0
   8  133  152   0

** K=   5  L=   4 **

  -7  142  154   0
  -3  157  127   0
  -1  248  274   0
   1  153  132   0
   5  146  147   0
   6  132  136 180

** K=   6  L=   4 **

  -6  134  136   0
  -2  123  112   0
   0  204  193   0
   2  115   95   0

** K=   0  L=   5 **

  -7  214  214   0
  -5  295  305   0
  -3  560  533   0
```

```
   H /FO/ /FC/ PHI

  -1  180  209   0
   1  265  301   0
   3  401  399   0
   5  220  243   0
   7  175  155   0
   9  162  180   0

** K=   1  L=   5 **

 -10  176  153   0
  -7  187  176 180
  -6  337  303   0
  -5  331  310   0
  -4  244  272   0
  -2  435  440   0
  -1  231  213 180
   0  133  184   0
   1  166  173 180
   2  645  607   0
   3  451  406   0
   4  203  213   0
   5  142  133 180
   6  157  150   0
   8  169  195   0

** K=   2  L=   5 **

  -9  127  119   0
  -5  346  347   0
  -3  275  301   0
  -2  152  158   0
  -1  280  331   0
   1  330  361   0
   3  246  249   0
   5  283  289   0
   7  154  155   0

** K=   3  L=   5 **

  -8  164  159   0
  -5  133  164 180
  -4  501  503   0
  -2  193  240   0
  -1  315  344   0
   0  205  235   0
   1  218  223 180
   4  461  425   0
   6  175  159   0

** K=   4  L=   5 **
```

```
    H  /FO/  /FC/  PHI          H  /FO/  /FC/  PHI          H  /FO/  /FC/  PHI

   -7   180   165    0         -7   199   207  180        ** K=  1  L=  7 **
   -5   119   121    0         -6   144   134    0
   -1   202   224    0         -4   294   282    0         -8   122   125    0
    1   221   216    0         -2   263   287    0         -6   228   245    0
    3   215   235    0          0   246   279    0         -5   135   124    0
                                2   305   337    0         -4   188   180    0
  ** K=  5  L=  5 **            3   125   117  180         -3   105   102  180
                                4   146   137    0         -2   307   324    0
   -6   224   236    0          5   115    97  180          0   292   313    0
   -5   134   145  180          6   144   145    0          2   246   244    0
   -3   154   173    0          7   123   131    0          4   185   180    0
    0   336   326    0          8   180   222    0          6   194   194    0
    2   169   181    0                                      8   162   177    0
    6   165   162    0        ** K=  3  L=  6 **
                                                          ** K=  2  L=  7 **
  ** K=  7  L=  5 **           -7   384   380    0
                               -5   235   241    0         -7   144   120    0
   -2   122   164    0         -1   241   272    0         -6   141   130    0
                                1   408   430    0         -5   228   222    0
  ** K=  0  L=  6 **            3   211   200    0         -3   277   278    0
                                7   154   162    0         -2   170   174  180
  -10   170   191    0                                     -1   247   270    0
   -6   383   399    0        ** K=  4  L=  6 **            1   192   211    0
   -4   334   329    0                                      2   133   115    0
   -2   323   354    0         -8   179   183    0          3   170   171    0
    0   390   380    0         -4   166   163    0          5   263   272    0
    4   322   335    0         -2   185   182    0          6   174   183  180
    6   367   386    0          0   171   186    0
                                2   222   205    0        ** K=  3  L=  7 **
  ** K=  1  L=  6 **            3   109    43    0
                                4   168   173    0         -8   148   151    0
   -9   227   242    0                                     -4   227   234    0
   -8   303   333    0        ** K=  5  L=  6 **           -2   131   172    0
   -6   185   191  180                                      0   260   269    0
   -5   236   232    0         -3   119   136    0          2   183   190    0
   -4   367   345  180          3   183   180    0          4   138   139    0
   -3   648   619    0                                      6   165   146    0
   -2   438   411    0        ** K=  6  L=  6 **
   -1   274   286    0                                    ** K=  4  L=  7 **
    0   211   193    0          2   123    97    0
    1   159   182    0                                     -5   187   181    0
    2   230   215  180        ** K=  0  L=  7 **           -3   163   166    0
    3   250   246    0                                     -1   131   132    0
    5   275   290    0         -7   313   326    0          1   170   167    0
    7   205   180    0         -5   153   146    0          3   115   121    0
                               -1   482   480    0          4   118   137  180
  ** K=  2  L=  6 **            1   526   508    0          5   164   175    0
                                3   168   158    0
   -9   162   154    0          7   329   355    0        ** K=  5  L=  7 **
   -8   211   198    0
```

```
   H /FO/ /FC/ PHI


  -6  125  124   0
  -4  118   93   0
  -2  113  111   0
   0  125   94   0
   4  169  115   0

** K=  6  L=  7 **

  -3  134  104   0
   3  160  181   0

** K=  0  L=  8 **

  -6  160  141   0
  -4  263  218   0
  -2  196  166   0
   0  654  582   0
   6  228  249   0

** K=  1  L=  8 **

  -9  185  185   0
  -7  195  193   0
  -3  176  157   0
  -2  132  109 180
  -1  403  388   0
   1  277  282   0
   3  163  150   0
   5  162  126   0
   7  200  196   0

** K=  2  L=  8 **

  -8  174  184   0
  -6  224  210   0
  -2  258  278   0
  -1  260  219 180
   0  292  288   0
   1  298  300   0
   2  179  180   0
   4  160  129   0
   5  181  165 180
   6  173  177   0

** K=  3  L=  8 **

  -7  164  145   0
  -5  136  136   0
  -3  220  216   0
  -1  170  167   0
```

```
   H /FO/ /FC/ PHI


   1  208  197   0
   5  201  182   0
** K=  4  L=  8 **

  -6  115  105   0
  -5  117  120   0
  -4  192  182   0
  -3  111  126 180
  -2  183  188   0
   2  245  248   0
   4  220  205   0

** K=  5  L=  8 **

  -5  181  174   0
   3  176  163   0

** K=  0  L=  9 **

  -7  296  311   0
  -3  142  157   0
  -1  490  490   0
   3  238  246   0
   5  195  192   0

** K=  1  L=  9 **

  -8  203  210   0
  -6  123  101   0
  -4  135  134   0
  -2  204  220   0
   0  303  296   0
   2  190  175   0
   4  154  128   0

** K=  2  L=  9 **

  -6  113  126   0
  -5  208  212   0
  -3  119  123   0
  -2  114  113 180
  -1  135  134   0
   0  188  174   0
   1  338  343   0
   2  133  124 180

** K=  3  L=  9 **

  -6  179  200   0
```

```
   H /FO/ /FC/ PHI


  -2  170  186   0
   2  166  149   0
   4  182  166   0

** K=  4  L=  9 **

  -3  162  161   0
   0  122  101 180
   1  158  162   0
   2  143  148   0

** K=  0  L= 10 **

  -8  141  137   0
  -6  241  256   0
  -4  204  215   0
  -2  249  241 180
   0  476  455   0
   2  311  324   0

** K=  1  L= 10 **

  -7  122  139   0
  -5  159  114   0
  -3  141  148   0
  -1  217  219   0
   3  201  198   0

** K=  2  L= 10 **

  -3  160  169   0
  -2  370  376   0
  -1  285  312 180
   3  128  132   0
   4  194  206   0

** K=  3  L= 10 **

  -3  121  145   0
   1  179  173   0

** K=  4  L= 10 **

  -3  133  162 180
  -2  173  192   0

** K=  5  L= 10 **

  -3  124  117   0
```

```
    H /FO/ /FC/ PHI        H /FO/ /FC/ PHI         H /FO/ /FC/ PHI

** K=  0  L= 11 **       -1  164  176   0

   -3  281  297   0     ** K=  0  L= 13 **
   -1  232  229   0
    3  225  213   0       -3  175  160   0

** K=  1  L= 11 **      ** K=  1  L= 13 **

   -4  199  194   0       -2  177  138   0
   -2  151  155   0
    2  153  152   0
    4  159  178   0

** K=  2  L= 11 **

   -5  242  232   0
   -4  122   96 180
    1  192  201   0
    3  140  130   0

** K=  3  L= 11 **

   -2  118  119   0
    0  145  120   0
    2  149  142   0

** K=  4  L= 11 **

   -3  140  131   0

** K=  0  L= 12 **

   -6  169  167   0
   -4  235  228   0
    2  186  173   0

** K=  1  L= 12 **

   -5  166  159   0
   -3  183  153   0
    0  129  141 180
    1  144  159   0

** K=  2  L= 12 **

   -3  117  126   0
   -2  159  141   0

** K=  3  L= 12 **
```

Observed and calculated structure factors for [clgeH]ClO$_4$

```
    H  /FO/  /FC/  PHI          H  /FO/  /FC/  PHI          H  /FO/  /FC/  PHI

** K=  0  L=  0 **              8    33    36  180      ** K= 11  L=  0 **
                                9    52    51  180
    1    26    11    0                                      2    30    34  180
    2   318   335  180      ** K=  5  L=  0 **
    3   210   220    0                                  ** K=  1  L=  1 **
    4   431   449  180          1   164   166  180
    5   103    99    0          2    34    14  180         -9    77    78    0
    6   255   257    0          3    53    41    0         -8   138   137  180
    7   160   155  180          5   228   227    0         -7   135   137    0
    8    52    49  180          6   164   163  180         -6   235   229    0
    9    68    66    0          7   171   174  180         -5   217   220  180
                                8   107   109    0         -4   133   131    0
** K=  1  L=  0 **                                         -3   293   297    0
                            ** K=  6  L=  0 **             -2   863   965  180
    1   165   159  180                                     -1   272   283    0
    2   317   314    0          0   501   493  180          0    51    24    0
    3   230   221    0          1   177   179    0          1   708   724  180
    4   398   374    0          2   138   128    0          2   838   855    0
    5   309   300    0          4    86    86    0          3   561   548  180
    8   173   172    0                                      4   174   173  180
                            ** K=  7  L=  0 **              5   223   218    0
** K=  2  L=  0 **                                          7   106   103  180
                                1   146   150  180          9    88    95  180
    0   340   354    0          2   180   185    0
    1   593   598  180          3    42    36    0      ** K=  2  L=  1 **
    2   336   340  180          4   121   119  180
    3   205   188  180          5   156   152    0         -9    36    33  180
    4   275   271  180          6    46    48  180         -8    36    47    0
    5   257   260    0                                     -7   227   225    0
    6   250   247    0      ** K=  8  L=  0 **             -6   219   226  180
    7   128   136  180                                     -5   225   225    0
    9    75    77    0          0   180   172  180         -4   137   135    0
                                1    82    89    0         -3    41    50  180
** K=  3  L=  0 **              3   103    96  180         -2   121   134    0
                                4   130   129    0         -1   550   608    0
    1  1138  1306  180          5    64    65  180          0    38    18  180
    2   189   180  180          6   104   102  180          1   549   552    0
    4   119   123  180          7    80    84    0          3   534   531  180
    5   219   216    0                                      4   102   104    0
    7   187   186  180      ** K=  9  L=  0 **              5    88    92    0
    8   155   158    0                                      6   154   157  180
    9    78    73  180          3    66    67  180          7    54    39    0
                                5    57    57    0          9    61    57  180
** K=  4  L=  0 **
                            ** K= 10  L=  0 **          ** K=  3  L=  1 **
    0   173   164  180
    1   199   185    0          0   117   112  180         -8    85    84  180
    2   142   142  180          2    57    55    0         -6    66    67    0
    3   131   131    0          3   160   163  180         -5   144   142  180
    5   131   128  180          4    45    42    0         -4   123   117  180
```

```
   H /FO/  /FC/ PHI         H /FO/  /FC/ PHI         H /FO/  /FC/ PHI


  -2   35    31 180        -1  205   208   0         4  165   164   0
  -1  433   452   0         0  265   257 180         5   83    77 180
   0  612   631   0         1  352   332 180         6   32    33   0
   1  175   183   0         2   33    52 180
   2   42    45 180         3  216   203 180      ** K= 10  L=   1 **
   3   40    28   0         4  126   120   0
   4   84    88 180         5  123   126   0        -5   49    47 180
   5  164   162   0         6  135   130 180         2   61    65 180
   6   59    61   0         7   78    78   0         4   31    33 180
   8   57    59   0                                  5   31    39 180
                         ** K=  7  L=   1 **
** K=  4  L=   1 **                               ** K= 11  L=   1 **
                           -8   63    58   0
  -9   74    79 180        -6   53    45 180        -4   40    41 180
  -8   43    40 180        -5   79    75   0        -2   83    88   0
  -7  173   163   0        -4   47    33 180        -1   48    59 180
  -6  234   237 180        -3  112   112 180         1   72    84   0
  -4   76    69 180        -2  270   270   0         4   27    30   0
  -3  357   344 180         1  181   167   0
  -2  246   251 180         2  173   178 180      ** K= 12  L=   1 **
  -1  162   176   0         5  150   150 180
   0  149   151 180         6   50    48 180        -2   31    52 180
   2  215   218   0                                 -1   36    49 180
   3  200   199 180      ** K=  8  L=   1 **         0   46    69   0
   4  207   202   0
   5  188   184   0        -7   41    43   0      ** K=  0  L=   2 **
   6  212   218 180        -5   38    40 180
   7   61    60   0        -4  107    99   0        -9   59    70 180
                           -3  110   106 180        -8  155   152 180
** K=  5  L=   1 **        -2  130   128   0        -7  263   272   0
                           -1  103   104   0        -6  291   293 180
  -8   28    23   0         0  132   128 180        -5  201   199 180
  -3  169   171 180         1   62    67   0        -4  251   258   0
  -2   81    80   0         2  132   125   0        -3  242   260 180
   0  114   107 180         3   63    61   0        -2  167   171   0
   1   84    80 180         4  156   152   0        -1  808   989   0
   2  498   494 180         6   87    91 180         0  610   632 180
   3  129   129   0                                  1  210   213   0
   4   49    46   0      ** K=  9  L=   1 **         2  272   239 180
   5  128   123   0                                  3  386   401 180
                           -6   78    76 180         4  500   488   0
** K=  6  L=   1 **        -5  115   116   0         5  118   113 180
                           -4   50    49 180         6  164   164 180
  -8   40    43 180        -3   54    49 180         7   85    86   0
  -7  114   115   0        -2  135   135   0         8   72    79   0
  -6   91    88 180        -1  237   234 180         9   83    88 180
  -5   63    56 180         0  116   117 180
  -4  173   167   0         1  120   110   0      ** K=  1  L=   2 **
  -3   68    66 180         2   41    33 180
  -2  242   241   0         3  107   107   0        -9   92    97 180
```

```
   H  /FO/  /FC/ PHI

  -7    86    92 180
  -6    61    54   0
  -5    99   101   0
  -4   368   376 180
  -3   152   150   0
  -2    34    29 180
  -1   488   543 180
   0   301   306 180
   1   555   555   0
   3   175   176   0
   4   159   156   0
   5   166   158 180
   6   116   122 180
   8    56    59 180

** K=   2  L=    2 **

  -8    47    47 180
  -7   126   129   0
  -6   123   122 180
  -5    84    91 180
  -4   164   168   0
  -3   317   323 180
  -2   109   101   0
  -1   385   430   0
   0   901   990 180
   1   130   138 180
   2   302   292   0
   3   167   172 180
   4   277   269   0
   5   214   217   0
   6    80    76 180

** K=   3  L=    2 **

  -9   123   123 180
  -8   199   206   0
  -7    58    58 180
  -6   125   122 180
  -5   289   291   0
  -4    35    43 180
  -3   113   115   0
  -2    21     1 180
   0   671   686 180
   1    28    26   0
   2   243   252 180
   3    33    32   0
   4   125   122   0
   5   284   272 180
   6    46    47   0
```

```
   H  /FO/  /FC/ PHI

   7   152   152   0
   8   114   117 180

** K=   4  L=    2 **

  -9    33    36 180
  -8    63    70   0
  -7   160   158   0
  -6   100    99   0
  -5   156   156 180
  -4   165   160   0
  -3   160   159   0
  -1   102   110   0
   0   372   368   0
   2    60    57   0
   3    67    55 180
   4   200   201 180
   5    45    45 180
   6   154   155 180

** K=   5  L=    2 **

  -9    92    92 180
  -8    73    75   0
  -7    79    76 180
  -6   181   176 180
  -5   154   149   0
  -4    38    27 180
  -2   268   281   0
  -1    40    38 180
   0   125   128 180
   1   627   620   0
   2   124   119   0
   3    91    86 180
   4   357   347   0
   5   132   130 180
   6    47    43 180
   7   110   112   0
   8    82    84 180

** K=   6  L=    2 **

  -8    38    44   0
  -7   107   112 180
  -4   235   228 180
  -3   118   110 180
  -2    28    34   0
  -1   264   278 180
   0    77    68   0
   3    95    92   0
```

```
   H  /FO/  /FC/ PHI

   4    72    72 180
   5    93    96   0
   6    75    74   0

** K=   7  L=    2 **

  -8   117   110   0
  -6   168   168 180
  -5    92    90   0
  -3   150   148 180
  -2   134   134   0
  -1   141   152 180
   0    32    25 180
   2   163   161 180
   3   108   104 180
   5   127   126 180
   6    31    26   0
   7    45    50   0

** K=   8  L=    2 **

  -7    94    92 180
  -6    69    60   0
  -5   107   109   0
  -4   125   126 180
  -3   172   169   0
  -1   132   140 180
   0   248   235   0
   1    88    85 180
   2   170   179 180
   3   139   130   0
   5    43    42 180
   6    68    73   0

** K=   9  L=    2 **

  -2    93    99   0
  -1    93    97 180
   2    66    66 180

** K=  10  L=    2 **

  -6    60    61   0
  -5    66    67   0
  -4    98   101 180
  -3    89    93   0
  -1    31    31 180
   0   116   118   0
   2    81    77 180
   3    57    55   0
```

```
   H /FO/ /FC/ PHI


   4   43   42 180
   5   38   40 180

** K= 11  L=  2 **

  -4   35   35   0
  -2   40   42 180
   1   41   43 180
   2   76   86   0
   3   86  103   0

** K= 12  L=  2 **

  -1   40   56 180

** K=  1  L=  3 **

  -9   79   83 180
  -8  216  226   0
  -7  130  136   0
  -6  379  386 180
  -5  118  117   0
  -4  206  210 180
  -3  168  151   0
  -2  676  772   0
  -1  183  192 180
   0  343  355 180
   1  432  439   0
   2  225  229 180
   3  222  214   0
   4  206  210   0
   5  158  146 180
   7   69   64   0
   8   50   54 180

** K=  2  L=  3 **

  -9   86   84   0
  -8   56   55   0
  -7  327  338 180
  -5  149  148 180
  -4  145  145   0
  -3  194  199   0
  -2  249  249 180
  -1  112  122 180
   1  187  179   0
   2  280  275 180
   3  233  235   0
   4   69   65 180
   5   47   51   0
```

```
   H /FO/ /FC/ PHI


   6  213  212   0

** K=  3  L=  3 **

  -9   66   66 180
  -8   69   68   0
  -7   70   70   0
  -6  129  133 180
  -3  327  338 180
  -2  341  365   0
  -1   94  100 180
   0  476  480 180
   1   92   71 180
   2  175  169 180
   3  109  107 180
   4  155  154   0
   5  131  127 180
   6  104  108 180
   7   66   63   0

** K=  4  L=  3 **

  -9   66   75   0
  -8  116  116   0
  -7  265  269 180
  -6   82   77   0
  -5  141  135   0
  -4   41   40   0
  -3  250  252   0
  -2   44   50   0
  -1  406  427 180
   0   89   90   0
   1  420  402   0
   2  263  259 180
   3  315  302   0
   4  131  132 180
   5  276  278 180
   6  112  108   0
   7   88   90 180
   8   56   59 180

** K=  5  L=  3 **

  -9   30   19 180
  -8   75   74 180
  -7   90   89 180
  -6   85   87   0
  -4   83   75   0
  -3   57   53 180
   1  198  188 180
```

```
   H /FO/ /FC/ PHI


   2  131  123   0
   3  101   89   0
   4  199  203   0
   5  100  100   0

** K=  6  L=  3 **

  -8  101  108   0
  -7   89   87 180
  -5   92   91   0
  -4  193  196 180
  -3  184  186   0
  -2   80   81   0
  -1  430  442 180
   2  124  119 180
   3  170  169   0
   4  105  100 180
   5  183  183 180
   6  146  146   0

** K=  7  L=  3 **

  -8   36   33 180
  -6  200  199   0
  -5   45   52 180
  -3  157  160   0
  -2  179  181 180
  -1  170  172   0
   0  261  258   0
   1  111  110 180
   2   76   74   0
   3   51   54 180
   4  173  165 180

** K=  8  L=  3 **

  -7   29   34 180
  -4   87   91 180
  -3   75   78   0
  -1  116  120 180
   0  114  113   0
   1   35   25   0
   2  166  164   0
   3  147  146   0
   5   73   73 180

** K=  9  L=  3 **

  -6   44   42   0
  -5  125  131 180
```

```
    H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

   -3    67    72    0       -3   217   214    0       -6    65    66  180
   -2   245   256  180       -2   432   423    0       -5    41    17  180
    0    64    57    0       -1   106   105  180       -4    51    54    0
    1    79    83  180        0   146   147    0       -3   181   174    0
    2    57    55    0        1   409   388    0       -2   143   145    0
    4   102   103  180        2   222   215    0       -1   218   228  180
    5    97    99    0        4   189   192  180        0   260   250    0
                              5    58    61  180        1    55    42    0
  ** K= 10  L=  3 **          6   120   118  180        2   196   194  180
                              7    66    68  180        5    82    81  180
    1    88    92  180                                  6    67    70    0
    3    63    71  180     ** K=  2  L=  4 **
                                                     ** K=  5  L=  4 **
  ** K= 11  L=  3 **         -9    35    36  180
                             -8    82    88    0       -9   104   103    0
   -3    40    46    0       -7   277   273  180       -8   152   152  180
   -2    63    69  180       -6    71    74  180       -7   122   123  180
    0    53    62    0       -5   161   159    0       -6   171   170    0
                             -4   430   440  180       -5   170   168  180
  ** K= 12  L=  3 **         -3   182   190    0       -4    48    50  180
                             -2   374   388    0       -3   341   342    0
   -1    46    73    0       -1   166   188  180       -2   243   245  180
                              0    44    21  180       -1   234   227  180
  ** K=  0  L=  4 **          1    31    32  180        0   202   199    0
                              2    46    43    0        1   186   181  180
  -10    26    43  180        3   445   440    0        2   172   173    0
   -9    62    65  180        4   144   152    0        3   207   202    0
   -8   231   233    0        7    62    63  180        4   248   239  180
   -7    48    47    0        8    50    53  180        5    84    82    0
   -6   273   275    0                                  7    87    87  180
   -5   170   171    0     ** K=  3  L=  4 **
   -4   424   443  180                               ** K=  6  L=  4 **
   -3   342   355    0       -9   129   133    0
   -2    95    95  180       -8    61    59    0       -8    45    41  180
   -1   202   211  180       -6    61    58    0       -6    68    72  180
    0   132   121  180       -5   341   349  180       -5   105   106  180
    1   432   414  180       -4    75    74    0       -4   198   199    0
    2   385   376  180       -2    65    71  180       -3   142   143  180
    3   291   287    0       -1   270   272  180       -2    59    61  180
    4    86    82  180        0    96    99    0       -1    69    70    0
    5   342   330  180        1   229   223  180        0   144   147  180
    6   126   132  180        2   129   128    0        2    99    98    0
    7    27    29  180        3   257   254    0        3   189   186  180
                              4   422   417  180        4    44    48  180
  ** K=  1  L=  4 **          6   103   103    0        5    80    70    0

   -8    39    33  180     ** K=  4  L=  4 **        ** K=  7  L=  4 **
   -7    58    55    0
   -6   197   205    0       -9    56    50    0       -8    63    58  180
   -4   177   181    0       -8    63    64    0       -7    53    52  180
```

```
   H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI

  -6    54    63    0        -7   327   333  180        -6   124   127    0
  -4    64    71    0        -6   174   175    0        -4   319   319    0
  -3   163   162    0        -5   154   152  180        -3    85    81  180
  -2   223   222  180        -4   122   108    0        -2   124   126  180
  -1    60    61    0        -3   293   313    0        -1   365   365    0
   0    80    73    0        -2   398   409  180         1   172   170  180
   1   187   192  180         0   160   151    0         2   362   350    0
   2    68    69    0         1   111   107  180         3   123   115  180
   3    81    75    0         3   152   152    0         5   138   134    0
   4    55    57  180         4    78    73  180         6   194   190  180
                              5   122   123    0
** K=   8   L=   4 **         6    95    94    0      ** K=   5   L=   5 **
                              7   110   109  180
  -7   109   106    0                                  -9    36    36  180
  -5    87    91  180      ** K=   2   L=   5 **        -8    68    64  180
  -4   204   206    0                                  -7    62    56    0
  -3    89    91  180        -8   118   123  180        -6   117   120  180
  -2   124   118  180        -6    80    91    0        -4    69    70  180
  -1   144   143    0        -5    63    66  180        -2   136   143    0
   0   114   109  180        -3   290   289  180         2   140   136    0
   1    31    49    0        -2   175   176  180         3    62    66    0
   2   109   107    0        -1    91    84  180         5    46    45  180
   3    73    71  180         0    64    67    0         6    27    16  180
   4    27     1    0         1   404   393  180
                              2   129   132    0      ** K=   6   L=   5 **
** K=   9   L=   4 **         3    45    50  180
                              5   112   107    0        -8    69    65  180
  -5    28    23    0         6   139   137  180        -7   111   114    0
  -1    40    35    0                                  -6    71    74  180
   3    58    60  180      ** K=   3   L=   5 **        -5   223   215  180
   4    41    42    0                                  -4    83    77    0
                             -9   134   129    0        -3    63    68  180
** K=  10   L=   4 **        -7    47    53    0        -2   143   145  180
                             -6   233   242    0        -1   319   305    0
  -4    52    53    0        -4    41    33  180         0   110   114  180
  -3    82    84  180        -3   222   224    0         2   157   158    0
  -2    42    48  180        -2   265   272  180         3   189   191  180
  -1   104   111    0         0   169   162    0         4    48    43  180
   0    62    61  180         1   205   210  180         5   143   144    0
   2   106   111    0         2    78    79    0
                              3    53    46    0      ** K=   7   L=   5 **
** K=  11   L=   4 **         4   225   221  180
                              5    74    73  180        -8    58    56    0
  -3    66    71  180         7    59    62  180        -7   104   111    0
   1    43    57    0                                  -6   137   135  180
                           ** K=   4   L=   5 **        -5    74    76    0
** K=   1   L=   5 **                                   -3   204   202  180
                             -9    67    58  180        -2   165   174    0
  -9   101   106    0        -8   181   182  180        -1    97   100  180
  -8   182   181  180        -7   168   161    0         0   137   130  180
```

```
   H  /FO/  /FC/  PHI


   1   105   102    0
   3    34    40  180
   4    55    49    0
   5    55    52  180

** K=    8  L=    5 **

  -7    40    36    0
  -4    65    63    0
  -2    92    87  180
   0    61    64  180
   3    64    68  180
   4    64    59  180

** K=    9  L=    5 **

  -6   115   120  180
  -5    65    68    0
  -4    96    98    0
  -2   144   147    0
   0    98    99  180
   1    80    76    0
   3    49    50  180
   4    96   102    0

** K=   10  L=    5 **

   1    39    44    0
   3    26    33    0

** K=   11  L=    5 **

  -3    59    64  180
   0    49    58  180

** K=    0  L=    6 **

  -9   103   102    0
  -8    80    80  180
  -7   236   230    0
  -6   235   246    0
  -5   347   347  180
  -4   397   400    0
  -3    73    69  180
  -2   296   312  180
  -1    54    56    0
   0   119   112    0
   1    75    64    0
   2   163   169    0
   3   116   114  180
```

```
   H  /FO/  /FC/  PHI


   4   252   256  180
   5    63    57    0
   7    60    69    0

** K=    1  L=    6 **

  -9    48    54  180
  -8    85    88  180
  -6    51    53    0
  -5    78    73    0
  -4   176   165    0
  -3   113   100    0
  -2    75    75    0
   0    69    64  180
   1    54    50    0
   2    69    65    0
   3   168   172  180
   4   111   109    0
   5    55    53    0
   6    40    27  180

** K=    2  L=    6 **

  -9    25    35    0
  -8   201   198  180
  -7    63    69  180
  -5   152   146  180
  -4   318   319    0
  -3    62    74  180
  -2    87    87  180
  -1   230   232    0
   0   115   114  180
   2   256   252    0
   3    95    93  180
   4   131   137  180
   5   126   121    0

** K=    3  L=    6 **

  -9    80    83  180
  -7    68    74    0
  -6   278   280  180
  -5    44    51  180
  -4   115   115    0
  -3   314   332  180
  -1   235   233    0
   0    79    82  180
   1    69    74    0
   3   240   243  180
   4   211   210    0
```

```
   H  /FO/  /FC/  PHI


   5    57    55    0
   6    46    46    0

** K=    4  L=    6 **

  -8    61    59  180
  -7    82    77    0
  -6    39    42  180
  -4    53    49    0
  -3    64    58  180
  -2   325   320  180
  -1    88    90  180
   0    95    87  180
   3    58    47  180
   6    42    41  180

** K=    5  L=    6 **

  -7   134   136    0
  -5   193   189    0
  -4    71    65    0
  -3   279   272  180
  -2   164   161    0
  -1    56    51    0
   0   200   200  180
   1   212   209    0
   2   115   123  180
   3   258   248  180
   4   124   126    0
   5    43    52  180
   6    91    91  180

** K=    6  L=    6 **

  -8    44    51    0
  -7    76    71  180
  -5   218   214    0
  -4    96   101  180
  -3   134   138    0
  -2   114   115    0
   0    93    94    0
   3    77    77    0
   4    48    47    0

** K=    7  L=    6 **

  -7    57    54    0
  -6    54    47  180
  -5    60    56    0
  -3   227   225  180
```

```
   H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI

  -1   117   116    0         1   177   177    0        -5    70    63    0
   0    37    36  180         2   179   181  180        -4   117   106  180
   1   112   112    0         4    46    48    0        -3    59    52  180
   4    56    58    0         5   116   120  180        -2   117   120    0
                              6    48    53    0        -1    95    92  180
** K=  8  L=  6 **                                     0    97    99    0
                           ** K=  3  L=  7 **            1   114   118    0
  -7    37    38  180                                    2   138   137  180
  -4   161   161  180        -9    66    65  180         4    57    51    0
  -3    65    66    0        -7    61    62    0
  -2   118   108    0        -6    96   103  180      ** K=  7  L=  7 **
  -1   124   119  180        -5    73    64    0
   0    60    59    0        -3    99    93  180        -6   123   119    0
   2   120   116  180        -2    59    56    0        -5    76    75  180
   4    33    34    0         0    46    33  180        -4   124   128  180
                              1   198   196    0        -2   164   164  180
** K= 10  L=  6 **            2    63    71    0         0    42    29    0
                              3    43    41  180         1    99    97  180
  -4   109   115  180                                    3    54    61    0
  -3    46    46  180      ** K=  4  L=  7 **            4    34    36  180
  -2    98    99    0
  -1    55    53  180        -8    57    61    0      ** K=  8  L=  7 **
                             -7    55    49  180
** K=  1  L=  7 **           -5   219   224    0        -6    29    36    0
                             -4   184   192  180        -5   129   124    0
  -9    79    75  180        -3   139   141  180        -4    70    69    0
  -8    57    61  180        -2   145   141    0        -1    79    84  180
  -7   123   117    0        -1   210   213  180         0    36    32  180
  -6   171   163  180         0    64    64    0         2    53    51  180
  -5   121   122    0         1   108   108    0
  -4   295   302    0         2   258   260  180      ** K=  9  L=  7 **
  -3   400   404  180         3    48    45    0
  -1    43    43  180         4    89    88    0        -3   103   102    0
   0   121   113  180         5    85    84  180         0   115   121    0
   1   156   155    0
   2    88    92    0      ** K=  5  L=  7 **         ** K= 10  L=  7 **
   3   199   211  180
   6   104   102  180        -7    51    53  180        -1    44    47    0
                             -5    43    41  180
** K=  2  L=  7 **           -3   233   231    0      ** K=  0  L=  8 **
                             -2    34    35    0
  -8    67    68    0        -1    70    68    0        -9   137   134  180
  -7    65    70    0         0    67    71  180        -8   135   129    0
  -6    43    41  180         1    50    50  180        -6   226   232  180
  -5   187   186    0         3    39    28  180        -5    95    83    0
  -4   187   184  180                                   -4   245   240  180
  -3   170   167  180      ** K=  6  L=  7 **           -3    98    95  180
  -2   294   301    0                                   -2   166   167    0
  -1    63    63    0        -7   128   123  180        -1   362   368  180
   0    79    79    0        -6    71    70  180         1   233   233    0
```

```
   H /FO/  /FC/ PHI

   2   39    41 180
   3   39    42   0
   4  165   173   0
   5   75    83 180
** K=   1  L=   8 **

  -6  104   109   0
  -5  132   139   0
  -4  129   128 180
  -3   71    73   0
  -2  176   179 180
  -1  318   328 180
   1   67    58 180
   2   81    82 180
** K=   2  L=   8 **

  -8  132   123   0
  -7   78    79 180
  -6   53    60 180
  -5  236   242   0
  -3   72    71   0
  -2  285   286   0
  -1   83    81 180
   0   49    47 180
   1   50    40   0
   2   95   102 180
   5   72    80 180
** K=   3  L=   8 **

  -7  136   140 180
  -6   46    41 180
  -5   46    46   0
  -4  147   140 180
  -3  183   190   0
  -2  134   139 180
  -1  101    96 180
   0  316   315   0
   3  140   146   0
   4   87    95 180
** K=   4  L=   8 **

  -8   38    44   0
  -7   43    43   0
  -6   91    89   0
  -5   34    34 180
  -4   84    89 180
```

```
   H /FO/  /FC/ PHI

  -3  122   114 180
  -2  113   119 180
   0   54    57   0
   1   67    55   0
   2   75    75 180

** K=   5  L=   8 **

  -7   72    74 180
  -6  153   155   0
  -5   33    36   0
  -4   80    77 180
  -3  217   218   0
  -1  118   117 180
   0  144   141   0
   1   64    67 180
   2   37    32 180
   3   72    77   0
   4   59    70 180

** K=   6  L=   8 **

  -3   88    79 180
  -1  155   154   0

** K=   7  L=   8 **

  -5   89    84 180
  -4  103   100 180
  -3   52    46   0
   0   67    60   0
   1   87    91 180
   2   53    48 180
   3   66    66   0

** K=   8  L=   8 **

  -5   74    78 180
  -4   90    88   0
  -3   52    49   0
  -2   93    94 180
   1   72    76 180

** K=   9  L=   8 **

  -2   37    34   0

** K=   1  L=   9 **

  -8   35    43   0
```

```
   H /FO/  /FC/ PHI

  -7   73    71 180
  -6  181   176   0
  -4  271   267 180
  -3  186   189   0
  -2   95    94   0
   0  186   182   0
   1  131   136 180
   2  147   156 180
   3   96   101   0

** K=   2  L=   9 **

  -8   83    79 180
  -5  190   196 180
  -3  271   270   0
  -2   58    54 180
  -1  174   170   0
   1  121   116 180
   2  163   161   0
   3   39    42   0
   4   45    47 180

** K=   3  L=   9 **

  -7   70    71 180
  -5   59    67 180
  -4  139   131 180
  -3   70    72 180
  -2   67    69 180
  -1   73    75 180
   0   55    54   0
   3   70    73   0

** K=   4  L=   9 **

  -7   65    62   0
  -6   75    76   0
  -5  151   143 180
  -4   41    41   0
  -3  160   160   0
  -2  186   187 180
   0  113   117 180
   1  203   197 180
   2  108   111   0

** K=   5  L=   9 **

  -5   60    65   0
  -4  133   140   0
  -3   42    36   0
```

```
   H /FO/  /FC/ PHI

  -2   32    39   0
  -1   71    64 180
   0   34    40 180

** K=   6  L=   9 **

  -6   33    37   0
  -5  137   131 180
  -3   63    62   0
  -2   46    52 180
  -1  105   104   0
   0   79    79   0
   1   72    72 180
   2   68    73   0

** K=   7  L=   9 **

  -4   49    52   0
  -3   77    79 180
  -2   29    38 180
   1   73    69   0

** K=   8  L=   9 **

  -2   72    73 180

** K=   0  L= 10 **

  -7   91    76   0
  -6   95   102   0
  -5  226   223 180
  -4   70    68 180
  -2  324   326 180
  -1   74    75   0
   0  136   131   0
   1   78    74 180
   2   60    63   0

** K=   1  L= 10 **

  -7   56    62   0
  -6   36    46   0
  -3   90    89 180
   0  143   141 180
   3   43    42 180

** K=   2  L= 10 **

  -6  108   105   0
  -4   59    56   0
```

```
   H /FO/  /FC/ PHI

  -3   93    92   0
  -1  105   104   0
   1  152   151 180

** K=   3  L= 10 **

  -7   92    93   0
  -6   91    92 180
  -5   90    91 180
  -4  136   134   0
  -3   85    87 180
  -1  267   260   0
   0   75    74 180

** K=   4  L= 10 **

  -6   44    37   0
  -5   77    76 180
  -4   41    41 180
  -3   47    40   0
  -2   30    39   0
  -1   27    14   0
   0   82    83   0

** K=   5  L= 10 **

  -5   94    91 180
  -4   63    63   0
  -3   66    66 180
  -1   45    51   0
   0  164   165 180

** K=   6  L= 10 **

  -3   39    34 180
  -1   28    31 180
   0   76    75 180

** K=   1  L= 11 **

  -6   65    61 180
  -4  108   111   0
  -3   49    48 180
  -1  115   114   0
   0  104   114 180
   1   38    26 180

** K=   2  L= 11 **

  -6   52    59 180
```

```
   H /FO/  /FC/ PHI

  -3   99   103 180
  -2   58    66   0
  -1   86    87 180
   0   63    59 180
   1   84    82   0

** K=   3  L= 11 **

  -5   48    41 180
  -4   56    57   0
  -3   49    46 180
  -2   69    67 180
  -1   78    67   0

** K=   4  L= 11 **

  -3   93    93 180
  -2  103   100   0

** K=   0  L= 12 **

  -2   81    81   0
```

Observed and calculated structure factors for

$[\text{clgeH}]_2[CuCl_4(H_2O)_2]$

```
   H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI


** K=  0  L=  0 **            1   191   170  180            1   115   110    0
                              2   357   337  180            3    56    56  180
   1   716   723    0         3    88    81    0
   2  1646  1807  180         4   314   306    0      ** K= 12  L=  0 **
   3   148   143    0         5    90    92  180
   4   879   868    0         6   185   190  180            0   265   258    0
   5   369   357    0                                       1   176   169    0
   6   216   211    0      ** K=  6  L=  0 **               2    61    51    0
   7    57    56    0                                       3    96    96    0
                              0   967  1124    0
** K=  1  L=  0 **            1   499   476    0      ** K=  1  L=  1 **
                              2   209   192  180
   1   133   122  180         3    70    70    0           -7   182   184    0
   2   732   708    0         4   389   372    0           -6   446   446    0
   3    98   103    0         5   336   334    0           -5   170   167    0
   4   557   540  180         6   191   190    0           -4    32    22  180
   5    36    39  180                                      -3   507   488    0
   6   248   251    0      ** K=  7  L=  0 **              -2   716   721    0
                                                           -1   255   249    0
** K=  2  L=  0 **            1    49    48  180            0   557   544    0
                              2    42    45  180            1   823   842    0
   0   685   925    0         4    32    33    0            2   326   320    0
   1   657   637    0         6    62    62  180            3   226   218    0
   2   162   156    0                                       4   405   387    0
   3   107   108    0      ** K=  8  L=  0 **               5   282   282    0
   4   443   426    0                                       6   132   140    0
   5   475   464    0         0   746   775    0            7    53    52    0
   6   141   143    0         1   371   358    0
                              2   113   100  180      ** K=  2  L=  1 **
** K=  3  L=  0 **            3    50    46    0
                              4   305   292    0           -7   136   145    0
   1   229   219  180         5   318   319    0           -6    97    93  180
   2   245   230    0                                      -5   185   181  180
   3    63    61    0      ** K=  9  L=  0 **              -4   259   250    0
   4   261   249  180                                      -3   237   217    0
   5    28    10  180         1    32    32    0           -2   261   246  180
   6   126   133    0         2    92    89    0           -1    48    44  180
                              3    92    89  180            1   408   364  180
** K=  4  L=  0 **            4   141   141  180            2   192   177    0
                              5    71    74    0            3   399   373    0
   0   115   116    0                                       4   172   171  180
   1   664   653    0      ** K= 10  L=  0 **               5   193   188  180
   2   617   590    0                                       6    68    68    0
   3    61    51  180         0   384   374    0
   4   254   246    0         1   345   334    0      ** K=  3  L=  1 **
   5   519   512    0         2    71    64    0
   6   107   109    0         3    86    89  180           -7   115   104    0
                              4   228   226    0           -6   166   157    0
** K=  5  L=  0 **                                         -5   450   441    0
                           ** K= 11  L=  0 **              -4   164   156    0
```

```
  H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

 -3   279   259  180        2   246   232  180       -4    76    75    0
 -2   744   751    0        3   169   166  180       -1    94    98    0
 -1  1166  1548    0        4   227   224    0        0    75    74  180
  0   269   256    0        5    37    41    0        1   122   123  180
  1   331   296  180        6   145   147  180        2   160   159    0
  2   321   306    0                                 3    84    88    0
  3   475   454    0      ** K=  7  L=  1 **          4   179   176  180
  4   515   497    0
  5   371   370    0       -6   313   310    0      ** K= 11  L=  1 **
  6    63    50  180       -5    31    20    0
                           -4    96    90    0       -2   367   364    0
** K=  4  L=  1 **         -3   365   347    0       -1   326   339    0
                           -2   135   131    0        0    32    27  180
 -6   113   115    0       -1   372   394    0        1   140   137    0
 -5    38    33    0        0   764   779    0        2   278   269    0
 -4   182   174  180        1    88    81    0        3    64    64    0
 -3    87    82    0        2   162   154  180
 -2   179   173    0        3   498   481    0      ** K= 12  L=  1 **
 -1   317   319  180        4   415   409    0
  0    60    55    0                                -3   127   121    0
  1   523   483    0      ** K=  8  L=  1 **         -2   146   143    0
  2   178   169  180                                -1   156   165  180
  3   331   314  180       -5    51    54    0        0    53    60  180
  4   113   111    0       -4   133   131    0        1   157   150    0
  5    71    80    0       -3   189   179  180        2    72    67  180
  6    84    91  180       -2    74    73  180
                           -1   366   379    0      ** K= 13  L=  1 **
** K=  5  L=  1 **          0    62    55  180
                            1   412   391  180       -1   205   215    0
 -6   218   213    0        2   194   182    0        0   182   176    0
 -5   224   217    0        3   223   220    0
 -4   170   164    0        4   241   233  180      ** K=  0  L=  2 **
 -3   223   217    0        5    85    95  180
 -2   430   421    0                                -7   222   223    0
 -1   485   529    0      ** K=  9  L=  1 **         -6   445   445    0
  0   434   425    0                                -5    55    49    0
  1   282   260    0       -5   188   184    0       -4    69    62  180
  2   247   235    0       -4    87    82    0       -3   499   502    0
  3   401   378    0       -3    70    68    0       -2   722   775    0
  4   429   412    0       -2   272   263    0       -1   759  1055    0
  5   183   186    0       -1   372   387    0        0   623   614    0
                            0   308   294    0        1   693   663  180
** K=  6  L=  1 **          1   194   183    0        2   109   116    0
                            2   138   135    0        3  1212  1233    0
 -6    79    81    0        3   153   140    0        4   523   509    0
 -4   160   154  180        4   231   224    0        5   309   322  180
 -3   151   144    0        5   219   223    0        6    38    31    0
 -2   206   202    0
 -1   236   241  180      ** K= 10  L=  1 **        ** K=  1  L=  2 **
  1   251   236    0
```

```
   H  /FO/  /FC/  PHI


  -7    62    65    0
  -6    75    74  180
  -5    90    88  180
  -4   237   228    0
  -3    30    31    0
  -2   323   315  180
  -1   166   187    0
   0   223   195    0
   1   208   193  180
   2    66    65    0
   3    52    53    0
   4   184   173  180
   6   130   134    0

** K=   2   L=   2 **

  -7   267   269    0
  -6   250   249    0
  -5    67    61    0
  -4    44    45    0
  -3   440   437    0
  -2   802   863    0
  -1   586   735    0
   0   138   148    0
   1    29    37    0
   2   588   564    0
   3   710   687    0
   4   270   269    0
   6    57    56    0

** K=   3   L=   2 **

  -6    92    95  180
  -4   322   309    0
  -3    33    26  180
  -2   394   396  180
  -1    88   103    0
   0   109   102    0
   1   167   158  180
   2   226   210    0
   3   111   111    0
   4   233   227  180
   5    44    48  180
   6   117   117    0

** K=   4   L=   2 **

  -7   271   274    0
  -6    81    82    0
  -5    48    41    0

   H  /FO/  /FC/  PHI


  -4    42    38    0
  -3   376   366    0
  -2  1097  1264    0
  -1   577   718    0
   0   804   791  180
   1    30    15  180
   2  1090  1088    0
   3   571   554    0
   4    74    70    0
   5   126   127    0
   6    68    46    0

** K=   5   L=   2 **

  -7    70    69  180
  -6   128   127    0
  -5   159   158    0
  -4   336   323  180
  -3   157   151  180
  -2   531   548    0
  -1    85    90    0
   0   451   424  180
   1    82    80    0
   2    95    89    0
   3   148   145  180
   4    68    64    0
   5    50    49    0
   6   105   101  180

** K=   6   L=   2 **

  -6   314   314    0
  -4    97    93  180
  -3   473   463    0
  -2   692   726    0
  -1   287   331    0
   0    94   101    0
   1   132   131    0
   2   297   283    0
   3   550   540    0
   4   367   359    0
   5    52    52  180

** K=   7   L=   2 **

  -5    53    57  180
  -4    39    34  180
  -3    71    69    0
  -2    70    73    0
   0    33    28    0

   H  /FO/  /FC/  PHI


   2   110   100  180

** K=   8   L=   2 **

  -6   313   314    0
  -5    64    57    0
  -4    87    83  180
  -3   294   290    0
  -2   416   430    0
  -1   242   276    0
   0   311   299    0
   1   182   177    0
   2   120   119    0
   3   390   374    0
   4   296   286    0
   5    42    29  180

** K=   9   L=   2 **

  -5   100    98  180
  -4   342   337    0
  -3   165   161    0
  -2   390   402  180
  -1    66    78  180
   0   288   279    0
   1    55    55  180
   2    58    52  180
   3   114   116    0
   4    93    95  180

** K=  10   L=   2 **

  -5   101   107    0
  -4    34    32    0
  -3    48    50    0
  -2   531   558    0
  -1   417   494    0
   0   283   282  180
   1   142   137  180
   2   557   549    0
   3   398   390    0

** K=  11   L=   2 **

  -4    98    97  180
  -2   155   155    0
  -1    59    62  180
   0    96    91  180
   1   110   106    0
   3   115   110  180
```

```
   H  /FO/  /FC/  PHI

** K= 12   L=  2 **

  -3   168   166    0
  -2   241   247    0
  -1   198   225    0
   0    45    46    0
   2   195   188    0

** K= 13   L=  2 **

   0    94    89  180

** K=  1   L=  3 **

  -7   101   101    0
  -6   145   136    0
  -5    94    96    0
  -4   361   350    0
  -3   797   836    0
  -2   304   339    0
  -1   337   336  180
   0   666   655    0
   1  1061  1109    0
   2   319   314    0
   3   118   119    0
   4   258   257    0
   5   119   122    0
   6   142   140    0

** K=  2   L=  3 **

  -7   103   104    0
  -6    88    86  180
  -5   198   196  180
  -4   310   296    0
  -3   291   286    0
  -2   423   469  180
  -1   158   171  180
   0   336   316    0
   1   174   162  180
   2    69    59    0
   3   313   298    0
   4   203   204  180
   5   225   229  180
   6   152   160    0

** K=  3   L=  3 **

  -7   154   154    0
  -6   115   111  180
```

```
   H  /FO/  /FC/  PHI

  -5   209   204    0
  -4   493   486    0
  -3   275   281    0
  -2   558   637    0
  -1   582   637    0
   0   349   321  180
   1   174   175    0
   2  1043  1065    0
   3   488   468    0
   4   129   127  180
   5   100    99    0
   6   206   217    0

** K=  4   L=  3 **

  -4    49    42  180
  -3   214   206    0
  -2   120   132    0
  -1   341   347  180
   1   291   275    0
   2   149   137  180
   3   155   152  180
   4   144   142    0
   5    42    45    0
   6   101   110  180

** K=  5   L=  3 **

  -7   188   184    0
  -5    40    32    0
  -4   330   331    0
  -3   426   435    0
  -2   371   409    0
  -1   451   466    0
   0   215   205    0
   1    97   108    0
   2   519   496    0
   3   495   482    0
   4    74    79    0

** K=  6   L=  3 **

  -6    81    83    0
  -5   242   243    0
  -4   129   125  180
  -3   283   284  180
  -2   120   130    0
  -1   184   185    0
   0    29    27    0
   1    96    97    0
```

```
   H  /FO/  /FC/  PHI

   2   132   128  180
   3   230   224  180
   4   111   113    0
   5   128   129    0

** K=  7   L=  3 **

  -6   155   147    0
  -4   225   218    0
  -3   633   653    0
  -2   199   214    0
  -1   258   269  180
   0   375   353    0
   1   686   672    0
   2   291   277    0
   3   176   171    0
   4   122   117    0

** K=  8   L=  3 **

  -5   110   110  180
  -4    76    74    0
  -3   120   119    0
  -2    55    57  180
  -1    43    36    0
   1   155   144  180
   2    38    41    0
   3   121   117    0
   4   102   104  180
   5    66    67  180

** K=  9   L=  3 **

  -5   135   138    0
  -4   328   328    0
  -3   214   212    0
  -2    83    84    0
  -1   180   194    0
   0   264   258    0
   1   268   252    0
   2   291   280    0
   3   182   179    0
   4    51    52    0

** K= 10   L=  3 **

  -5    54    52  180
  -4   146   144    0
  -3   132   132    0
  -2    71    84  180
```

```
    H  /FO/  /FC/  PHI


   -1    79    87  180
    2    90    87    0

** K= 11   L=   3 **

   -4   227   225    0
   -3   154   156    0
   -2   193   202    0
   -1   230   239    0
    1    90    88    0
    2   339   329    0
    3   181   173    0

** K= 12   L=   3 **

   -3    87    87  180
   -2    39    48    0
    0    44    35  180
    1   125   124    0

** K= 13   L=   3 **

   -1   106   112  180

** K=  0   L=   4 **

   -7    62    69  180
   -6   242   238    0
   -5   321   320    0
   -4   401   404    0
   -3   664   718    0
   -2   116   104  180
   -1   626   632  180
    0  1063  1082    0
    1  1390  1528    0
    2   193   181    0
    3   250   240  180
    4   124   123    0
    5   263   269    0
    6   281   300    0

** K=  1   L=   4 **

   -7   103    99    0
   -6    59    60  180
   -5   233   227  180
   -4   341   337    0
   -3   406   423    0
   -2   524   589  180
   -1   411   407  180

    H  /FO/  /FC/  PHI


    0   452   422    0
    2   105   103  180
    3   209   204    0
    5   162   168  180

** K=  2   L=   4 **

   -7    82    79    0
   -6    80    78  180
   -5   182   184    0
   -4   688   705    0
   -3   536   568    0
   -2    31    16  180
   -1   104   118    0
    0   553   546    0
    1   672   647    0
    2   538   517    0
    3   125   123    0
    4    29    19  180
    5   248   254    0
    6   294   316    0

** K=  3   L=   4 **

   -7    67    69    0
   -5    83    77  180
   -4    33    37    0
   -3    50    49    0
   -1   104   104    0
    0    29    19  180
    1   151   147  180
    2    55    53    0
    3    85    90    0
    4    65    64  180
    5    49    48  180

** K=  4   L=   4 **

   -7   129   124    0
   -6   157   152  180
   -5   191   189    0
   -4   696   713    0
   -3   342   360    0
   -2    35    20  180
   -1   236   250    0
    0   439   421    0
    1   603   582    0
    2   536   529    0
    3    35    36    0
    4    36    35  180

    H  /FO/  /FC/  PHI


    5   312   325    0

** K=  5   L=   4 **

   -7    81    79  180
   -6    33    22    0
   -5   228   232    0
   -4   174   174  180
   -3   263   274  180
   -2   376   412    0
   -1   184   179    0
    0   408   383  180
    1    98    95    0
    2   166   158    0
    3   249   245  180
    5   163   175    0

** K=  6   L=   4 **

   -6   103   105    0
   -5   239   237    0
   -4   313   314    0
   -3   407   430    0
   -2    97   107    0
   -1   161   150  180
    0   572   547    0
    1   840   835    0
    2   138   133    0
    3   104   101  180
    4   193   193    0
    5   210   215    0

** K=  7   L=   4 **

   -5    57    51    0
   -4   126   121    0
   -2   152   157  180
    0   195   181    0
    2   132   128  180
    4    35    41    0

** K=  8   L=   4 **

   -6    48    44    0
   -5   177   178    0
   -4   300   301    0
   -3   370   390    0
   -2    83    93    0
   -1   140   134  180
    0   359   351    0
```

```
    H  /FO/  /FC/  PHI

    1   646   634    0
    2   221   209    0
    3    40    43  180
    4    75    71    0

** K=   9   L=   4 **

   -5    85    81  180
   -4    70    68    0
   -3   104   110    0
   -2   135   144  180
   -1    37    34    0
    0   211   199    0
    1   165   155  180
    2   135   126  180
    3   166   168    0

** K=  10   L=   4 **

   -5   124   121    0
   -4   376   382    0
   -3   175   188    0
   -1    79    80    0
    0   210   201    0
    1   382   377    0
    2   365   356    0
    3    54    53  180

** K=  11   L=   4 **

   -3    47    50    0
   -2    97   100    0
   -1    72    71  180
    0   114   105  180
    1    61    65    0
    2    60    60    0

** K=  12   L=   4 **

   -3   138   145    0
   -2    48    56    0
   -1   128   126    0
    0   155   153    0
    1   156   151    0

** K=   1   L=   5 **

   -7    84    81  180
   -6   333   329    0
   -5   522   531    0
```

```
    H  /FO/  /FC/  PHI

   -4   146   151    0
   -3    91    98    0
   -2   312   342    0
   -1   309   321    0
    0   680   663    0
    1   717   707    0
    2    45    47    0
    4   381   382    0
    5   275   284    0

** K=   2   L=   5 **

   -7    46    44    0
   -6   109   111    0
   -5   238   240  180
   -4    50    47  180
   -3   462   495    0
   -1   434   423  180
    0    64    62    0
    1    25    10    0
    2    69    61  180
    3   208   206    0
    5   171   179  180

** K=   3   L=   5 **

   -7   165   162    0
   -6   147   142    0
   -5   291   293    0
   -4   342   359    0
   -3    74    63  180
   -2   163   168    0
   -1   950  1000    0
    0   632   619    0
    1    86    72  180
    2   160   156    0
    3   303   302    0
    4   193   196    0
    5   272   282    0

** K=   4   L=   5 **

   -7    70    68  180
   -5   183   182    0
   -4    58    57    0
   -3   206   216  180
   -2   105   104  180
   -1   167   162    0
    0   146   133    0
    2    53    56  180
```

```
    H  /FO/  /FC/  PHI

    3    56    56  180

** K=   5   L=   5 **

   -7    79    76    0
   -6   166   163    0
   -5   273   271    0
   -4   283   286    0
   -3   123   132    0
   -2   198   211    0
   -1   465   468    0
    0   383   377    0
    1   267   251    0
    2   278   264    0
    3   152   152    0
    4   142   140    0
    5   239   257    0

** K=   6   L=   5 **

   -6    41    32    0
   -5   104   106    0
   -4   124   125  180
   -3   132   145  180
   -2   247   273    0
   -1   146   140    0
    0   226   218  180
    2    66    68    0
    3   120   123  180

** K=   7   L=   5 **

   -6   311   309    0
   -5   274   281    0
   -4    49    45    0
   -3   196   207    0
   -2   170   189    0
   -1    95    89    0
    0   568   548    0
    1   552   543    0
    2   100    99  180
    3    65    62  180
    4   335   342    0

** K=   8   L=   5 **

   -6    66    67    0
   -5   117   119  180
   -4    39    39    0
   -3   153   162    0
```

```
   H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI

  -2    85    95  180         0   619   584    0      ** K=  4   L=  6 **
  -1    57    54  180         1   250   250    0
   0   140   144    0         2   127   115  180        -7   268   269    0
   1    65    57  180         3   219   222    0        -6   199   205    0
   2   103   108  180         4   542   560    0        -5   115   110    0
   3   101   102    0         5   184   194    0        -4   172   174    0
                                                        -2   301   320    0
** K=  9   L=  5 **        ** K=  1   L=  6 **          -1   931   943    0
                                                         0   433   417    0
  -5   272   276    0        -7    39    32    0         1   363   343  180
  -4   196   199    0        -5   103   101  180         2    97    90    0
  -3    47    56  180        -4    74    77    0         3   560   558    0
  -2    53    56    0        -3   106   121    0         4   298   303    0
  -1   424   429    0        -2   216   220  180         5    57    65    0
   0   392   376    0         0   304   278    0
   1    89    81    0         1   113   112  180      ** K=  5   L=  6 **
   2    72    69    0         2   175   175  180
   3   155   154    0         3   142   151    0        -6    49    54  180
                              4    48    53    0        -5   180   189    0
** K= 10   L=  5 **           5   121   130  180        -3   283   297  180
                                                        -2   176   186    0
  -4    83    81    0      ** K=  2   L=  6 **          -1   272   268    0
  -3    39    40    0                                  0   263   250  180
  -2    63    74  180        -7   156   157    0         1    34    41  180
   0    68    67    0        -6   281   282    0         2   192   190    0
   1    35    44  180        -5   282   282    0         3   126   123  180
   3    51    51    0        -4   179   178    0         4    88    88  180
                             -2   225   259    0
** K= 11   L=  5 **          -1   761   767    0      ** K=  6   L=  6 **
                              0   603   568    0
  -4   217   222    0         1    28    28    0        -6   329   333    0
  -2    41    37    0         2    64    64    0        -5   343   359    0
  -1   379   387    0         3   343   342    0        -4   133   142  180
   0   228   222    0         4   340   348    0        -3    45    43  180
   2   130   130    0         5   154   165    0        -2   528   568    0
                                                        -1   553   544    0
** K= 12   L=  5 **        ** K=  3   L=  6 **           0   216   206    0
                                                         1    71    70    0
  -2   125   136    0        -7    42    41    0         2    41    34    0
  -1   123   126    0        -6    65    68  180         3   254   255    0
   0   137   143  180        -5   117   116  180         4   384   389    0
                             -4   133   139    0
** K=  0   L=  6 **          -3   250   256    0      ** K=  7   L=  6 **
                             -2    92   100  180
  -6   389   394    0        -1   246   238  180        -6    85    86    0
  -5   389   405    0         0    33    23    0        -5    87    90    0
  -4    45    48  180         1    74    68    0        -4    49    53  180
  -3    84    84    0         3    44    56    0        -3   130   134  180
  -2   455   506    0         5    86    88  180        -2    35    30    0
  -1   579   575    0                                  -1   189   178    0
```

```
    H  /FO/  /FC/  PHI

    0    60    56    0
    1    96    95  180
    2    70    71  180

** K=   8   L=   6  **

   -6   252   254    0
   -5   341   357    0
   -4    32    18  180
   -3    35    27  180
   -2   279   294    0
   -1   290   290    0
    0   303   288    0
    1   276   267    0
    3    54    59    0

** K=   9   L=   6  **

   -5   151   158  180
   -3   312   341    0
   -1   288   293  180
    0   112   113    0
    1   102    98    0
    2    90    88  180
    3    63    62    0

** K=  10   L=   6  **

   -4   190   196    0
   -3    73    70    0
   -2    35    33    0
   -1   419   420    0
    0   326   326    0
    1   121   125  180

** K=  11   L=   6  **

   -2    91    86    0
    0   109   106  180
    1    40     5  180

** K=  12   L=   6  **

   -1   307   299    0

** K=   1   L=   7  **

   -7    95    97    0
   -6   186   187    0
   -5   159   159    0
```

```
    H  /FO/  /FC/  PHI

   -3   418   441    0
   -2   706   753    0
   -1    62    71    0
    0   100    86  180
    1   491   478    0
    2   460   451    0
    3   178   179    0
    4   145   155    0

** K=   2   L=   7  **

   -7    54    67    0
   -6   177   189    0
   -5   269   275  180
   -4   159   160  180
   -3   531   550    0
   -2    57    56    0
   -1   563   541  180
    0    86    87    0
    1   231   219    0
    2   129   131  180
    3    53    50    0
    4    79    85    0

** K=   3   L=   7  **

   -7   321   321    0
   -6    97   107    0
   -5   104   102  180
   -4   229   232    0
   -3   394   406    0
   -2   382   392    0
   -1   530   526    0
    0   138   132    0
    1   189   182  180
    2   364   368    0
    3   579   593    0
    4   107   106    0

** K=   4   L=   7  **

   -5    41    33    0
   -4    56    51  180
   -3    61    61  180
   -2   154   160    0
   -1   127   120    0
    0   162   156  180
    1    81    77  180
    2   282   100    0
    4    45    57  180
```

```
    H  /FO/  /FC/  PHI

** K=   5   L=   7  **

   -7   269   267    0
   -6   147   151    0
   -5    54    59  180
   -4   105   107    0
   -3   342   362    0
   -2   360   371    0
   -1   345   329    0
    0   223   214    0
    1    82    76    0
    2   181   183    0
    3   316   318    0
    4   206   214    0

** K=   6   L=   7  **

   -6   100   102  180
   -5   133   137    0
   -4   192   198    0
   -3   183   188  180
   -2   183   189  180
   -1   150   141    0
    0   109   113    0
    1    32    25    0
    3   116   120  180
    4    54    60  180

** K=   7   L=   7  **

   -6    52    45    0
   -5    96    94    0
   -4   124   130    0
   -3   321   340    0
   -2   375   385    0
    1   349   343    0
    2   296   301    0
    3   135   129    0

** K=   8   L=   7  **

   -5    83    88  180
   -3   191   196    0
   -2    46    52    0
   -1   159   150  180
    1    55    54    0
    2    45    49  180

** K=   9   L=   7  **
```

```
   H  /FO/  /FC/  PHI

  -4   100   102    0
  -3   240   256    0
  -2   262   271    0
  -1   178   170    0
   0    38    33    0
   1    61    67    0
   2   254   260    0

** K= 10   L=   7 **

  -3    75    71    0
  -2    67    71    0
   0    60    55  180
   1    39    37  180

** K= 11   L=   7 **

  -3   148   156    0
  -2   182   190    0
  -1   251   242    0
   0    88    79    0

** K=  0   L=   8 **

  -6    47    37    0
  -5   283   282    0
  -4   220   222    0
  -3   284   294    0
  -2   486   501    0
  -1    69    61    0
   0   129   130  180
   1   505   501    0
   2   586   602    0
   3    93    94    0
   4    49    40  180

** K=  1   L=   8 **

  -7    86    91  180
  -6    63    65    0
  -4    93    88  180
  -3   154   163    0
  -2   111   106    0
  -1   201   207  180
   0    47    43  180
   1    88    91    0
   2    52    49  180
   3    38    24    0
   4    67    70    0

   H  /FO/  /FC/  PHI

** K=  2   L=   8 **

  -7   224   224    0
  -5    90    91  180
  -4   321   327    0
  -3   551   586    0
  -2   265   267    0
  -1    73    59    0
   0   166   163    0
   1   285   281    0
   2   369   373    0
   3   267   269    0

** K=  3   L=   8 **

  -7   209    73  180
  -5    90    92    0
  -3    68    66  180
  -1    69    64    0
   0    58    55    0
   1    51    48  180
   2    67    64  180
   3    45    43    0

** K=  4   L=   8 **

  -7   244   244    0
  -6    38    36    0
  -5   135   141  180
  -4   320   319    0
  -3   536   568    0
  -2   170   176    0
  -1    61    56    0
   0   188   186    0
   1   232   220    0
   2   375   374    0
   3   277   285    0

** K=  5   L=   8 **

  -6   111   114  180
  -5    83    83    0
  -4   139   141    0
  -3   186   189  180
  -1   231   222    0
   0   117   107  180
   1   101    95  180
   2   166   165    0

** K=  6   L=   8 **

   H  /FO/  /FC/  PHI

  -6   113   118    0
  -5   144   144    0
  -3   316   324    0
  -2   551   567    0
  -1    35    27  180
   0   223   215  180
   1   423   418    0
   2   505   509    0
   3    58    52    0

** K=  7   L=   8 **

  -6    59    63    0
  -3    52    62    0
  -2    55    55    0
  -1    50    53  180
   1    54    53    0
   3    36    45  180

** K=  8   L=   8 **

  -5    86    87    0
  -4    76    73    0
  -3   295   300    0
  -2   360   363    0
   0    58    59  180
   1   323   320    0
   2   311   314    0

** K=  9   L=   8 **

  -4    61    52  180
  -3   131   137    0
  -1   118   115  180
   0   159   162    0
   1    63    60    0

** K= 10   L=   8 **

  -3   270   268    0
  -1    57    60    0
   0   188   189    0

** K=  1   L=   9 **

  -7   126   120  180
  -5   413   405    0
  -4   381   383    0
  -3   150   153    0
  -2    85    85    0
```

```
   H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI


  -1    35    38    0    ** K=  6  L=  9 **           -1   355   345    0
   0   303   291    0                                  0   165   158    0
   1   587   584    0      -5   133   128    0         1   245   250    0
   2   233   240    0      -4    98    93    0         2   195   200    0
   3   141   140  180      -3   238   248  180
                           -2    74    74  180    ** K=  1  L= 10 **
** K=  2  L=  9 **         -1   318   318    0
                            0    51    47    0      -7    64    67  180
  -7    34    34    0       1   208   204  180      -6   144   139    0
  -6    69    67    0                               -5    61    68    0
  -5   198   193  180    ** K=  7  L=  9 **           -4   220   214  180
  -4   134   130  180                               -2   183   182    0
  -3   367   382    0      -5   384   380    0      -1    43    34  180
  -2   134   138    0      -4   316   323    0       0    50    48  180
  -1   381   368  180      -3    34    43  180       1    50    51    0
   1   205   192    0      -2    33    35    0       2    55    55  180
   2    89    93  180      -1   170   167    0
                            0   214   207    0    ** K=  2  L= 10 **
** K=  3  L=  9 **          1   355   354    0
                            2   180   181    0      -6    96    94    0
  -7   127   116    0                               -5   304   297    0
  -6   194   194    0    ** K=  8  L=  9 **           -4   341   337    0
  -5    91    94    0                               -2   102    98  180
  -4   225   218    0      -5    38    44    0      -1   330   326    0
  -3   264   270    0      -4    61    68  180       0   518   514    0
  -2    44    51    0      -3    64    73    0       1   175   175    0
  -1   200   199    0      -2    57    63    0       2    39    35  180
   0   461   450    0      -1   126   123  180       3    61    78    0
   1   239   236    0       1   113   121    0
   2    76    81    0                            ** K=  3  L= 10 **
   3   139   137    0    ** K=  9  L=  9 **
                                                    -6    82    79    0
** K=  4  L=  9 **         -4   257   260    0      -5    66    65    0
                           -3   173   164    0      -4   158   161  180
  -4   121   118    0      -2    38    44  180      -2   243   241    0
  -2   145   149  180      -1    37    30    0       0   197   189  180
   0   121   116    0       0   258   261    0       2    79    76    0

** K=  5  L=  9 **       ** K= 10  L=  9 **       ** K=  4  L= 10 **

  -5   175   171    0      -2    82    81    0      -6   228   217    0
  -4   377   384    0      -1    48    47  180      -5   158   150    0
  -3   165   167    0                               -4   188   190    0
  -2    56    57  180    ** K=  0  L= 10 **           -3   137   143    0
  -1   239   227    0                               -2    78    83  180
   0   389   387    0      -6    33    26    0      -1   240   233    0
   1   167   168    0      -5   361   346    0       0   613   605    0
   2   107   104    0      -4   225   226    0       1   175   172    0
   3   144   153    0      -3    35    38  180       2   198   199  180
                           -2   235   237    0
```

```
   H  /FO/  /FC/  PHI

** K=   5   L= 10 **

  -6   101   102  180
  -4   199   195    0
  -3    60    58  180
  -2   148   150  180
  -1   112   111    0
   0    51    43    0
   1    69    71  180
   2    62    62    0

** K=   6   L= 10 **

  -5   246   232    0
  -4   106   102    0
  -3    54    51    0
  -2   168   174    0
  -1   173   169    0
   0   215   208    0
   1   274   276    0

** K=   7   L= 10 **

  -4    46    45    0
  -2    69    69  180
   0    92    94    0

** K=   8   L= 10 **

  -4   190   185    0
  -2    64    63    0
  -1   153   153    0
   0   177   179    0

** K=   9   L= 10 **

  -3   100    92    0
  -2   143   148    0
  -1    91    86  180

** K=   1   L= 11 **

  -6   186   173    0
  -5   219   211    0
  -2   328   333    0
  -1   390   388    0
   0    95    92    0
   1    45    31    0
   2   114   127    0
```

```
   H  /FO/  /FC/  PHI

** K=   2   L= 11 **

  -4    36    31  180
  -3   103   104    0
  -2    67    60    0
  -1   184   186  180
   1   151   159    0
   2    44    48  180

** K=   3   L= 11 **

  -6   302   279    0
  -5    96    87  180
  -4    67    68  180
  -3   334   347    0
  -2   298   296    0
  -1   144   141    0
   0   211   210    0
   1    58    51    0

** K=   4   L= 11 **

  -6    35    25  180
  -5    58    57  180
  -4    68    72    0
  -2    71    74  180
  -1   126   126    0
   0    79    71    0
   1   143   149  180

** K=   5   L= 11 **

  -5   136   132    0
  -4    46    46  180
  -2   286   293    0
  -1   389   386    0
   0   118   112    0
   1    50    55  180

** K=   6   L= 11 **

  -4    49    51    0
  -2    58    62  180

** K=   7   L= 11 **

  -4   104   100    0
  -3    62    70  180
  -2   226   227    0
  -1   361   355    0
```

```
   H  /FO/  /FC/  PHI

** K=   8   L= 11 **

  -3    42    32    0
  -2   144   139    0
  -1    61    60  180

** K=   0   L= 12 **

  -6    74    67  180
  -5   107   105    0
  -4   247   240    0
  -3   115   110    0
  -2   231   234    0
  -1   234   241    0
   0    84    88  180
   1    35    36    0

** K=   1   L= 12 **

  -5    35    30    0
  -4   142   143  180
  -2   234   244    0
  -1    49    49  180
   0   205   207  180
   1    46    49    0

** K=   2   L= 12 **

  -5    35    32    0
  -4    45    38  180
  -3   176   178    0
  -2   354   365    0
  -1   215   214    0
   1    34    13    0

** K=   3   L= 12 **

  -4    92    94  180
  -3    35    37    0
  -2   134   135    0
  -1    67    66  180
   0    89    90  180
   1    75    80    0

** K=   4   L= 12 **

  -4    77    75  180
  -3   223   220    0
  -2   273   276    0
  -1   152   152    0
```

```
    H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI


    0   124   123    0

 ** K=   5   L= 12  **

   -4   150   145    0
   -2   174   178  180
   -1    33    38    0
    0   131   136    0

 ** K=   6   L= 12  **

   -4    86    87    0
   -3   136   140    0
   -2   226   221    0
   -1   172   165    0

 ** K=   1   L= 13  **

   -5    60    45    0
   -4   267   265    0
   -3   216   226    0
   -2    93    92    0
   -1    36    31    0

 ** K=   2   L= 13  **

   -5    85    81    0
   -4    70    60  180
   -3    69    80  180
   -2   116   109    0
   -1    56    59    0

 ** K=   3   L= 13  **

   -4   127   125    0
   -3   277   273    0
   -2    93    84    0
   -1    79    75  180

 ** K=   4   L= 13  **

   -3    42    38    0
   -2    37    41  180

 ** K=   0   L= 14  **

   -3    76    78    0
```

Observed and calculated structure factors for $[Cu(aOeu)Cl_2]_2$

```
  H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

** K=  0  L=  0 **          5   243   231  180      ** K= 15  L=  0 **

  1   825   872    0      ** K=  7  L=  0 **          1   166   137    0
  2  1823  1939  180                                  2   365   353    0
  4    97    98  180        1   130   134  180
  5   203   235    0        2   283   271  180      ** K= 16  L=  0 **
                            5   176   135    0
** K=  1  L=  0 **                                    0   852   856    0
                          ** K=  8  L=  0 **          1   234   204    0
  1   548   545  180                                  2   217   208  180
  2  1402  1460  180        0   535   546  180        4   140   117  180
  4   280   294    0        1   541   532  180
  5   161   184    0        2   121   116  180      ** K= 18  L=  0 **
                            4   437   425    0
** K=  2  L=  0 **                                    0   391   362    0
                          ** K=  9  L=  0 **
  0  1916  1957    0                                ** K= 19  L=  0 **
  1   388   390    0        1   462   487    0
  2  1496  1483  180        2   308   314    0        1   200   199  180
  4   483   475    0        4   124   120  180        2   177   213  180
  5   269   290    0
  8   139    18  180      ** K= 10  L=  0 **        ** K=  1  L=  1 **

** K=  3  L=  0 **          0   115    98  180       -5   366   408    0
                            1    97    86  180       -2   296   320  180
  1   909   867  180        4   143   164    0       -1   118   134  180
  2   857   843  180        5   154   106  180        0  1087  1069    0
  4   740   736    0                                  1  1102  1149    0
  5   351   359    0      ** K= 11  L=  0 **          4   265   292  180
  7   150   187  180
                            1   568   573    0      ** K=  2  L=  1 **
** K=  4  L=  0 **          2   388   371    0
                            4   195   180  180       -4   103    97  180
  0   330   335    0        5   114   129  180       -2   411   409    0
  1   363   347  180                                 -1   917   906    0
  2   356   351  180      ** K= 12  L=  0 **          0   140   116  180
  4   456   438    0                                  1   157   165  180
                            0   382   371    0        2   423   460  180
** K=  5  L=  0 **                                    5   323   349    0
                          ** K= 13  L=  0 **
  2   182   204  180                                ** K=  3  L=  1 **
  4   356   357    0        1   368   386    0
  5   297   299    0        4   297   296  180       -8   131    95  180
  7   211   204  180        5   147   138  180       -5   325   324    0
                                                     -4   140   128    0
** K=  6  L=  0 **        ** K= 14  L=  0 **         -2   781   765  180
                                                     -1    92    89    0
  0   357   317    0        2   201   227  180        0   352   346    0
  1   143   102    0        5   189   174    0        1   380   332  180
  4   243   234    0                                  2   215   206  180
```

```
   H  /FO/  /FC/  PHI

   5   185   172    0

** K=   4   L=   1 **

  -7   213   190    0
  -4   725   724  180
  -1   628   644    0
   0   917   922    0
   2   285   310  180
   4   197   221    0
   5   334   355    0
   7   163   182  180

** K=   5   L=   1 **

  -5   153   138  180
  -4   200   196  180
  -2   333   342    0
  -1   823   798    0
   0   699   664    0
   1   474   460  180
   2   373   341  180
   4   105   117    0

** K=   6   L=   1 **

  -5   168   150  180
  -4   396   392  180
  -2   694   679    0
  -1   506   509    0
   1   494   451  180
   2   689   695  180
   4   269   263    0
   5   260   264    0
   7   133    88  180

** K=   7   L=   1 **

  -5   129   150  180
  -2   639   656    0
  -1   222   246    0
   0  1054  1073  180
   1   893   893  180
   4   377   376    0
   5   140   141  180

** K=   8   L=   1 **

  -2   209   194    0
  -1   160   142  180
```

```
   H  /FO/  /FC/  PHI

   0   272   263  180
   2   104    96  180

** K=   9   L=   1 **

  -2   351   352    0
   0  1350  1356  180
   1   762   779  180
   2   160   144    0
   4   408   401    0

** K=  10   L=   1 **

  -4   179   184    0
  -2   522   527  180
  -1   631   658  180
   1   591   603    0
   2   647   643    0
   4   193   194  180

** K=  11   L=   1 **

  -4   108   111  180
  -2   296   299    0
  -1   410   429    0
   0   175   189    0
   1   165   180  180
   5   221   230  180

** K=  12   L=   1 **

  -5   123    99    0
  -4   511   491    0
  -2   220   196  180
  -1   408   404  180
   0   296   300  180
   1   291   288    0
   2   243   246    0
   4   139   167  180

** K=  13   L=   1 **

  -2   236   229  180
  -1   239   261    0
   0   234   227    0
   1   247   248  180

** K=  14   L=   1 **

  -4   257   261    0
```

```
   H  /FO/  /FC/  PHI

  -2   276   246  180
  -1   400   400  180
   1   263   268    0

** K=  15   L=   1 **

  -5   235   240    0
  -2   318   313  180
  -1   124   118    0
   0   346   346    0

** K=  16   L=   1 **

  -2   215   200  180
  -1   207   219  180
   0   281   291    0
   1   171   188    0

** K=  17   L=   1 **

  -2   120   136  180
  -1   173   195    0
   0   546   545    0
   1   249   250    0

** K=  18   L=   1 **

  -1   195   206    0
   0   211   207    0
   1   128   104  180
   2   356   336  180

** K=  19   L=   1 **

  -2   135   118  180

** K=   0   L=   2 **

  -8   209   189  180
  -7   188   190  180
  -5   391   384    0
  -4   140    83    0
  -2   445   499  180
  -1  1307  1208    0
   0   771   689    0
   1   348   392    0
   2   514   515    0
   4   593   627  180
   5   227   242  180
   7   165   179    0
```

```
   H  /FO/  /FC/  PHI

** K=   1   L=   2 **

  -2   217   138     0
  -1   468   445     0
   0   573   557     0
   1   908   891   180
   2   450   472   180
   5   129   165     0

** K=   2   L=   2 **

  -5   551   557     0
  -2   298   319   180
  -1   271   243   180
   0   172    98   180
   2   337   324     0
   4   312   309   180
   5   130   107   180
   7   123   102     0

** K=   3   L=   2 **

  -7   151   166     0
  -4   479   495   180
  -1  1004   997     0
   0   966   915     0
   1   193   186   180
   2   648   659   180
   4   125   115     0
   5   122   121     0

** K=   4   L=   2 **

  -5   147   165     0
  -4   312   304   180
  -2   243   237     0
  -1   222   185     0
   0   544   507   180
   1   309   296   180
   2   156   162     0
   5   131   147   180

** K=   5   L=   2 **

  -7   175   163     0
  -4   618   617   180
  -2   109   138     0
  -1   768   767     0
   0  1088  1065     0
   1   162   176   180
```

```
   H  /FO/  /FC/  PHI

   2   356   324   180
   5   119   151     0

** K=   6   L=   2 **

  -5   273   281   180
  -4   339   342   180
  -2  1040  1054     0
  -1   727   747     0
   0   447   430   180
   1   511   477   180
   2   170   183   180
   5   165   140   180

** K=   7   L=   2 **

  -5   140   140     0
  -2   285   250     0
  -1   841   845     0
   0   410   299   180
   1   560   534   180
   2   447   423   180
   5   137   152     0

** K=   8   L=   2 **

  -5   192   181   180
  -4   236   211   180
  -2   428   420     0
  -1   325   300     0
   0  1035  1055   180
   1  1157  1150   180
   4   398   405     0

** K=   9   L=   2 **

  -5   148   139     0
  -2   157   137   180
  -1   116   120   180
   0   103    76     0
   2   244   244     0
   5   145   139   180

** K=  10   L=   2 **

  -7   125    83     0
  -5   193   205   180
  -4   234   224   180
  -2   584   588     0
  -1   510   508     0
```

```
   H  /FO/  /FC/  PHI

   0   481   475   180
   1   694   668   180
   2   113   100   180
   4   224   187     0

** K=  11   L=   2 **

  -7   156   139   180
  -4   322   305     0
  -2   155   153   180
  -1   366   375   180
   0   484   493   180
   2   338   391     0
   5   263   257   180

** K=  12   L=   2 **

  -4   189   169   180
  -2   160   135     0
  -1   358   371     0
   0   185   155     0

** K=  13   L=   2 **

  -4   279   281     0
  -1   290   300   180
   0   604   606   180
   1   235   241   180
   2   248   239     0

** K=  14   L=   2 **

  -5   325   322     0
  -2   327   331   180
  -1   261   269   180
   0   179   153     0
   1   146   153     0
   4   124    79   180

** K=  15   L=   2 **

  -4   124    71   180
   0   115   128   180
   2   154   131     0

** K=  16   L=   2 **

  -5   184   156     0
  -2   183   203   180
   0   236   240     0
```

```
   H  /FO/  /FC/  PHI

   1   192   191    0
   2   146   137    0
   4   218   188  180

** K= 17   L=   2 **

  -1   170   191    0
   0   211   198    0
   2   164   126  180

** K= 19   L=   2 **

  -1   169   177    0
   0   200   213    0

** K=  1   L=   3 **

  -8   167   139  180
  -1   732   741  180
   0   182   173  180
   1   800   797    0
   2   559   588    0
   4   548   565  180
   5   167   178  180
   7   158   138    0

** K=  2   L=   3 **

  -5   299   316    0
  -4   138   124  180
  -2   159   143    0
  -1   121   130    0
   0   185   220    0
   1   146   126  180
   2   556   557  180
   5   215   204    0

** K=  3   L=   3 **

  -5   209   211    0
  -4   101    94    0
  -2   272   258  180
  -1  1165  1102  180
   0  1104  1083  180
   1   619   602    0
   2   766   768    0
   4   229   227  180

** K=  4   L=   3 **
```

```
   H  /FO/  /FC/  PHI

  -7   139   157    0
  -5   146   133    0
  -4   525   533  180
  -2   412   408  180
  -1   838   823    0
   0  1630  1638    0
   1   529   540    0
   2   347   340  180
   5   125   132    0

** K=  5   L=   3 **

  -5   372   388  180
  -4   326   333  180
  -2   818   814    0
  -1   491   493    0
   0   704   694  180
   1   214   211  180
   2   238   230    0
   4   181   176  180

** K=  6   L=   3 **

  -5   173   163    0
  -4   116   132  180
  -2   390   387  180
  -1   569   556    0
   0  1113  1109    0
   1   167   151  180
   2   520   513  180
   5   143   130    0

** K=  7   L=   3 **

  -7   251   228    0
  -5   457   470  180
  -4   672   676  180
  -2  1048  1050    0
  -1   434   435    0
   0   770   759  180
   1   572   562  180
   2   169   162  180
   4   176   174    0
   5   132   144    0

** K=  8   L=   3 **

  -4   110   102    0
   0    95    75  180
   1   305   302  180
```

```
   H  /FO/  /FC/  PHI

** K=  9   L=   3 **

  -7   219   210    0
  -5   299   283  180
  -4   535   523  180
  -2   633   640    0
   0   616   609  180
   1   323   330  180
   4   218   216    0
   5   159   128    0

** K= 10   L=   3 **

  -5   119   161  180
  -2   139   163    0
  -1   131   124  180
   0   555   571  180
   2   379   352    0
   4   113    92    0
   5   197   191  180

** K= 11   L=   3 **

  -5   231   215  180
  -4   160   201  180
  -2   382   392    0
  -1   142   174    0
   4   175   157  180

** K= 12   L=   3 **

  -4   204   223    0
  -2   278   282    0
  -1   206   200  180
   0   686   725  180
   1   352   364  180
   4   126   103    0
   5   135   109  180

** K= 13   L=   3 **

  -1   328   332  180
   0   352   373  180
   1   236   228    0
   2   321   329    0
   4   188   138  180

** K= 14   L=   3 **

   0   203   200  180
```

```
    H  /FO/  /FC/  PHI

    1   120   121  180
    2   125   111    0

 ** K=  15   L=   3 **

   -5   131   122    0
   -2   220   202  180
   -1   268   289  180
    0   149   142  180
    1   268   256    0
    2   257   255    0

 ** K=  16   L=   3 **

   -1   120   121    0
    0   151   171    0

 ** K=  17   L=   3 **

    0   194   207    0
    1   190   175    0

 ** K=  18   L=   3 **

   -1   140   109    0

 ** K=   0   L=   4 **

   -7   244   232  180
   -5   156   144    0
   -4   480   498    0
   -2    97    83  180
   -1   740   708  180
    0   353   349  180
    1   881   884    0
    2   478   486    0
    4   426   445  180
    5   175   150  180

 ** K=   1   L=   4 **

   -5   234   238    0
   -4   130   137    0
   -2   170   175  180
   -1   218   187    0
    2   206   214  180

 ** K=   2   L=   4 **

   -5   144   128    0
```

```
    H  /FO/  /FC/  PHI

   -4   269   276    0
   -2   370   366  180
   -1   937   939  180
    0   599   579  180
    1   511   513    0
    2   641   639    0
    4   193   164  180

 ** K=   3   L=   4 **

   -5   262   256    0
   -4   157   149  180
   -2   438   426  180
   -1   441   414    0
    0  1020  1007    0
    1   335   320    0
    4   260   279  180

 ** K=   4   L=   4 **

   -5   258   243  180
   -1   217   188  180
    0   234   230  180

 ** K=   5   L=   4 **

   -5   183   197    0
   -4   244   260  180
   -2   444   437  180
   -1   230   208    0
    0   717   744    0
    1   487   486    0
    2   120   112    0
    4   227   221  180

 ** K=   6   L=   4 **

   -5   263   279  180
   -4   347   349  180
   -2   479   479    0
   -1   366   345    0
    0   505   502    0
    1   234   224  180
    2   382   357  180

 ** K=   7   L=   4 **

   -5   342   352    0
   -2   169   169    0
   -1   271   258  180
```

```
    H  /FO/  /FC/  PHI

    0   205   214  180
    2   131   194  180
    5   121    63    0

 ** K=   8   L=   4 **

   -7   284   264    0
   -5   166   162  180
   -4   279   290  180
   -2   107   108    0
   -1   236   230    0
    0   205   195  180
    2   172   138  180
    4   169   177    0
    5   213   195    0

 ** K=   9   L=   4 **

   -5   136   140  180
   -4   204   204  180
   -2   127   118    0
   -1   254   247    0
    0   125    99  180
    2   136   145    0

 ** K=  10   L=   4 **

   -7   145   153    0
   -5   212   197  180
   -4   306   303  180
   -2   356   355    0
   -1   288   278    0
    0   130    72    0
    1   177   176  180
    2   154   165  180

 ** K=  11   L=   4 **

   -5   254   263  180
   -2   385   403    0
    0   577   577  180
    1   308   300  180
    2   181   168    0

 ** K=  12   L=   4 **

   -5   188   175  180
   -2   196   181    0

 ** K=  13   L=   4 **
```

```
   H  /FO/  /FC/  PHI

  -5   168   148  180
  -4   118   131    0
  -2   369   358    0
  -1   204   223  180
   0   906   944  180
   1   351   338  180
   2   143   153    0
   4   140    92    0

** K= 14   L=   4 **

  -4   227   223    0
  -2   368   370  180
  -1   514   534  180
   0   191   156  180
   1   261   269    0
   2   310   303    0

** K= 15   L=   4 **

  -2   124   134    0
   0   143   133  180
   2   185   186    0

** K= 16   L=   4 **

  -4   231   234    0
  -2   163   164  180
  -1   324   326  180
   1   310   331    0
   2   168   162    0

** K= 18   L=   4 **

  -1   176   196  180

** K=  1   L=   5 **

  -7   278   265  180
  -4   804   849    0
  -2   476   484  180
  -1   664   649  180
   1   275   264    0
   2   141   187    0

** K=  2   L=   5 **

  -8   137   152  180
  -5   379   404    0
  -4   272   287    0
```

```
   H  /FO/  /FC/  PHI

  -2   568   572  180
  -1   346   347  180
   0   328   327    0
   1   225   244    0

** K=  3   L=   5 **

  -8   131    99    0
  -4   345   344    0
  -2   739   721  180
  -1   600   586  180
   0   178   167    0
   1   417   414    0
   2   189   193    0

** K=  4   L=   5 **

  -7   135    88  180
  -5   289   286    0
  -2   719   701  180
   0  1341  1348    0
   1   630   623    0
   4   269   267  180

** K=  5   L=   5 **

  -2   192   175    0
  -1   189   190    0
   0   525   552    0
   2   472   475  180
   5   130   121    0

** K=  6   L=   5 **

  -5   278   288    0
  -4   314   325    0
  -2   455   447  180
   0   292   293    0
   1   190   183    0

** K=  7   L=   5 **

  -7   218   219    0
  -5   198   190  180
  -4   177   167  180
  -1   367   372    0
   0   682   680    0
   2   486   490  180
   4   182   169    0
   5   167   188    0
```

```
   H  /FO/  /FC/  PHI

** K=  8   L=   5 **

  -4   221   241    0
  -1   121   107  180
   0   218   224  180

** K=  9   L=   5 **

  -7   223   219    0
  -5   167   150  180
  -4   131   105  180
  -2   389   399  180
  -1   159   129    0
   0   686   702    0
   2   268   267  180
   4   159   144    0

** K= 10   L=   5 **

  -5   362   345  180
  -4   163   163  180
  -2   224   229    0

** K= 11   L=   5 **

  -4   129   119    0
   0   406   431    0
   1   123   104    0
   2   334   328  180

** K= 12   L=   5 **

  -5   147   186  180
  -2   275   279    0
   0   460   461  180
   1   277   286  180

** K= 13   L=   5 **

  -4   174   155    0
  -2   171   191  180
  -1   284   285  180
   1   169   171    0

** K= 14   L=   5 **

  -5   194   171  180
  -2   200   214    0
   0   240   254  180
   1   143   136  180
```

```
   H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI

** K= 15   L=  5   **    ** K=  4   L=  6   **       1   127   110    0

  -4   222   211    0      -5   196   189    0    ** K= 10   L=  6   **
  -2   144   163  180      -4   158   143    0
  -1   352   338  180      -2   338   341  180      -4   216   206  180
   0   151   139  180      -1   261   259    0      -1   304   345    0
   1   178   166    0       0   499   490    0       0   345   320    0
   2   159   149    0       1   111   108  180       2   225   242  180

** K= 17   L=  5   **    ** K=  5   L=  6   **    ** K= 11   L=  6   **

  -1   201   217  180      -4   249   242    0      -5   274   265  180
                           -2   423   418  180      -4   163   152  180
** K=  0   L=  6   **      -1   329   319  180      -2   341   353    0
                            0   483   489    0       0   228   204  180
  -7   293   298  180       1   591   589    0       1   129   135  180
  -4   627   661    0       2   107    70    0       2   116    69  180
  -2   205   207    0       4   186   177  180
  -1   290   277  180                             ** K= 12   L=  6   **
   0   532   530  180    ** K=  6   L=  6   **
   1   296   280  180                               -1   118   111    0
                           -5   216   182    0
** K=  1   L=  6   **      -2   188   154  180    ** K= 13   L=  6   **
                           -1   568   583    0
  -5   274   286    0       0   599   604    0      -5   176   176  180
  -4   349   377    0       1   182   150  180      -2   175   177    0
  -2   385   381  180       2   412   391  180       0   357   366  180
  -1   389   385  180                                1   180   189  180
   0   188   222  180    ** K=  7   L=  6   **
   1   170   159    0                             ** K= 14   L=  6   **
                           -4   165   176    0
** K=  2   L=  6   **      -2   367   365  180      -1   162   174  180
                           -1   382   385  180       0   155   135  180
  -7   173   158  180       0   109   107    0
  -5   132    71    0                             ** K=  1   L=  7   **
  -4   303   308    0    ** K=  8   L=  6   **
  -2   329   328  180                               -4   155   179    0
  -1   213   184  180      -5   197   189    0      -2   226   237    0
   2   125   114    0      -4   360   367  180      -1   108   114    0
                           -2   235   223  180       0   394   400  180
** K=  3   L=  6   **      -1   232   237    0       1   355   361  180
                            0   744   744    0
  -5   322   335    0       2   289   279  180    ** K=  2   L=  7   **
  -4   373   344    0
  -2   551   554  180    ** K=  9   L=  6   **      -5   187   165    0
  -1   487   475  180                               -4   254   259    0
   0   316   329    0      -5   254   255  180      -2   253   254  180
   1   600   589    0      -4   139   146  180      -1   369   367  180
   2   231   232    0      -2   176   175    0       0   253   258  180
   4   199   186  180       0   111   120    0       2   175   172    0
```

```
   H  /FO/  /FC/  PHI

** K=   4   L=   7 **

  -7   191   195  180
  -4   220   225    0
  -2   189   210  180
   0   126   129    0
   1   345   352    0
   2   235   233    0

** K=   5   L=   7 **

  -5   149   142    0
  -4   110    73    0
  -1   145   148    0
   0   179   187    0
   1   169   166  180
   2   132   147  180

** K=   6   L=   7 **

  -5   337   358    0
  -4   234   231    0
  -2   298   299  180
  -1   420   413  180
   1   284   288    0
   2   156   166    0

** K=   7   L=   7 **

  -5   321   300    0
  -4   171   165  180
  -2   191   194  180
  -1   378   387    0
   0   503   530    0
   2   179   166  180

** K=   8   L=   7 **

  -5   128   125    0

** K=   9   L=   7 **

  -5   273   286    0
  -4   241   226  180
  -2   246   247  180
  -1   393   418    0
   0   481   518    0
   2   124    83  180

** K=  10   L=   7 **

   H  /FO/  /FC/  PHI

  -5   214   256  180
  -4   239   219  180
  -2   277   279    0
  -1   419   424    0
   0   202   178    0
   1   176   163  180
   2   167   168  180

** K=  11   L=   7 **

  -5   167   191    0
  -1   263   269    0
   1   219   218  180

** K=  12   L=   7 **

  -1   188   189    0
   1   274   268  180

** K=   0   L=   8 **

  -5   276   254  180
  -2   636   641    0
  -1   207   193  180
   0   904   919  180
   1   345   349  180
   2   176   175    0

** K=   1   L=   8 **

  -5   255   253    0
  -4   180   158    0
  -2   232   219  180
  -1   315   330  180

** K=   2   L=   8 **

  -5   293   294  180
  -4   303   316  180
  -2   466   467    0
   0   603   624  180
   2   224   228    0

** K=   3   L=   8 **

  -5   184   193    0
  -4   273   276    0
  -2   227   210  180
  -1   261   266  180
   0   114    72  180

   H  /FO/  /FC/  PHI

   1   172   181    0
   2   153   171    0

** K=   4   L=   8 **

  -4   351   353  180
  -2   325   316    0
  -1   140   133    0
   0   314   280  180
   2   138   130    0

** K=   5   L=   8 **

  -4   274   274    0
  -1   178   135  180
   0   168   142  180
   2   196   177    0

** K=   6   L=   8 **

  -5   233   221    0

** K=   7   L=   8 **

  -5   158   139    0
  -4   204   182    0
  -2   160   146  180
  -1   141   137  180
   0   312   307  180

** K=   8   L=   8 **

  -4   195   164  180
  -2   286   268  180
   0   264   259    0
   1   226   214    0

** K=   9   L=   8 **

  -4   155   163  180
  -2   143    95    0
  -1   217   229    0
   0   223   209    0

** K=  10   L=   8 **

   0   149   132    0

** K=  11   L=   8 **
```

```
   H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI


  -2   131   152    0
  -1   250   281    0

** K=   1   L=   9 **

  -5   245   251  180
  -4   203   196  180
  -2   480   476    0
   0   448   464  180
   1   190   207  180

** K=   2   L=   9 **

  -4   252   218    0
  -1   245   224  180
   0   366   384  180

** K=   3   L=   9 **

  -5   276   278  180
  -4   215   201  180

** K=   4   L=   9 **

  -5   115    60  180
  -4   243   229    0
  -1   162   141  180
   0   163   206  180

** K=   5   L=   9 **

  -4   130   144    0
  -1   178   161  180

** K=   6   L=   9 **

  -1   165   184  180
   0   192   183  180

** K=   7   L=   9 **

  -2   203   195  180
  -1   189   191  180
```

Observed and calculated structure factors for $[Cu(aOeu)_2]Cl_2.2H_2O$

```
    H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

** K=  0  L=  0 **        ** K=  8  L=  0 **            2   319   294    0
                                                        3   273   283    0
    1   563   460    0        0   254   299    0        4   355   442    0
    2   269   232  180        1   177   173    0
    3   342   345    0        2   458   427    0    ** K=  4  L=  1 **
    4   250   267    0        3   163   187    0
    5   161   209    0        4   183   242    0       -3   285   291    0
                                                       -2   301   333    0
** K=  1  L=  0 **        ** K=  9  L=  0 **           -1   618   545  180
                                                        0   442   539  180
    1   181   164    0        3   176   161    0        1   361   194  180
    2   342   347  180                                  2   101    58  180
    4   156   119    0    ** K= 10  L=  0 **            3   211   181    0
    5   174   182    0
                              0   393   432    0    ** K=  5  L=  1 **
** K=  2  L=  0 **            1   299   262    0
                              3   183   249    0       -4   180   235    0
    0   450   505    0                                 -3   387   403    0
    1   627   587    0    ** K= 11  L=  0 **           -2   343   282    0
    2   561   529    0                                 -1   451   330    0
    3   614   631    0        2   128    73  180        0   332   368    0
    4   352   398    0                                  1   740   699    0
                          ** K=  1  L=  1 **            2   580   558    0
** K=  3  L=  0 **                                      3   389   406    0
                             -4   346   405    0
    1  1689  1458    0       -3   451   438    0    ** K=  6  L=  1 **
                             -2   446   264    0
** K=  4  L=  0 **           -1   375   238  180       -2   511   460  180
                              0   773  1003    0       -1   123    82  180
    0   257   256  180        1   652   645    0        0   392   416    0
    1  1160  1013    0        2   653   782    0        2   230    55    0
    2   519   565    0        3   418   544    0        3   238   280  180
    4   167   161    0        4   237   232    0
                              5   183   243    0    ** K=  7  L=  1 **
** K=  5  L=  0 **
                          ** K=  2  L=  1 **           -4   159    82    0
    4   264   205    0                                 -3   141   117    0
                             -2   127    32    0       -2   779   740    0
** K=  6  L=  0 **            0   211   295  180       -1   410   405    0
                              2   226   254  180        0   386   510    0
    1   368   306    0        4   147   167  180        1   227   137    0
    2   684   665    0                                  2   376   169    0
    3   228   227    0    ** K=  3  L=  1 **            3   210   208    0
    4   150   179    0                                  4   243   328    0
                             -4   159   175    0
** K=  7  L=  0 **           -3   163   158    0    ** K=  8  L=  1 **
                             -2   294   307    0
    1   494   449  180       -1  1426  1388    0        0   233   278  180
    2   304   269    0        0   250   331    0        1   167   171  180
                              1   844   592    0        3   213   167    0
```

```
   H  /FO/ /FC/ PHI

** K=  9   L=   1 **

  -3   233  238    0
  -2   282  230    0
  -1   160   77    0
   1   395  386    0
   2   406  345    0
   3   185  160    0

** K= 10   L=   1 **

  -3   260  215  180
   1   149  137    0

** K= 11   L=   1 **

  -1   295  300    0
   0   117  178    0
   1   173  159    0

** K= 12   L=   1 **

   2   139   73    0

** K=  0   L=   2 **

  -4   221  215    0
  -3   374  357    0
  -2  1092 1141    0
  -1   285  243    0
   1   213  106  180
   2   864  524    0
   3   714  628    0
   4   293  250    0

** K=  1   L=   2 **

  -4   291  286    0
  -3   168  149    0
  -2   487  433  180
  -1   120   87  180
   0   236  319  180
   1   233  166    0
   2   530  420    0
   3   233  217    0
   4   321  301  180

** K=  2   L=   2 **

  -4   272  341    0
```

```
   H  /FO/ /FC/ PHI

  -2   228   78    0
  -1   655  466    0
   0   462  556    0
   1   968  914    0
   2   502  551    0
   4   172  220    0

** K=  3   L=   2 **

  -3   178  190  180
  -2   182   55    0
  -1   644  656    0
   0   134  100    0
   1   383  278  180
   2   365  322  180

** K=  4   L=   2 **

  -4   188  184    0
  -3   548  563    0
  -2   222  185    0
  -1   413  413    0
   0   147  200    0
   1   323  339    0
   2   359  383    0
   3   510  525    0
   4   383  445    0

** K=  5   L=   2 **

  -2   111  100    0
  -1   398  291  180
   1   222  156  180
   2   103   95    0
   3   118  113  180

** K=  6   L=   2 **

  -3   279  214    0
  -2   243  209    0
  -1   201  211    0
   0   569  752    0
   1   359  360    0
   2   233  201    0
   3   418  426    0
   4   164  255    0

** K=  7   L=   2 **

  -3   154  141    0
```

```
   H  /FO/ /FC/ PHI

  -1   234  176  180
   1   136  128  180

** K=  8   L=   2 **

  -2   390  310    0
  -1   300  259    0
   0   229  329    0
   1   331  337    0
   2   396  343    0
   3   116  147    0

** K=  9   L=   2 **

   0   112  147  180
   2   281  291  180

** K= 10   L=   2 **

  -3   286  296    0
  -2   369  306    0
  -1   291  307    0
   1   147  151    0
   2   275  255    0
   3   185  204    0

** K= 11   L=   2 **

  -1   120  112  180

** K= 12   L=   2 **

  -1   190  230    0
   0   206  202    0
   1   240  243    0

** K=  1   L=   3 **

  -4   186  236    0
  -3   279  301    0
  -2   243  289    0
  -1   260  244    0
   0   593  738    0
   1   352  257    0
   2   239  253    0
   3   605  641    0
   4   267  220    0

** K=  2   L=   3 **
```

```
   H  /FO/  /FC/  PHI


  -3   163   167    0
  -2   147    73    0
  -1   153   102    0
   0   281   289  180
   1   217   167  180
   2   339   314  180
   3   175   204    0
   4   183   184    0

** K=    3   L=    3  **

  -4   268   292    0
  -3   369   400    0
  -2   369   271    0
  -1   335   283    0
   1   453   467    0
   2   744   625    0
   3   253   198    0
   4   252   315    0

** K=    4   L=    3  **

  -3   153   124  180
  -1   401   364  180
   0   124   151    0
   1   499   443    0
   2   214   205  180
   3   216   180  180

** K=    5   L=    3  **

  -4   143    81    0
  -3   150   134    0
  -2   290   344    0
  -1   509   498    0
   0   387   445    0
   1   358   316    0
   2   101    56    0
   4   301   330    0

** K=    6   L=    3  **

  -3   150   132    0
  -2   312   263    0
  -1   194    95    0
   1   437   452  180
   2   174    80    0

** K=    7   L=    3  **
```

```
   H  /FO/  /FC/  PHI


  -4   363   396    0
  -3   340   275    0
  -2   355   298    0
  -1   167    62    0
   1   351   368    0
   2   480   441    0
   3   331   264    0
   4   173   166    0

** K=    8   L=    3  **

  -2   175   136  180
  -1   117   128    0
   3   182   134  180

** K=    9   L=    3  **

  -2   267   269    0
  -1   447   425    0
   0   290   352    0
   1   226   152    0
   2   211   179    0
   3   134   175    0

** K=   10   L=    3  **

  -3   150   111    0
  -2   190   143    0
  -1   120    68    0
   0   106   121  180
   1   111    54  180
   2   177   134  180

** K=   11   L=    3  **

  -2   154   130    0
  -1   221   186    0
   0   163   276    0
   1   185   209    0
   2   244   201    0

** K=    0   L=    4  **

  -4   391   390    0
  -3   312   325    0
  -2   184   187  180
  -1    85    71    0
   0   795   996    0
   1   151   215    0
   3   535   580    0
```

```
   H  /FO/  /FC/  PHI


   4   220   174    0

** K=    1   L=    4  **

  -2   253   161  180
  -1   203   254    0
   0   538   597    0
   1   108    90    0
   2   491   432  180
   3   254   255  180

** K=    2   L=    4  **

  -4   208   230    0
  -3   342   368    0
  -2   447   474    0
  -1   628   632    0
   0    88   129    0
   1   382   251  180
   2   358   209    0
   3   499   461    0
   4   377   387    0

** K=    3   L=    4  **

  -3   312   314    0
  -2   126   110    0
  -1   477   435  180
   1   337   325    0
   2   262   290  180
   3   150    54  180

** K=    4   L=    4  **

  -4   192   246    0
  -3   190   219    0
  -2   369   300    0
  -1   319   239    0
   0   150   203    0
   1   599   620    0
   2   597   561    0
   4   137   110    0

** K=    5   L=    4  **

  -2   244   198    0
   0   182   237    0
   2   332   263  180

** K=    6   L=    4  **
```

```
   H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI

  -3   282   297    0       2   430   339    0       1   319   319    0
  -2   555   501    0       3   231   218    0       2   137   103    0
  -1   287   203    0       4   239   172    0       4   131   103  180
   0   111   173    0
   1   525   538    0    ** K=  2   L=   5 **    ** K=  7   L=   5 **
   2   320   262    0
   3   130    94    0      -4   108   140    0      -2   201   202    0
   4   195   200    0      -3   132   106    0      -1   249   220    0
                           -2   282   267  180       0   327   378    0
** K=  7   L=   4 **       0   324   339    0       1   399   431    0
                            2   309   221    0       2   176   194    0
  -1   249   247    0       4   178   178  180
   1   174   177  180                             ** K=  8   L=   5 **
   2   155   164    0    ** K=  3   L=   5 **
                                                    -2   295   256    0
** K=  8   L=   4 **      -4   193   231    0      -1   183   175    0
                           -3   162   139    0       1   101    92  180
  -3   170   143    0      -2   237   237    0
  -2   352   315    0      -1   679   633    0    ** K=  9   L=   5 **
  -1   354   326    0       0   493   589    0
   0   196   249    0       1   306   286    0      -3   234   173    0
   1   278   319    0       2   150   168    0      -2   290   236    0
   2   215   203    0       4   173   209    0      -1   172   154    0
   3   185   131    0                                1   209   209    0
                         ** K=  4   L=   5 **       2   369   338    0
** K=  9   L=   4 **                                3   218   207    0
                           -2   117   120    0
  -2   178   140    0      -1   303   262    0    ** K= 11   L=   5 **
   0   169   173  180       0   184   243    0
   2   219   157    0       2   211   160  180      -1   256   255    0
                            4   119    79    0       0   200   246    0
** K= 10   L=   4 **                                1   150   122    0
                         ** K=  5   L=   5 **
  -1   130   145    0                             ** K=  0   L=   6 **
   0   244   347    0      -4   179   144    0
   1   199   205    0      -3   505   499    0      -3   120   113    0
   2   196   206    0      -2   420   387    0      -2   475   542    0
                           -1   142    39  180      -1   654   753    0
** K= 12   L=   4 **       0   206   223    0       0   494   573    0
                            1   311   326    0       1   258   134    0
  -1   264   270    0       2   339   277    0       2   306   233    0
                            3   509   456    0       3   276   256    0
** K=  1   L=   5 **       4   181   226    0       4   319   309    0

  -4   286   303    0    ** K=  6   L=   5 **    ** K=  1   L=   6 **
  -3   283   292    0
  -2   490   451    0      -3   105    79    0      -3   227   178    0
  -1   560   578    0      -2   182   133  180      -1   143   142  180
   0   185   277    0      -1   199   126  180       1   241   284  180
   1   280   224    0       0   183   203    0       2   175   168    0
```

```
   H  /FO/  /FC/  PHI

   3   269   223     0

** K=    2   L=    6 **

  -4   304   334     0
  -3   200   233     0
  -2   240   129     0
  -1   378   254     0
   0   358   397     0
   1   571   636     0
   2   527   526     0
   3   194   178     0
   4   168   106     0

** K=    3   L=    6 **

  -2   235   194   180
   0   290   263     0

** K=    4   L=    6 **

  -3   326   321     0
  -2   409   396     0
  -1   363   346     0
   0   261   327     0
   1   315   306     0
   2   177    92     0
   3   287   291     0
   4   206   208     0

** K=    5   L=    6 **

  -2   100    44     0
   0   170   216   180
   1   131   145     0
   2   143   137     0

** K=    6   L=    6 **

  -3   291   248     0
  -2   293   263     0
  -1   188   206     0
   0   247   346     0
   1   198   222     0
   2   198   158     0
   3   252   228     0

** K=    8   L=    6 **

  -3   175   155     0

   H  /FO/  /FC/  PHI

  -2   246   193     0
  -1   216   244     0
   0   108   143     0
   1   149   115     0
   2   309   327     0
   3   156   132     0

** K=    9   L=    6 **

   0   169   171     0

** K=   10   L=    6 **

  -2   176   141     0
  -1   220   222     0
   0   145   175     0
   1   149   151     0

** K=    1   L=    7 **

  -4   157   204     0
  -3   235   274     0
  -2   230   137     0
  -1   148   122     0
   0   530   596     0
   1   227   294     0
   2   266   280     0
   3   273   269     0
   4   178   170     0

** K=    2   L=    7 **

  -2   191   199     0
  -1   140   125   180
   2   199   163   180
   3   112    61     0

** K=    3   L=    7 **

  -3   308   244     0
  -2   378   365     0
  -1   457   457     0
   1   270   282     0
   2   345   315     0
   3   340   301     0

** K=    4   L=    7 **

  -1   178   180   180
   0   131   152   180

   H  /FO/  /FC/  PHI

   1   163   193     0

** K=    5   L=    7 **

  -2   199   196     0
  -1   420   358     0
   0   271   351     0
   1   406   485     0
   2   231   199     0

** K=    6   L=    7 **

  -1   254   234     0
   1   186   148   180

** K=    7   L=    7 **

  -3   205   182     0
  -2   327   282     0
  -1   190   185     0
   0   139   186     0
   1   133   107     0
   2   300   301     0
   3   201   168     0

** K=    8   L=    7 **

  -2   211   148   180
  -1   139   110   180
   2   150   122     0

** K=    9   L=    7 **

  -1   175   154     0
   0   231   272     0
   1   161   179     0
   2   135   125     0

** K=    0   L=    8 **

  -3   226   237     0
  -2   333   301     0
   0   269   313     0
   1   177   232     0
   2   472   441     0
   3   294   287     0

** K=    1   L=    8 **

  -3   134   126   180
```

```
   H /FO/ /FC/ PHI

   0  204  223    0
   1   96  124    0

** K=  2  L=  8 **

  -2  231  213    0
  -1  461  474    0
   0  259  319    0
   1  198  173    0
   2  234  210    0
   3  176  182    0

** K=  3  L=  8 **

  -2   99   88    0
   3  231  174    0

** K=  4  L=  8 **

  -3  211  171    0
  -1  268  206    0
   0  114  112    0
   1  343  390    0
   2  252  248    0
   3  249  234    0

** K=  5  L=  8 **

  -2  223  125  180

** K=  6  L=  8 **

  -3  158  153    0
  -2  198  207    0
  -1  141   66    0
   0  193  234    0
   1  170  203    0
   2  119  114    0
   3  181  166    0

** K=  7  L=  8 **

  -2  124   81  180

** K=  8  L=  8 **

  -2  188  156    0
   0  189  246    0
   2  122  149    0
```

```
   H /FO/ /FC/ PHI

** K=  9  L=  8 **

   0  121  151  180

** K=  1  L=  9 **

  -2  293  266    0
  -1  174  168    0
   1  130  145    0
   2  351  348    0
   3  222  222    0

** K=  2  L=  9 **

  -2  123  101  180
   3  266  204    0

** K=  3  L=  9 **

  -3  165  174    0
  -1  219  201    0
   0  132  158    0
   1  234  256    0
   2  193  188    0
   3  149  152    0

** K=  4  L=  9 **

  -1  151  125    0
   1  145  152  180
   2  123  113  180

** K=  5  L=  9 **

  -2  177  156    0
  -1  170  133    0
   0  144  200    0

** K=  6  L=  9 **

  -1  185  161  180

** K=  7  L=  9 **

   0  258  294    0
   1  146  204    0
   2  114  114    0

** K=  0  L= 10 **
```

```
   H /FO/ /FC/ PHI

  -2  189  210    0
  -1  137  171    0
   0  185  225    0

** K=  1  L= 10 **

  -1  128  118    0
   1  123   69  180
   2  154  146  180

** K=  2  L= 10 **

  -2  175  119    0
   2  253  179    0

** K=  3  L= 10 **

  -2  158   78  180
   1  136  109    0
   2  124  100  180

** K=  4  L= 10 **

  -1  203  191    0
   0  160  148    0
   1  197  198    0
   2  118  107    0

** K=  5  L= 10 **

  -2  132   94    0

** K=  6  L= 10 **

   0  123  145    0
   1  158  195    0

** K=  1  L= 11 **

  -1  122   74    0
   0  221  226    0
   1  148  166    0

** K=  2  L= 11 **

   1  147  174    0

** K=  3  L= 11 **

  -1  231  212    0
```

```
   H /FO/ /FC/ PHI      H /FO/ /FC/ PHI      H /FO/ /FC/ PHI

** K=  0  L= 12 **

   1  171  144   0

** K=  2  L= 12 **

   0  151  141   0
```

Observed and calculated structure factors for [Cu(aOeu)$_2$]Br$_2$

```
   H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI       H  /FO/  /FC/  PHI

** K=  0  L=  0 **          3   222   233    0       1   143   147    0
                            4   391   399    0
   1   260   247    0       5   138   127    0    ** K=  1  L=  1 **
   2   681   671  180
   3   507   507    0    ** K=  7  L=  0 **         -5   223   246    0
   4   565   575    0                               -4   113   114    0
   5   173   183    0       1   735   735    0      -3   121   126    0
   6   102    98  180       3   485   491  180      -2   573   582    0
                            5   114   104    0      -1   464   446    0
** K=  1  L=  0 **                                   0   631   649    0
                         ** K=  8  L=  0 **          1    59    30    0
   1   454   445    0                                2   616   628    0
   2   165   154    0       0   273   293  180       3   551   542    0
   3   576   594  180       1   291   297    0       4   158   168    0
   5   195   211    0       2   911   914    0       5   120   139    0
                            3   167   160    0       6   111    88    0
** K=  2  L=  0 **          4   204   208  180
                            5   206   213    0    ** K=  2  L=  1 **
   0    71    44  180
   1   275   270    0    ** K=  9  L=  0 **         -6   119   103  180
   2  1157  1193    0                               -5   153   133    0
   3   211   218    0       1   490   494  180      -4   263   266    0
   5   280   289    0       3   143   132    0      -3    78    50    0
                                                    -2   456   476  180
** K=  3  L=  0 **       ** K= 10  L=  0 **         -1   311   307    0
                                                     0   570   560    0
   1   208   212  180       0   567   568    0       1   618   620  180
   2   131   122    0       1   165   166    0       2   536   540  180
   4   178   181    0       3   297   298    0       4   100    98    0
                            4   210   210    0       5    97   103  180
** K=  4  L=  0 **
                         ** K= 11  L=  0 **      ** K=  3  L=  1 **
   0   119   116    0
   1    77    75    0       2   120   131    0      -5   100    84    0
   2   375   385    0                               -4   403   412    0
   3   428   429    0    ** K= 12  L=  0 **         -3   909   938    0
   4   195   201    0                               -2   128   123  180
   5   132   144    0       0   153   148    0      -1   590   590  180
                            1   262   252    0       0  1225  1234    0
** K=  5  L=  0 **          2   142   143    0       1  1097  1111    0
                            3   131   119    0       2   167   156  180
   1   167   183  180                                3   141   148  180
   2   253   252    0    ** K= 13  L=  0 **          4   425   438    0
   3   163   160    0                                5   286   301    0
                            1   243   243    0
** K=  6  L=  0 **          2    85    23    0    ** K=  4  L=  1 **

   0  1245  1238    0    ** K= 14  L=  0 **         -5   161   167  180
   1   341   347    0                               -4   373   390  180
   2   223   226  180       0   153   140  180      -3   454   463    0
```

```
   H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

  -2   499   510    0       -2   122   130  180        1   405   403    0
  -1   702   699  180       -1   243   247    0
   0  1185  1193  180        0   116   131    0     ** K= 14   L=  1 **
   1   683   690    0        2    86    84  180
   2   697   720    0                                   0   101    88  180
   3   360   369  180     ** K=  9   L=  1 **
   4   285   296  180                               ** K=  0   L=  2 **
   5   158   160    0       -4   247   237    0
                            -3   221   213    0       -6   198   187    0
** K=  5   L=  1 **         -2   259   257    0       -5   112    98  180
                             0   260   265    0       -4   108   107    0
  -5   310   331    0        1   393   394    0       -3  1131  1071    0
  -4   207   201    0        2   134   132    0       -2  1019   944    0
  -3   100   112  180        3   170   172    0       -1  1006   922  180
  -2   596   616    0        4    94   103    0        0   378   373    0
  -1  1351  1361    0                                  1  2759  2842    0
   0   124   120    0     ** K= 10   L=  1 **          3   363   369  180
   1   148   138  180                                  4   166   160    0
   2   763   776    0       -4   203   213  180        5   242   251    0
   3   440   444    0       -3   229   229    0        6   113   119    0
                            -2   328   331    0
** K=  6   L=  1 **         -1   356   350  180     ** K=  1   L=  2 **
                             0   472   465  180
  -4   100   105    0        1   347   341    0       -6    93    86    0
  -3   250   256  180        2   358   366    0       -4   340   338  180
  -2   277   293  180        3   223   227  180       -3   166   164  180
  -1   368   372    0        4   129   129  180       -2   881   846    0
   0   132   162    0                                 -1   737   689    0
   1   115    97    0     ** K= 11   L=  1 **          0   258   242  180
   2   379   374  180                                  1   632   622  180
   3   158   175    0       -3   136   129  180        2   382   386    0
   4   254   261    0       -2   389   385    0        3   277   282    0
                            -1   484   470    0        4   312   322  180
** K=  7   L=  1 **          1   117   136  180
                             2   274   267    0     ** K=  2   L=  2 **
  -5    99    78    0        3   405   407    0
  -4    81    80    0                                 -5   295   290    0
  -3   353   350    0     ** K= 12   L=  1 **         -4   549   550    0
  -2   480   475    0                                 -1  1466  1460    0
  -1    63    65    0       -3   129   136  180        0   497   497    0
   0   626   619    0       -2   411   399  180        1   161   159  180
   1   498   501    0       -1   232   215    0        2   139   142    0
   2   144   150    0        0   372   376    0        3   590   596    0
   3   342   341    0        1   329   339  180        4   225   227    0
   4   104   120    0        2   215   219  180
                             3   199   186    0     ** K=  3   L=  2 **
** K=  8   L=  1 **
                          ** K= 13   L=  1 **         -2   241   223    0
  -5    91    68  180                                  0   312   319    0
  -4    88    60    0        0   310   301    0        1   390   389    0
```

```
     H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI

     2   129   143  180    ** K=  8   L= 2 **         ** K= 13   L= 2 **
** K=  4   L= 2 **             -5   321   329    0        -2   168   174    0
                               -4   392   400    0         0   215   189  180
    -5   181   178    0        -3   383   376  180         2   184   174    0
    -4   178   163    0        -2   142   131    0
    -3   339   350    0        -1   958   959    0    ** K= 14   L= 2 **
    -2   410   408    0         0   554   561    0
    -1   400   403    0         1   229   237  180        -1   346   337    0
     0   206   214    0         3   596   593    0         0   280   281    0
     1   268   271    0         4   101   104    0         1    93    66  180
     2   275   287    0
     3   372   367    0    ** K=  9   L= 2 **         ** K=  1   L= 3 **
     4   318   330    0
     5    98   125    0        -4   139   127    0        -6   124   125    0
                               -3   115   107    0        -4   524   499    0
** K=  5   L= 2 **             -2   206   210  180        -3   228   222    0
                               -1   212   202  180        -2   126   128    0
    -5   134   126  180         0   362   367    0        -1   793   769    0
    -4   149   148    0         1   195   184    0         0   603   595    0
    -3   133   121    0         2   378   381  180         1  1196  1208    0
    -2   372   374  180         3   126   127  180         3   398   395    0
    -1   427   412  180         4    95    88    0         4   348   348    0
     0    63    80    0                                    5   103   102    0
     1   410   410    0    ** K= 10   L= 2 **
     2   117   137  180                               ** K=  2   L= 3 **
                               -4   132   143    0
** K=  6   L= 2 **             -3   307   294    0        -5   228   232  180
                               -2   512   518    0        -4    91    78    0
    -3   534   546    0        -1   112   115  180        -3   401   385    0
    -2   510   528    0         0    81    71    0        -2   286   269    0
    -1   178   185  180         1   435   440    0        -1  1133  1112  180
     0   199   202    0         2   123   127    0         0    61    45  180
     1  1071  1082    0         3   101    71    0         1   671   673    0
     2   497   514    0         4    86    88    0         2   139   135  180
     4   126   113    0                                    3   260   264  180
     5   223   231    0    ** K= 11   L= 2 **              4    76    68  180
                                                           5   131   116    0
** K=  7   L= 2 **              0   100   103    0
                                3    97   104    0    ** K=  3   L= 3 **
    -4   185   184  180
    -3   224   219  180    ** K= 12   L= 2 **             -6   268   273    0
    -2   505   521    0                                   -5   216   222    0
    -1   302   294    0        -3   158   153    0        -4    80    26  180
     0   907   917  180        -2   245   248    0        -3   373   372    0
     1   181   188  180        -1   135   136    0        -2  1277  1283    0
     2   380   389    0         0   135   140    0        -1   144   148    0
     3   118   114    0         1   174   155    0         0   851   860  180
     4   239   223  180         2   242   248    0         1   676   687    0
     5    90    69  180         3   141   132    0         2   716   734    0
```

```
   H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI

   3   120   115    0        -3   186   186    0        -2   325   318    0
   4    77    32  180        -2   128   130    0        -1   164   162    0
   5   148   155    0        -1   139   142  180         0    85    14  180
                              0   189   198    0         1   145   132    0
** K=  4   L=  3 **           1    99   110    0         2   350   340    0
                              2    74    81  180
  -5   246   251    0                                   ** K= 14   L=  3 **
  -4   176   167  180       ** K=  9   L=  3 **
  -3   737   728  180                                    -1   170   168    0
  -2   337   317    0        -4    99    94    0
  -1   538   547    0        -3   171   157    0        ** K=  0   L=  4 **
   0   324   321  180        -2   485   490    0
   1   861   877  180        -1   409   404    0        -6   305   306    0
   2   229   225    0         0   125   126  180        -5   305   304    0
   4   132   139  180         1   177   174    0        -3   321   303  180
   5   118    98  180         2   409   405    0        -2  1234  1150    0
                              3   244   251    0        -1  1042  1000    0
** K=  5   L=  3 **                                      0   897   896  180
                            ** K= 10   L=  3 **          1   470   466    0
  -5   144   131    0                                    2   987  1004    0
  -4   651   656    0        -3   386   386  180         3   250   251    0
  -3   345   355    0        -2   217   208    0         5   100    71    0
  -2   448   451  180        -1   346   344    0
  -1   417   414    0         0   195   188  180       ** K=  1   L=  4 **
   0  1209  1224    0         1   368   363  180
   1   208   209    0         2   122   135    0        -6   138   117  180
   2   220   223  180         3   247   245    0        -5   172   161    0
   3   246   255    0         4    89   105  180        -4   343   324    0
   4   275   279    0                                   -3   336   320  180
   5   117   102    0       ** K= 11   L=  3 **         -2   407   400  180
                                                       -1   634   611    0
** K=  6   L=  3 **          -4   350   344    0         0  1037  1053    0
                             -3   136   120    0         1   369   366  180
  -3   151   155    0        -2   159   174  180         2   764   768  180
  -1   321   328  180        -1   218   224    0         3   189   187    0
   1   365   363    0         0   633   637    0         4   155   158    0
   3   259   266  180         1   181   170    0         5   122   122  180
   5   117   114    0         2   135   131  180
                              3   151   142    0       ** K=  2   L=  4 **
** K=  7   L=  3 **
                            ** K= 12   L=  3 **         -6   161   142    0
  -5   147   159    0                                   -4   546   524    0
  -2   566   579    0        -3   187   198    0        -3   784   769    0
  -1   426   425    0        -2   112   116  180        -2    66    55  180
   1   521   503    0        -1   518   513  180        -1   197   182  180
   2   285   291    0         0    91   121    0         0   890   896    0
   3   192   198    0         1   318   312    0         1   684   699    0
   4   179   176    0         2   147   141  180         2    73    68  180
                                                        3   112   116    0
** K=  8   L=  3 **         ** K= 13   L=  3 **          4   267   271    0
```

```
   H  /FO/  /FC/  PHI

   5   165   148    0

** K=   3   L=   4 **

  -3    86    52  180
  -2   408   396    0
  -1   148   127    0
   0   248   247  180
   2   151   169    0
   3   114   119  180
   4   144   143  180

** K=   4   L=   4 **

  -5   182   189    0
  -4   282   281    0
  -3   315   304    0
  -2   620   607    0
  -1   392   391    0
   0   377   395    0
   1   386   387    0
   2   219   210    0
   3   221   220    0
   4   217   213    0
   5   151   144    0

** K=   5   L=   4 **

  -4   281   282  180
  -3   169   175    0
  -2   329   331    0
  -1   520   506  180
   0   394   398  180
   2   404   401    0

** K=   6   L=   4 **

  -5   227   237    0
  -2   650   655    0
  -1   880   895    0
   1   109    94    0
   2   626   624    0
   3   387   381    0

** K=   7   L=   4 **

  -5   105   102    0
  -4   143   147    0
  -3   243   238  180
  -2   457   464  180
```

```
   H  /FO/  /FC/  PHI

  -1   373   385    0
   0   550   562    0
   1   525   523  180
   2   163   183  180
   3   202   196    0
   4   137   135    0

** K=   8   L=   4 **

  -4   448   458    0
  -3   532   552    0
  -2   369   360  180
   0   650   667    0
   1   609   619    0
   2    77    76  180
   4   296   297    0

** K=   9   L=   4 **

  -4   219   224  180
  -2   388   389    0
  -1   193   184  180
   0   311   311  180
   1   198   203    0
   2   235   236    0
   3   156   149  180
   4   127   114  180

** K=  10   L=   4 **

  -4   116   124    0
  -3    82    56    0
  -2   268   269    0
  -1   519   515    0
   0   140   134  180
   2   263   258    0
   3   133   122    0
   4   108   114    0

** K=  11   L=   4 **

  -1   103    87  180
   2   104   109  180

** K=  12   L=   4 **

  -3   124   120    0
  -2   145   158    0
  -1   305   320    0
   0   140   145    0
```

```
   H  /FO/  /FC/  PHI

   2   146   152    0

** K=  13   L=   4 **

  -2   176   162  180
  -1   153   144    0
   0   134   124    0
   1   122   117  180

** K=  14   L=   4 **

   0   315   308    0

** K=   1   L=   5 **

  -6   254   235    0
  -5    82    71    0
  -3   759   721    0
  -2   574   559    0
  -1   197   185    0
   0   494   506    0
   1   538   551    0
   2   683   681    0
   4   152   141    0
   5   148   149    0

** K=   2   L=   5 **

  -4   357   336  180
  -3    95    91  180
  -2   630   609    0
  -1   603   566    0
   0   766   768  180
   2   484   489    0
   4   121   116  180
   5    86    58  180

** K=   3   L=   5 **

  -5   475   482    0
  -4   477   472    0
  -3   225   226  180
  -2   155   168    0
  -1  1156  1149    0
   0   461   464    0
   1   462   471  180
   2   243   230    0
   3   442   441    0
   4   183   179    0
```

```
   H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI

** K=  4   L=  5 **       ** K=  9   L=  5 **          5   136    99    0

  -4   281   282    0       -4   210   206    0     ** K=  1   L=  6 **
  -2   729   738  180       -3   132   135    0
  -1    70    77  180       -1   680   685    0       -5   272   267  180
   0   579   595    0        0   413   409    0       -4    83    80    0
   1    91    82    0        1   116   125  180       -3   582   563    0
   2   365   376  180        3   246   237    0       -2   162   162  180
   4   247   243    0        4   191   190    0       -1   659   659  180
                                                       0   110   112    0
** K=  5   L=  5 **       ** K= 10   L=  5 **          1   786   781    0
                                                       2   199   197  180
  -3   817   822    0       -4   230   229    0        3   428   439  180
  -2   485   481    0       -3    92    65    0        4    86    83    0
  -1   571   565  180       -2   404   414  180
   0   196   193    0        0   263   263    0     ** K=  2   L=  6 **
   1   851   870    0        2   182   168  180
   2   346   348    0                                -5   225   221    0
   4    98    92    0     ** K= 11   L=  5 **         -4   264   255  180
   5   188   172    0                                -3   646   622    0
                            -3   496   496    0       -2   861   840    0
** K=  6   L=  5 **         -2   250   255    0        0    85    64  180
                            -1   130   122  180        1   353   353    0
  -5   147   152    0        1   535   528    0        2   592   596    0
  -4   216   213  180        2   208   217    0        4   100    84    0
  -3    82    91  180                                  5   116   115    0
  -2   133   138    0     ** K= 12   L=  5 **
  -1   186   180    0                               ** K=  3   L=  6 **
   0   308   312  180       -2   244   247    0
   1   304   298  180        0   354   358  180       -3   179   173  180
   2   293   305    0        1    84    42    0       -2   301   290  180
   4   127   120  180        2   183   187    0       -1   555   536    0
                                                       0   103    88  180
** K=  7   L=  5 **       ** K= 13   L=  5 **          1   321   327  180
                                                       3    92    81    0
  -5   166   181    0       -1   366   366    0
  -4   211   213    0        0   229   227    0     ** K=  4   L=  6 **
  -1   646   638    0
   0   300   318    0     ** K=  0   L=  6 **         -5   202   206    0
   1   133   125    0                                -4   266   254    0
   2   299   300    0       -5   333   332    0       -3   356   346    0
   3   168   166    0       -4   438   420    0       -2   462   452    0
   4   197   184    0       -3   160   155    0       -1   560   551    0
                            -2   578   575  180        0   209   208    0
** K=  8   L=  5 **         -1   780   750    0        1   168   176    0
                             0  1028  1038    0        2   245   250    0
  -4   164   163  180        1   116   116  180        3   104   100    0
  -2   199   203    0        2   458   456    0        4   124   114    0
   0    95   114  180        3   292   284    0        5   107   104    0
                             4   214   214    0
```

```
   H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI

** K=  5   L=  6  **       ** K= 10   L=  6  **         -4   610   597    0
                                                        -3   802   785    0
  -5   183   196    0        -4   294   305    0        -2   237   244  180
  -3   359   359  180        -3   179   171    0         0   773   769    0
  -1   421   412    0        -1   246   257    0         1   501   513    0
   0   321   322  180         0   414   404    0         2    84    72  180
   1   317   325  180         3   149   138    0         4   215   210    0
   3   225   226    0                                    5   140   124    0
   5    93    61  180      ** K= 11   L=  6  **
                                                     ** K=  4   L=  7  **
** K=  6   L=  6  **          0   138   133  180
                              1    98    87    0        -5   118   140  180
  -5   223   237    0                                   -4   141   134  180
  -4   423   428    0      ** K= 12   L=  6  **         -3   265   258    0
  -3   116   125    0                                   -2   344   352    0
  -2   190   197  180        -1   182   178    0        -1   377   390  180
  -1   485   486    0         0   277   292    0         0   422   420  180
   0   824   837    0         1   148   141    0         1   370   366    0
   1   125   136    0                                    2   159   161    0
   3   220   224    0      ** K= 13   L=  6  **          3   124   127  180
   4   197   184    0
                             -1   227   225  180     ** K=  5   L=  7  **
** K=  7   L=  6  **          1   103   104    0
                                                        -5   331   338    0
  -5   258   250  180      ** K=  1   L=  7  **         -4   141   133  180
  -3   440   454    0                                   -3    91    79  180
  -2    90    85  180        -5   420   422    0        -2   789   795    0
  -1   487   485  180        -4    85    68  180        -1   625   634    0
   0   190   190    0        -3    86    74    0         0   222   219  180
   1   481   481    0        -2   616   614    0         1    84    95    0
   2   127   133  180        -1   642   638    0         2   510   516    0
   3   155   155  180         0   150   134    0         3   294   294    0
                              2   393   396    0
** K=  8   L=  6  **          3   281   281    0     ** K=  6   L=  7  **
                              5    90    69    0
  -4   116   134  180                                   -4   256   265    0
  -3   421   423    0      ** K=  2   L=  7  **         -3   271   275  180
  -2   552   571    0                                   -2   337   340  180
   0    86    88  180        -5    87    74    0        -1   129   116    0
   1   333   339    0        -4   146   140    0         0   234   231    0
   2   479   485    0        -3   240   228  180         1   160   169  180
                             -2   290   280  180         2   228   234  180
** K=  9   L=  6  **         -1   704   690    0         3   175   166    0
                              0   495   500    0
  -3   311   330  180         1   363   370  180     ** K=  7   L=  7  **
  -1   571   577    0         2   149   146  180
   0    75    59  180         3   139   143    0        -4   214   200    0
   1   301   295  180                                   -3   258   251    0
   2    86    74    0      ** K=  3   L=  7  **         -2    81    54    0
   3   128   142    0                                   -1   116   117    0
```

```
   H  /FO/  /FC/  PHI

   0   505   498    0
   1   229   230    0
   2   159   162    0
   3   134   142    0
   4   104    97    0

** K=   8   L=   7 **

  -3   241   240  180
  -1   173   157    0

** K=   9   L=   7 **

  -4   276   264    0
  -3   360   363    0
  -2    96    91    0
  -1   126   131  180
   0   554   552    0
   1   263   260    0

** K=  10   L=   7 **

  -3   268   266    0
  -2   152   141    0
  -1   249   234  180
   0   152   143  180
   1   107   119    0
   2   106    81    0

** K=  11   L=   7 **

  -2   475   466    0
  -1   326   330    0
   1    95    86  180
   2   298   289    0

** K=  12   L=   7 **

  -2   169   181  180
  -1   218   205    0
   0   111   100    0
   1   161   156  180

** K=   0   L=   8 **

  -5   140   140  180
  -4   206   187    0
  -3   634   622    0
  -2   469   455    0
  -1   332   334  180

   H  /FO/  /FC/  PHI

   0   328   336    0
   1   742   740    0
   2   256   257    0
   3   237   241    0

** K=   1   L=   8 **

  -4   444   425  180
  -3   161   149  180
  -2   634   629    0
  -1   105   102    0
   0   570   560  180
   2   441   442    0
   4   164   164  180

** K=   2   L=   8 **

  -5   406   402    0
  -4   306   297    0
  -3   244   241  180
  -2   462   451    0
  -1   724   729    0
   0   256   259    0
   2   118   111    0
   3   318   321    0

** K=   3   L=   8 **

  -4   108    88    0
  -2   299   294  180
  -1   281   265  180
   0   439   438    0
   2   149   153  180

** K=   4   L=   8 **

  -5   180   191    0
  -4   277   264    0
  -3   205   217    0
  -2   238   236    0
  -1   425   421    0
   0   290   294    0
   1   102    90    0
   2    93    94    0
   3   147   138    0
   4    93    75    0

** K=   5   L=   8 **

  -4   326   327    0

   H  /FO/  /FC/  PHI

  -3    94    99  180
  -2   315   324  180
   0   271   268    0
   1    97    88  180
   2   214   213  180
   4    99    97    0

** K=   6   L=   8 **

  -4   142   132    0
  -3   498   507    0
  -2   252   260    0
  -1   249   256  180
   0   208   208    0
   1   513   526    0
   2   175   169    0

** K=   7   L=   8 **

  -4   290   280  180
  -3   119   126  180
  -2   593   604    0
   0   423   430  180
   2   202   206    0

** K=   8   L=   8 **

  -4   188   187    0
  -3   151   153  180
  -2   251   252    0
  -1   454   456    0
   0   271   266    0
   2   128   123    0
   3   258   263    0

** K=   9   L=   8 **

  -2   354   348  180
   0   445   450    0
   2   200   204  180

** K=  10   L=   8 **

  -3   365   362    0
  -2   277   291    0
   0   225   230    0
   1   256   246    0
   2   103    97    0

** K=  12   L=   8 **
```

```
   H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI         H  /FO/  /FC/  PHI

   0   178   174    0         0   554   557    0        -5   289   294    0
   1   209   202    0         3   229   221    0        -3    87    96  180
                              4   115   135    0        -2   668   681    0
** K=  1   L=  9 **                                     -1   574   563    0
                           ** K=  6   L=  9 **           0   109   102  180
  -5   260   245    0                                    2   295   293    0
  -4   515   506    0        -3   298   297    0         3   249   248    0
  -3   176   185  180        -2   146   150  180
  -2    85    81    0        -1   402   402  180      ** K=  1   L= 10 **
  -1   346   351    0         0   106   101    0
   0   471   466    0         1   217   218    0        -5   153   150    0
   1   168   162    0         3   110    91  180        -4   203   201    0
   3   268   268    0                                   -3   394   400  180
   4   126   117    0      ** K=  7   L=  9 **          -2   276   277  180
                                                        -1   475   485    0
** K=  2   L=  9 **          -4   104    91    0         0   268   266    0
                             -3   185   177    0         1   281   276  180
  -5   113   122  180        -2   250   255    0         3   168   163    0
  -3   347   341    0        -1    96    94    0
  -1   415   418  180         0   156   156    0      ** K=  2   L= 10 **
   0   378   364    0         1   294   287    0
   1   216   215    0         2   135   142    0        -4   498   496    0
   2   172   157  180         3   121   123    0        -3   334   325    0
   3   132   116  180                                   -1   159   158    0
                           ** K=  8   L=  9 **           0   441   445    0
** K=  3   L=  9 **                                      1   298   296    0
                             -2   132   133  180         4   144   123    0
  -4   107   110  180         0   143   124    0
  -3   531   532    0                                ** K=  3   L= 10 **
  -2   900   902    0      ** K=  9   L=  9 **
   0   138   139  180                                   -3   154   151    0
   1   375   376    0        -3   229   211    0        -2   160   147    0
   2   327   327    0        -2   409   419    0        -1   250   242  180
   4    84     6  180         1   318   321    0         1   244   247    0
                              2   154   141    0
** K=  4   L=  9 **                                  ** K=  4   L= 10 **
                           ** K= 10   L=  9 **
  -5   270   265    0                                   -4   210   203    0
  -3   388   391  180        -2   164   182    0        -3   234   234    0
  -2   120   112    0        -1   157   161    0        -2   168   152    0
  -1   416   417    0         0    86    39  180        -1   151   156    0
   0   121   109  180         1   207   191  180         0   325   332    0
   1   417   422  180                                    1   169   186    0
   3   116   105    0      ** K= 11   L=  9 **           2    94    77    0

** K=  5   L=  9 **          -2   135   128  180      ** K=  5   L= 10 **
                             -1   275   272    0
  -4   516   509    0         0   316   319    0        -4    91    59  180
  -2    80    76  180                                   -3   299   313    0
  -1   542   548    0      ** K=  0   L= 10 **          -1   234   230  180
```

```
    H  /FO/  /FC/  PHI

    1    89    92    0
    3    99    90  180

** K=    6   L= 10  **

   -2   424   438    0
   -1   346   342    0
    0   117   118  180
    1   104    85    0
    2   277   270    0
    3   157   159    0

** K=    7   L= 10  **

   -3   272   280  180
   -2   271   288  180
   -1   403   406    0
    0   149   141    0
    1   294   279  180

** K=    8   L= 10  **

   -3   330   332    0
    0   263   259    0
    1   316   314    0

** K=    9   L= 10  **

   -3   216   237    0
   -2   136   133    0
   -1   300   290  180
    0   112    99  180
    1   232   214    0

** K=   10   L= 10  **

   -2   312   313    0
   -1   295   299    0
    1   114   117    0

** K=    1   L= 11  **

   -4   222   223    0
   -3   412   420    0
   -1    85    96    0
    0   217   226    0
    1   323   322    0
    2   147   152    0

** K=    2   L= 11  **

    H  /FO/  /FC/  PHI

   -4   274   267  180
   -3   137   143  180
   -2   325   341    0
    0   329   324  180
    1    80    90    0
    2    86    83    0

** K=    3   L= 11  **

   -4   119    95    0
   -3   140   126  180
   -2   319   320    0
   -1   681   679    0
    0   132   120    0
    1   103   115  180
    2   143   130    0
    3   159   154    0

** K=    4   L= 11  **

   -4   360   364    0
   -3   116   111    0
   -2   512   522  180
    0   307   309    0
    2   213   223  180

** K=    5   L= 11  **

   -4   196   212    0
   -3   506   523    0
   -2   158   160    0
    0   212   199    0
    1   307   302    0

** K=    6   L= 11  **

   -2   242   244    0
    0   284   273  180
    2   134   125    0

** K=    7   L= 11  **

   -2    96   107    0
   -1   192   200    0
    0    97    97    0
    1   124   141    0
    2   112   125    0

** K=    8   L= 11  **

    H  /FO/  /FC/  PHI

   -3   118    84    0

** K=    9   L= 11  **

   -2   144   147    0
   -1   385   388    0

** K=    0   L= 12  **

   -4   389   388    0
   -3    90    73    0
   -2   331   330  180
   -1   424   435    0
    0   403   406    0
    3    89    88    0

** K=    1   L= 12  **

   -4   173   167    0
   -3   322   326    0
   -2   216   228  180
   -1   271   261  180
    0   224   213    0
    1   202   190    0
    2   102   100  180

** K=    2   L= 12  **

   -3   396   415    0
   -2   286   293    0
   -1   135   127    0
    1   220   193    0
    2   193   209    0

** K=    3   L= 12  **

   -3   130   114  180
   -2   140   138    0
   -1   160   139    0
    0   145   158  180

** K=    4   L= 12  **

   -3   237   234    0
   -2   210   214    0
   -1   145   148    0
    0   152   157    0
    1   218   220    0
    2    95   117    0
```

```
   H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI        H  /FO/  /FC/  PHI


** K=  5   L= 12 **         -3   338   330    0
                            -2   194   205    0
  -2   120   150    0       -1   374   373  180
  -1    84    41    0        0   137   126  180
   0   114   114  180        1   204   187    0

** K=  6   L= 12 **     ** K=  5   L= 13 **

  -2   137   124  180       -2   335   342    0
  -1   299   314    0       -1   214   214    0
   0   309   315    0
                        ** K=  6   L= 13 **
** K=  7   L= 12 **
                            -1   133   116    0
  -2   213   213  180        1   146   134  180
  -1   257   257  180
   0   182   178    0   ** K=  7   L= 13 **
   1   109   126    0
                             0   122   127    0
** K=  8   L= 12 **
                        ** K=  0   L= 14 **
  -2   356   369    0
   1   105   115    0       -2   120   132    0
                            -1   281   280  180
** K=  1   L= 13 **          0   216   204    0
                             1   264   244    0
  -3   217   219    0
  -2   235   242    0   ** K=  1   L= 14 **
  -1   128   121    0
   0   104   105    0       -2   264   274    0
   1   116   127    0       -1    96    80  180
   2   174   170    0        0   170   179  180

** K=  2   L= 13 **     ** K=  2   L= 14 **

  -3   296   313  180       -2   219   215    0
  -2   190   189  180       -1   241   241    0
  -1   285   276    0        0   166   154    0
   0   115   101    0
   1   104   109  180   ** K=  4   L= 14 **

** K=  3   L= 13 **         -2   195   203    0
                            -1   160   158    0
  -3   213   233    0        0   129   107    0
  -1   131   123    0
   0   366   356    0   ** K=  1   L= 15 **
   1   131   134    0
                            -1    92    64    0
** K=  4   L= 13 **
```

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PUBLICATIONS

Work from this thesis has been included in the following publications. Copies are appended overleaf.

M.J. Begley, P. Hubberstey and C.H.M. Moore:-

J.Chem.Research (S), 1985, 378-379;
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Structural and Spectroscopic Properties of Co-ordinated 1-Cyanoguanidine. Part 2.† Bis(1-cyanoguanidine)-di-μ-aquocopper(II) Dinitrate Dihydrate and Related Copper(II) Complexes

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Structural and Spectroscopic Properties of Co-ordinated 1-Cyanoguanidine. Part 2.† Bis(1-cyanoguanidine)-di-μ-aquocopper(II) Dinitrate Dihydrate and Related Copper(II) Complexes

J. Chem. Research (S),
1985, 378–379
J. Chem. Research (M),
1985, 4001–4034

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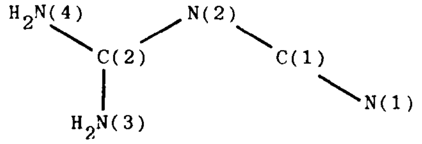
Following our attempted empirical correlation of the structural and spectroscopic properties of 1-cyanoguanidine (cnge) co-ordinated to cadmium(II),[5] we have now undertaken a corresponding study of copper(II)–cnge complexes.

Both anhydrous $Cu(cnge)_2X_2$ [X_2 = Cl_2, Br_2, $(NO_3)_2$, SO_4] and hydrated $Cu(cnge)_2X_2{\cdot}2H_2O$ [X_2 = Cl_2, Br_2, $(NO_3)_2$, SO_4], $Cu(cnge)_2(NO_3)_2{\cdot}4H_2O$, and $Cu(cnge)_2SO_4{\cdot}5H_2O$ complexes were synthesised and characterised spectroscopically. The structure of the nitrate tetrahydrate was determined by single-crystal *X*-ray-diffraction methods. As for the other copper(II)–cnge complexes for which structural data are available, $[Cu(cnge)_2Cl_2(H_2O)_2]$[1] and $[Cu(cnge)(aebg)]SO_4{\cdot}H_2O$ [aebg = 1-(2-aminoethyl)biguanide],[3] it contains monodentate cnge ligands co-ordinated to the copper atom through the nitrile nitrogen atom.



1-cyanoguanidine numbering scheme

Comparison of the i.r. spectra of the complexes with that of cnge reveals that the two absorption bands attributed to the antisymmetric and symmetric stretching vibrations of the nitrile group move to higher wavenumbers on co-ordination. Whereas ν_a[N(1)C(1)N(2)], which appears as a sharp doublet, moves from 2203/2157 cm^{-1} to between 2235/2180 and 2250/2200 cm^{-1}, ν_s[N(1)C(1)N(2)] moves from 1252 cm^{-1} into the range 1300 to 1275 cm^{-1}. The pertinent i.r. data are summarised in Table 9. It is probable that these increases, which are typical of monodentate co-ordinated nitriles and which are attributed to a more effective σ-donor than π-acceptor interaction,[13] are diagnostic of this co-ordination mode for cnge.

Several of the hydrates are novel; the properties of the others are consistent with those reported previously. A discrepancy occurs, however, between the anhydrous complexes prepared in this work by thermal dehydration of the hydrates and those synthesised by Panda *et al.*[10] by reaction of stoicheiometric quantities of cnge and the appropriate copper(II) salt in ethanol. A comparison of the properties of the two sets of compounds is effected in Table 8. We believe the discrepancy arises from the different synthetic routes employed. Despite many attempts we were unable to prepare the anhydrous halides by Panda's route: depending on the molar ratios of the reactants either mono- or bis-[1-(amidino-*O*-ethyl)urea] complexes of copper(II) were invariably obtained, presumably as a result of solvolysis of the nitrile group, a known facile reaction in the presence of copper(II) salts. A comparison of the properties of these products with those of the anhydrous compounds prepared by Panda is also included in Table 8. The remarkable similarity between the two sets of data and the marked difference between the properties of the two groups of anhydrous complexes lead us to question the reliability of the earlier work.

Table 8 Products of the reaction between cnge and copper(II) halides in refluxing ethanol

Product	Appearance	λ_{max}/nm
Anhydrous products obtained by thermal dehydration of hydrates[a]		
$Cu(cnge)_2Cl_2$	Bright green	870
$Cu(cnge)_2{\cdot}Br_2$	Pale brown	865
$Cu(cnge)_2(NO_3)_2$	Bright green	870
Anhydrous products obtained by refluxing cnge and copper(II) salt in ethanol[b]		
$Cu(cnge)_2Cl_2$	Pink	530
$Cu(cnge)_4Cl_2$	Blue	675
$Cu(cnge)_2Br_2$	Pink	525
$Cu(cnge)_4Br_2$	Blue	665
$Cu(cnge)_2(NO_3)_2$	Deep pink	520
Solvolysis products obtained by refluxing cnge and copper(II) salt in ethanol[a]		
$Cu(aOeu)_2Cl_2{\cdot}2H_2O$[c]	Pink	540
$Cu(aOeu){\cdot}Cl_2$	Blue	670
$Cu(aOeu)_2Br_2$	Purple	525
$Cu(aOeu)Br_2{\cdot}2H_2O$	Green	660

[a] Present work.
[b] Ref. 10.
[c] aOeu = 1-(amidino-*O*-ethyl)urea [$NH_2{\cdot}C(=NH){\cdot}NH{\cdot}C(=NH){\cdot}OEt$].

Crystal and Molecular Structure of $[Cu(cnge)_2(H_2O)_2](NO_3)_2{\cdot}2H_2O$.—After preliminary cell parameters had been determined from oscillation and Weissenberg photographs, reflection intensities were measured on a Hilger and Watts four-circle diffractometer. The structure was solved by heavy-atom methods and refined by least squares to R = 0.075 for 705 observed structure amplitudes.

Crystal Data.—$C_4H_{16}N_{10}O_{10}Cu$, M = 427.8, triclinic, space group $P\bar{1}$, a = 350.8(2), b = 1020.1(3), c = 1192.7(3) pm, α = 102.45(3), β = 101.58(3), γ = 101.60(3)°, U = 394.67 × 10^6 pm^3, D_m = 1.82 g cm^{-3}, D_c = 1.80 g cm^{-3} for Z = 1, $F(000)$ = 219, $\mu(Mo\text{-}K_\alpha)$ = 15.18 cm^{-1}.

The structure is shown in Figure 1(b). It comprises a series of planes parallel to (120) which contain $[Cu(cnge)_2(H_2O)_2]^{2+}$ cationic fragments and the nitrate anions, both of which are effectively planar, together with the free water molecules. Within the planes, the molecular units are held together by both electrostatic and hydrogen-bonding interactions. The planes are linked by Cu—O bridging contacts supported by weak hydrogen bonding between the free water molecule and a nitrate anion.

The Cu^{2+} ion lies in a tetragonally elongated centrosymmetric octahedral co-ordination sphere typical of Jahn–Teller distorted d^9 systems. The equatorial positions of the co-ordination sphere are occupied by two cnge nitrile nitrogen atoms, r[Cu(1)···N(1)] = 192 pm, and two water oxygen atoms, r[Cu(1)···O(1)] = 196 pm [Figure 1(b)]; the axial positions are occupied by two somewhat more remote water oxygen atoms, r[Cu(1)···O(1)] = 260 pm, located in the two adjacent planes.

---

*To receive any correspondence.
†Ref. 5 is taken as Part 1 of this series.

Table 6 Molecular geometries of cnge in the free molecule and in a number of copper(II)–cnge complexes

	cnge[a]	$[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$	$[Cu(cnge)_2Cl_2(H_2O)_2]$[b]	$[Cu(cnge)(aebg)]SO_4 \cdot H_2O$[c]
(a) *Bond distances* (pm)				
C(1)–N(1)	115	116(2)	116(1)	117(1)
C(1)–N(2)	129	129(2)	129(1)	128(1)
C(2)–N(2)	133	133(2)	133(1)	136(1)
C(2)–N(3)	133	134(2)	134(1)	133(1)
C(2)–N(4)	133	131(2)	132(1)	133(1)
(b) *Bond angles* (°)				
N(1)–C(1)–N(2)	175	173.0(1.1)	170.6(9)	172.6(6)
C(1)–N(2)–C(2)	119	122.8(1.0)	123.1(7)	118.6(6)
N(2)–C(2)–N(3)	123	123.3(1.1)	123.8(4)	124.4(5)
N(2)–C(2)–N(4)	117	117.7(1.1)	117.4(7)	116.6(5)
N(3)–C(2)–N(4)	120	118.9(1.1)	118.8(7)	118.9(6)

[a] N. V. Rannov, R. P. Ozerov, I. D. Datt, and A. N. Kshnyakina, *Sov. Phys. Crystallogr.*, 1966, **11**, 177. [b] Ref. 1. [c] Ref. 3.

Table 9 I.r. data/cm^{-1} for the N(1)C(1)N(2) stretching vibrations of the carbon–nitrogen skeleton of cnge in the free molecule and in a number of copper(II)–cnge complexes[a]

Species	ν_a[N(1)C(1)N(2)]	ν_s[N(1)C(1)N(2)]	Species	ν_a[N(1)C(1)N(2)]	ν_s[N(1)C(1)N(2)]
cnge	2203/2157	1252	cnge	2203/2157	1252
$Cu(cnge)_2Cl_2$	2240/2180	1280	$Cu(cnge)_2Cl_2 \cdot 2H_2O$	2250/2200	1300
$Cu(cnge)_2Br_2$	2240/2200	1280	$Cu(cnge)_2Br_2 \cdot 2H_2O$	2240/2200	1275
$Cu(cnge)_2(NO_3)_2$	2225/2185	1295	$Cu(cnge)_2(NO_3)_2 \cdot 2H_2O$	2240/2200	1275
$Cu(cnge)_2SO_4$	2235/2180	1280	$Cu(cnge)_2SO_4 \cdot 2H_2O$	2240/2200	1280
			$Cu(cnge)_2(NO_3)_2 \cdot 4H_2O$	2240/2200	1295
			$Cu(cnge)_2SO_4 \cdot 5H_2O$	2250/2210	1300

[a] The assignment is based on that of Jones and Orville-Thomas[12] for the unco-ordinated ligand; ν_a = antisymmetric A′ stretch, ν_s = symmetric A′ stretch.

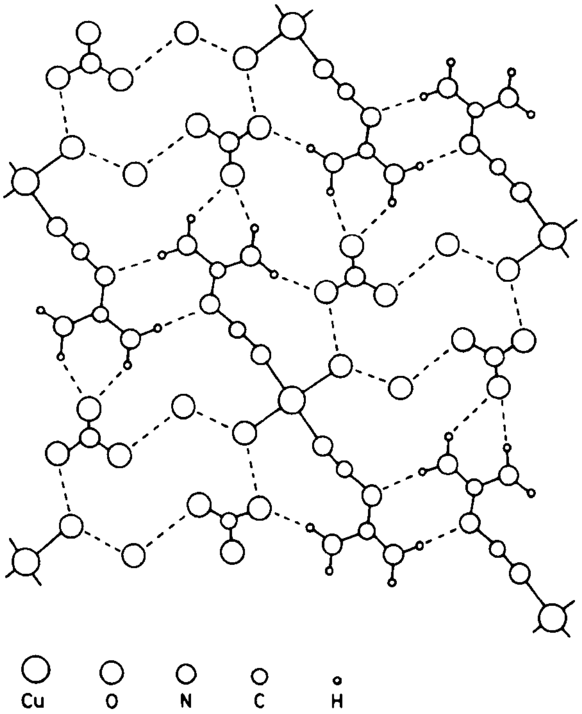


Figure 1(b) View of the structure of $[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ perpendicular to the (120) plane

The molecular geometry of the cnge molecule, which is effectively planar (the maximum deviation of the skeletal atoms from the best plane being 6 pm), is almost identical to that in $[Cu(cnge)_2Cl_2(H_2O)_2]$;[1] it differs somewhat, however, from that in $[Cu(cnge)(aebg)]SO_4 \cdot H_2O$.[3] Bond distances and angles for cnge in these complexes and in the free molecule are compared in Table 6. The differing geometries are tentatively attributed to the existence of a very weak Cu(1)—N(2) interaction, *r*[Cu(1)···N(2)] = 314 pm, in the sulphate complex.

We thank the S.E.R.C. for a maintenance grant (to C. H. M. M.).

References: 13

Figure 1(a): View of the structure of $[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ perpendicular to (001)

Figure 2: T.g.a. curves for hydrated copper(II)–cnge complexes

Table 1: Final positional parameters

Table 2: Thermal parameters

Table 3: Intermolecular contacts of less than 330 pm in $[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$; hydrogen bond and electrostatic interactions

Table 4: Bond distances and bond angles in $[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$

Table 5: Planarities of the cnge molecule and of the NO_3^- anion in $[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$

Table 7: Thermal behaviour of hydrated copper(II)–cnge complexes; isothermal experiments

Appendix: Observed and calculated structure factors for $[Cu(cnge)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$

Paper: E/137/85 Received: 21st June 1985

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Co-ordination Chemistry of Guanidine Derivatives. Part 1. Crystal and Molecular Structures of the 1 : 1 Ethanol Adduct of 1-Carbamoylguanidine and of 1-Carbamoylguanidinium Perchlorate

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We report the crystal and molecular structures of the 1 : 1 ethanol adduct of 1-carbamoylguanidine (clge·EtOH) and of 1-carbamoylguanidinium perchlorate ($[clgeH]^+ClO_4^-$), together with spectroscopic data for 1-carbamoylguanidine (clge), its ethanol adduct, and various 1-carbamoylguanidinium salts ($[clgeH]^+X^-$).

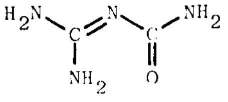
1-Carbamoylguanidine exhibits amphoteric properties readily forming both cationic and anionic derivatives by reaction with acids and bases respectively. All three species can form complexes with diverse metal cations. The literature on these resultant complexes is extremely confusing owing to the diversity of nomenclature used for 1-carbamoylguanidine and its two derivatives, resulting, presumably, from the plethora of molecular structures proposed for the three species; three tautomeric forms can be envisaged for the neutral molecule, eight for the cation and seven for the anion.

Our present understanding of the co-ordination chemistry of these species is somewhat limited and uncertain since it is generally inferred from spectroscopic (i.r., Raman, u.v.–visible), magnetic, and chemical analytical data.[4,5,8] There is a complete absence of structural data for both the uncomplexed species and the complexes in which they occur. The present paper which reports samples of such structural data, is a prelude to a study of the co-ordination chemistry of these species.

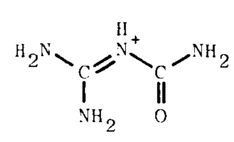
Structural Data.—After preliminary cell parameters had been determined from oscillation and Weissenberg photographs, reflection intensities were measured on a Hilger and Watts Y290 (clge·EtOH) or an Enraf–Nonius CAD4 ($[clgeH]^+ClO_4^-$) four-circle diffractometer using Mo-K_α or Cu-K_α radiation respectively. Whereas the structure of the adduct was solved by direct methods and refined by least squares to R = 0.046 for 715 observed structure amplitudes, that of the salt was solved by heavy-atom methods and refined by least squares to R = 0.041 for 1108 observed structure amplitudes.

Crystal Data.—$C_4H_{12}N_4O_2$, M = 148.2, orthorhombic, space group $P2_12_12_1$, a = 750.9(2), b = 889.6(3), c = 1156.5(3) pm, U = 772.5 × 10^6 pm^3, D_m = 1.25, D_c = 1.27 g cm^{-3} for Z = 4, $F(000)$ = 320, μ(Mo-K_α) = 1.1 cm^{-1}; $C_2H_7N_4ClO_5$, M = 202.6, monoclinic, space group $P2_1/c$, a = 802.0(3), b = 999.9(3), c = 961.1(3) pm, β = 105.54(3)°, U = 742.6 × 10^6 pm^3, D_m = 1.79, D_c = 1.81 g cm^{-3} for Z = 4, $F(000)$ = 416, μ(Cu-K_α) = 47.8 cm^{-1}

The molecular geometries of clge and its protonated derivative are shown in Figures 1(a) and (b) respectively. It is clear that the neutral molecule adopts the tautomeric form (**1**) (hence the nomenclature used in this publication) and that protonation occurs at the central nitrogen atom giving the tautomeric form (**4**) for the cationic species. It is important to note that the conformation of both species about the C(1)—N(2) bond is such that an intramolecular hydrogen bond can be formed between O(1) and N(4). The two molecules are effectively planar, the maximum deviation of the carbon and nitrogen atoms of the skeleton from the best plane being 9.8 pm (for clge) and 5.3 pm (for $[clgeH]^+$), inferring sp^2 hybridisation of all skeleton atoms and the presence of a delocalised π system over the entire C–N skeleton.



(**1**)



(**4**)

Significant aspects of the geometries of clge and of $[clgeH]^+$ are compared with those of the analogous species biuret (bu)[13,14] and biguanide (bg)[12] and the mono- and di-protonated derivatives of the latter ($[bgH]^+$ and $[bgH_2]^{2+}$)[15,16] in Table 7. Whereas bu exists as the carbamoylurea tautomer, bg adopts the (aminoiminomethyl)guanidine tautomeric form; protonation of the latter occurs first at the imino nitrogen atom and then at the bridging nitrogen atom. Although bu, clge, bg, and $[clgeH]^+$ are effectively planar, the dihedral angle between the normals to the two planar halves of the molecules not exceeding 12.5°, the out-of-plane distortion is extensive for $[bgH]^+$ and $[bgH_2]^{2+}$, with dihedral angles of *ca.* 40 and 48° respectively (Table 7). The planarity of the former species is attributed to the formation of an intramolecular hydrogen bond between an amine donor and an oxygen or imine acceptor; the lack of planarity of the latter species is due to steric interactions between hydrogen atoms on juxtapositioned amine groups. The electronic structures of the molecules, however, do not appear to be influenced by the dihedral angle; they are dependent solely on the adopted tautomeric form. Thus, whereas those species with a bridging C—NH—C group (bu, $[clgeH]^+$, and $[bgH]^{2+}$) all have longer bridging than terminal C—N bonds, those with a bridging C═N—C group (bg, clge, and $[bgH]^+$) exhibit near equivalence of C—N bond distances. Obviously, the out-of-plane distortion has little effect on the delocalised π-system which exists over the sp^2-hybridised CN skeleton.

Spectroscopic Data.—Infrared spectra for clge, clge·EtOH, and various $[clgeH]^+$ salts and for $[^2H_6]$-[clge] and $[^2H_7]$-$[clgeH]^+Cl^-$ have been measured. The spectra of clge and clge·EtOH are very similar; those of $[clgeH]^+$ are virtually independent of the associated anion. An unambiguous assignment of the spectra is not possible owing to extensive mixing of the internal co-ordinates of the planar clge and $[clgeH]^+$ species, both of which have C_s symmetry. Those bands attributable primarily to ν(N—H) and $\delta(NH_2)$ vibrations have been assigned, however, by comparison of the spectra of the protonated and deuterated samples.

Following earlier assignments of the spectra of cnge[17] and guanidine,[18] the majority of the bands associated with the A′ stretching vibrations of the C—N—O skeletons are expected to occur in the range 1800–1250 cm^{-1}. Although comparison of the spectra of cnge and clge in

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*To receive any correspondence.

Table 7 Significant features of the molecular geometries of bu, clge, bg, $[clgeH]^+$, $[bgH]^+$, and $[bgH_2]^{2+}$

						$[clgeH]^{+\,c}$	$[bgH]^+$			$[bgH_2]^{2+e}$
	bu[a]	bu[b]	clge[c]	bg[d]	bg[e]	ClO_4^-	$Cl^{-\,f}$	$CO_3^{2-\,e}$	$SO_4^{2-\,e}$	SO_4^{2-}
Dihedral angle/°[g]	5.6	6.3	7.5		12.5	4.4	39.5	42.1	46.6	48.4
Intramolecular hydrogen distance/pm	276	272	265	264		266				
Average r[C···N(bridge)]/pm	139.5	138.5	135.2	135.2	135.6	137.5	133.0	134.3	134.6	137.8
Average r[C···N(terminal)]/pm[h]	134.5	132.5	134.0	136.8	135.8	132.0	133.8	133.1	132.8	130.7

[a] Ref. 13. [b] Ref. 14. [c] Present results. [d] Ref. 12. [e] Ref. 16. [f] Ref. 15.
[g] This is the angle between the normals to the planes which best represent the two halves of the molecule.
[h] This average does not include those contacts, formally defined as double bonds, between carbon and terminal imine groups.

this region does not reveal unambiguously the bands due to the stretching vibrations of the carbamoyl fragment of clge (one occurs in the range 1600–1500 cm^{-1}, the other at 1425 cm^{-1}), the fact that for [$^2H_6$]-[clge] bands do not occur at wavenumbers higher than 1580 cm^{-1} suggests that the ν(C—O) band is moved to lower wavenumbers not only by mixing the other skeletal stretches but also by intramolecular hydrogen-bond formation. For $[clgeH]^+$, however, a similar comparison reveals intense bands at 1735 and 1460 cm^{-1} which are tentatively assigned to these vibrations. The movement of these bands to higher wavenumbers on protonation is indicative of less effective mixing of the internal coordinates for $[clgeH]^+$ rather than clge, a suggestion which is corroborated by the decrease observed in r[C(1)···N(1)] and r[C(1)···O(1)] from clge to $[clgeH]^+$ (Figure 1).

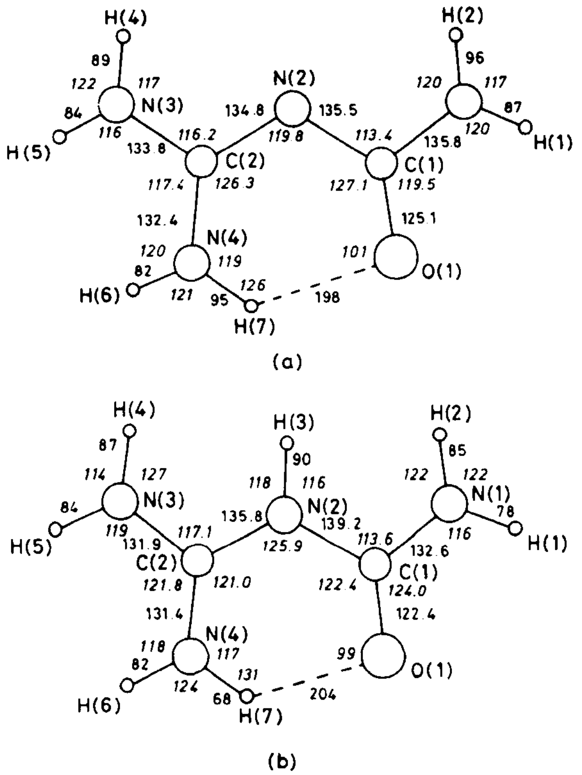

Figure 1 Molecular geometries of (a) 1-carbamoylguanidine and (b) its monoprotonated derivative: interatomic distances in pm; angles (in italics) in degrees

We thank the late Professor T. J. King for assistance in the determination of the structure of the perchlorate and Miss F. Leonard for sample preparation. One of us (C. H. M. M.) thanks the S.E.R.C. for a maintenance grant.

References: 18

Table 1: Final positional parameters for the adduct

Table 2: Thermal parameters for the adduct

Table 3: Final positional parameters for the perchlorate

Table 4: Thermal parameters for the perchlorate

Table 5: Bond distances and bond angles in 1-carbamoylguanidine and its protonated derivative

Table 6: Planarity of and torsion angles in the carbon–nitrogen skeletons of 1-carbamoylguanidine and its protonated derivative

Table 8: Geometry of the ethanol molecule

Table 9: Geometry of the perchlorate anion

Table 10: Intermolecular contacts of less than 330 pm in both structures; hydrogen bond and electrostatic interactions

Table 11: I.r. spectroscopic data for clge, [$^2H_6$]-[clge], clge·EtOH, various $[clgeH]^+$ salts, and $[clgeH]^+Cl^-$

Table 12: Analytical data for all products

Appendix A: Observed and calculated structure factors for the 1 : 1 ethanol adduct of 1-carbamoylguanidine

Appendix B: Observed and calculated structure factors for 1-carbamoylguanidinium perchlorate

Figure 2: Projection of the structure of the adduct onto the (100) plane

Figure 3: Projection of the structure of the adduct perpendicular to the plane of the 1-carbamoylguanidine molecule

Figure 4: Projection of the structure of the perchlorate onto the (001) plane

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Co-ordination Chemistry of Guanidine Derivatives. Part 2.† Crystal and Molecular Structures of Bis(1-carbamoylguanidine)dinitratocopper(II)

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1986

Co-ordination Chemistry of Guanidine Derivatives. Part 2.† Crystal and Molecular Structures of Bis(1-carbamoylguanidine)dinitratocopper(II)

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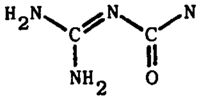
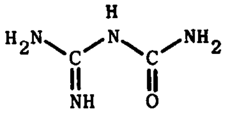
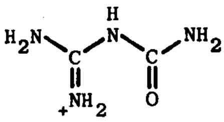
We report a structural analysis of bis(1-carbamoylguanidine)dinitratocopper(II) which shows that, on complex formation, 1-carbamoylguanidine (clge) undergoes proton transfer from a terminal amine group to the central nitrogen atom. The structure of the resultant ligand is very similar to that of the isoelectronic species, [clgeH]+.[8]



free clge

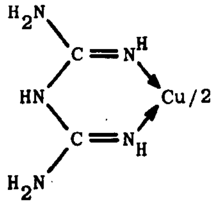


co-ordinated clge

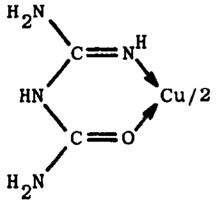


[clgeH]+

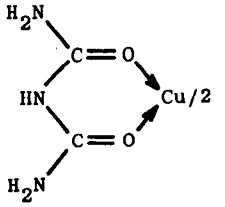
The co-ordination mode of clge is thus intermediate between those of biguanide (bg) and biuret (bu), bg co-ordinating *via* two imine groups (**1**),[3] clge *via* one imine and one carbonyl group (**2**), and bu *via* two carbonyl groups (**3**).[4] It is significant that in none of these complexes does the ligand co-ordinate the transition metal through an amine group, a co-ordination mode generally accepted by earlier workers in the field.[10] Since the ligands are planar, extensive delocalised π-systems must extend over the entire C—N—O skeleton of the molecules, resulting in sp^2 hybridisation of the amine groups. Consequently, these groups do not have lone pairs of electrons which can be directed towards a transition metal and hence co-ordination through amine residues is not possible; the only functional groups which act as co-ordinating centres in these ligands are imine and carbonyl fragments.



(**1**)



(**2**)



(**3**)

The observed tautomeric change in clge on co-ordination to copper(II) is analogous to that experienced by bg, a C—NH—C bridge being generated at the expense of a C—N=C bridge. No tautomeric change occurs in bu on co-ordination, both free and co-ordinated bu having a C—NH—C bridge. The formation of a C—NH—C rather than a C—N=C bridge has several structural ramifications, as evidenced by the structural features of free and co-ordinated clge, bg, and bu, collated in Table 4, together with corresponding data for [clgeH]+. It is clear that the bridging C—N bonds lengthen at the expense of the terminal C—N bonds, that the C—N—C bond angle increases, and that the molecule becomes flatter.

Crystal Structure of Bis(1-carbamoylguanidine)dinitratocopper(II). – After preliminary cell parameters had been determined from oscillation and Weissenberg photographs, reflection intensities were measured on a Hilger and Watts Y290 four-circle diffractometer. The structure was solved by heavy-atom methods and refined by least squares to R = 0.066 for 555 observed structure amplitudes.

Crystal Data. – $C_4H_{12}N_{10}O_8Cu$, M = 391.8, monoclinic, space group $P2_1/n$, a = 914.6(3), b = 665.4(3), c = 1118.3(3) pm, β = 98.56(3)°, U = 672.9 × 10^6 pm³, D_m = 1.90, D_c = 1.93 g cm^{-3} for Z = 2, $F(000)$ = 398, $\mu(\text{Mo-}K_\alpha)$ = 17.60 cm^{-1}.

The structure consists of ribbons of coplanar $[Cu(clge)_2]^{2+}$ cationic fragments and nitrate anions linked through the anions to give two sets of planes parallel to (120) and ($\bar{1}$20). The intra- and inter-ribbon contacts involve both electrostatic and hydrogen-bonding interactions.

In the cation, two bidentate clge molecules chelate the Cu^{2+} ion to form a centrosymmetric square planar CuO_2N_2 chromophore of D_{2h} symmetry. The molecular geometry of this moiety is summarised in Figure 1; its

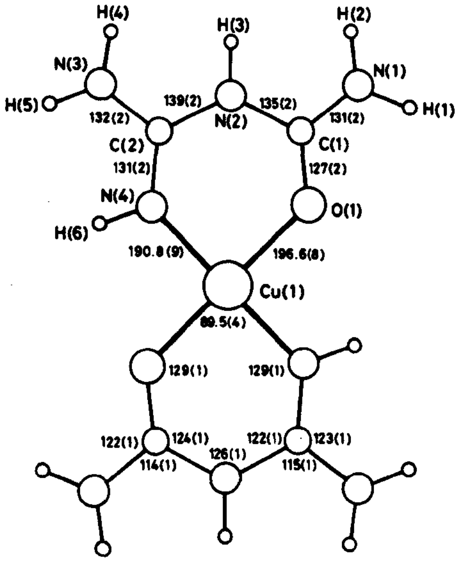


Figure 1 Molecular geometry of $[Cu(clge)_2]^{2+}$ cationic fragment (bond lengths/pm, bond angles/°)

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*To receive any correspondence.
†Part 1 is ref. 8.

Table 4 Significant features of the molecular geometries of free and co-ordinated clge, bg, and bu and of [clgeH]$^{+}$

Parameter	clge[a] (free)	clge (co-ord)	[clgeH]$^{+}$[a]	bg[b] (free)	bg[c] (co-ord)	bu[d] (free)	bu[e] co-ord
Dihedral angle[f]	7.5	1.7	4.4	12.5		6.3	
Average $r(C\cdots N_{bridge})$/pm	135.2	137.0	137.5	135.6	137.4	138.5	137.1
Average $r(C\cdots N_{terminal})$/pm[g]	134.0	131.5	132.0	135.8	134.9	132.5	132.1
C—N—C/°	119.8	126.0	125.9	119.9	127.3[h]	128.5	126.8

[a] Ref. 8.

[b] A. A. Pinkerton and D. Schwartzenbach, *J. Chem. Soc.*, *Dalton Trans*, 1978, 989.

[c] Ref. 3.

[d] B. M. Craven, *Acta Crystallogr, Sect. B.*, 1973, **29**, 1525.

[e] Ref. 4.

[f] This is the angle between the normals to the planes which best represent the two halves of the molecule.

[g] This average does not include those contacts, formally defined as double bonds, between carbon and terminal imine groups.

[h] Average of two determinations.

planarity is such that the maximum deviation of the constituent atoms from the best plane is 7.4 pm. A very weak bonding interaction exists between the copper atom and axially located oxygen atoms of a pair of centrosymmetrically related nitrate anions, $r[Cu(1)\cdots O(4)]$ = 289 pm [*cf.* the sum of the van der Waals' radii of copper (143 pm) and oxygen (152 pm)], O(1)—Cu(1)—O(4) = 86.1, N(4)—Cu(1)—O(4) = 85.9°. Thus, the Cu^{2+} ion lies in a tetragonally elongated centrosymmetric octahedral co-ordination sphere typical of Jahn–Teller distorted d^9 systems.

Spectroscopic Data. – I.r. spectra for protonated and deuterated samples of $[Cu(clge)_2(NO_3)_2]$ were compared with corresponding data, particularly in the 1800–1300 cm^{-1} range, for clge, [clgeH]Cl, $[clgeH]_2CuCl_4$, $Cu[clge]_2$, and the analogous complexes $Cu(clge)_2X_2$ (X = Cl, Br). The spectra exhibit sufficiently marked differences to permit the differentiation between free and co-ordinated clge, $[clgeH]^+$, and $[clge]^-$. Mixing of internal co-ordinates is, however, so extensive that absorption bands do not necessarily correspond to the vibration of one particular functional group and hence changes therein cannot be used for structural elucidation.

We thank Miss Gillian Eggleston and Miss W. Antoinette Groenewegen for assistance in sample preparation and the S.E.R.C. for a maintenance grant (to C. H. M. M.).

References: 11

Table 1: Final positional parameters

Table 2: Thermal parameters

Table 3: Planarities of the clge molecule, of the chelate complex, and of the nitrate anion in $[Cu(clge)_2(NO_3)_2]$

Table 5: Intermolecular contacts of less than 330 pm in $[Cu(clge)_2(NO_3)_2]$; hydrogen bond and electrostatic interactions

Appendix: Observed and calculated structure factors

Figure 2: View of the structure of $[Cu(clge)_2(NO_3)_2]$ perpendicular to (001)

Figure 3: View of the structure of $[Cu(clge)_2(NO_3)_2]$ perpendicular to (120)

Figure 4: I.r. spectra (1800–600 cm^{-1}) of $Cu(clge)_2X_2$ (X = NO_3, Cl, Br)

Figure 5: I.r. spectra (1800–1300 cm^{-1}) of $[Cu(clge)_2(NO_3)_2]$, $[Cu([^2H_6]\text{-}clge)_2(NO_3)_2]$, and clge

Figure 6: I.r. spectra (1800–1300 cm^{-1}) of $[Cu(clge)_2(NO_3)_2]$, $[clgeH]_2CuCl_4$, and $Cu[clge]_2$

Paper: E/228/85 Received: 28th October 1985

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Co-ordination Chemistry of Guanidine Derivatives. Part 3.[1] Crystal and Molecular Structures of the Bis(1-amidino-*O*-ethylurea)dichlorodi-μ-chlorodicopper(II) Dimer and of Bis(1-amidino-*O*-ethylurea)copper(II) Dichloride Dihydrate

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Co-ordination Chemistry of Guanidine Derivatives. Part 3.[1] Crystal and Molecular Structures of the Bis(1-amidino-O-ethylurea)dichlorodi-μ-chlorodicopper(II) Dimer and of Bis(1-amidino-O-ethylurea)copper(II) Dichloride Dihydrate

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J. Chem. Research (M), 1986, 1501–1545

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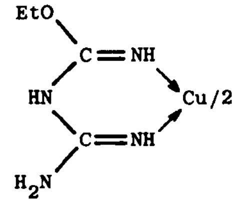
We report the crystal and molecular structures of the products of the reaction between cyanoguanidine (cnge) and copper(II) chloride in refluxing ethanol. Their identification as [Cu(aOeu)Cl_2]$_2$ and [Cu(aOeu)$_2$]Cl_2·$2H_2O$ (aOeu = 1-amidino-*O*-ethylurea) and the establishment of the tautomeric form (**5**) for the co-ordinated aOeu ligand has resolved uncertainty in this system.

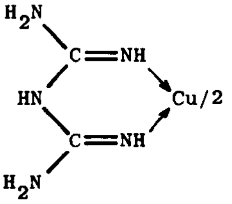
Previously the products had been reported both as anhydrous bis- or tetrakis-1-cyanoguanidine–copper(II) complexes[4] and as mono- or bis-(amidino-ethylurea)–copper(II) complexes;[5–8] whereas the former were thought to arise from simple complexation reactions, the latter were said to result from solvolysis of the nitrile function of cnge.

The authors identifying the products as amidinoethylurea complexes differed in their assessment of the geometrical conformation of the ligand, both 1-amidino-3-ethylurea (a3eu)[5,6] and aOeu[7,8] tautomers being suggested. Furthermore, the co-ordination mode of the ligand had not been ascertained.

Chemical evidence suggested that the products were, in fact, copper(II)–aOeu complexes[2,8] and, by analogy with the structure of co-ordinated biguanide [bg (**6**)] in [Cu(bg)$_2$]Cl_2·$2H_2O$[12] it was thought likely that the aOeu ligand co-ordinated the Cu^{2+} ion through the imine groups (**5**).[11]



(**5**)



(**6**)

Structural Data. – After preliminary cell parameters had been determined from oscillation and Weissenberg photographs, reflection intensities were measured on a Hilger and Watts Y290 four-circle diffractometer using graphite-monochromated Mo-K_α radiation. Both structures were solved by heavy-atom methods. Whereas the solution of [Cu(aOeu)Cl_2]$_2$ proceeded satisfactorily to a final *R* value of 0.047 for 790 observed structure amplitudes, that of [Cu(aOeu)$_2$]Cl_2·$2H_2O$ was disappointing owing to the presence of several elements of internal twinning which could not be resolved, a final *R* value of 0.148 being obtained for 557 observed structure amplitudes. Consequently, whereas detailed geometrical parameters can be quoted with confidence for [Cu(aOeu)Cl_2]$_2$, only gross aspects of the structure can be described for [Cu(aOeu)$_2$]Cl_2·$2H_2O$.

Crystal Data. – $C_4H_{10}N_4OCl_2Cu$, M = 264.6, monoclinic, space group $P2_1/c$, a = 717.5(2), b = 1677.3(3), c = 831.2(2) pm, β = 106.99(3)°, U = 956.66 × 10^6 pm^3, D_m = 1.85 g cm^{-3}, D_c = 1.84 g cm^{-3} for Z = 4, $F(000)$ = 532, μ(Mo-K_α) = 28.80 cm^{-1}.

$C_8H_{24}N_8O_4Cl_2Cu$, M = 430.8, monoclinic, space group $P2_1/c$, a = 529.9(2), b = 1373.9(3), c = 1280.6(3) pm, β = 89.89(3)°, U = 932.31 × 10^6 pm^3, D_m = 1.55 g cm^{-3}, D_c = 1.53 g cm^{-3} for Z = 2, $F(000)$ = 446, μ(Mo-K_α) = 15.33 cm^{-1}.

Whereas the mono-chelate complex solely comprises dimeric [Cu(aOeu)Cl_2]$_2$ units, the bis-chelate complex contains cationic {[Cu(aOeu)$_2$]$^{2+}$·$2H_2O$} fragments and chloride anions. The structures of the centrosymmetric chlorine-bridged [Cu(aOeu)$_2Cl_2$]$_2$ dimer and of the planar {[Cu(aOeu)$_2$]$^{2+}$·$2H_2O$} fragments are shown in Figures 1 and 5, respectively.

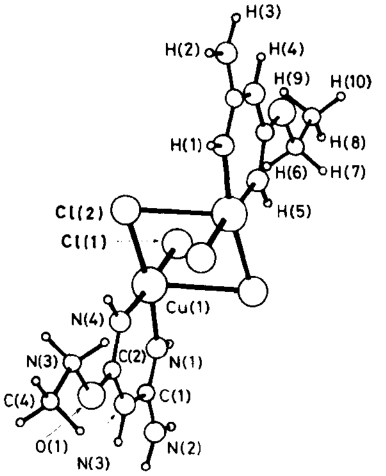


Figure 1 Molecular geometry of the [Cu(aOeu)Cl_2]$_2$ dimer

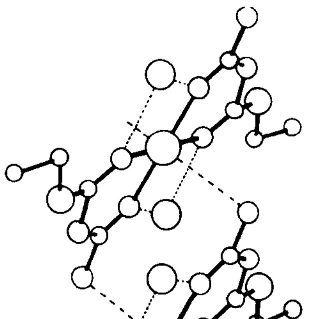


Figure 5 Molecular geometry of the [Cu(aOeu)$_2$]$^{2+}$·$2H_2O$ fragment

In the dimer (Figure 1), the Cu^{2+} ions are located 11.8 pm above the base of a square-pyramidal co-ordination sphere typical of five-co-ordinate copper. The equatorial plane is composed of the two imine nitrogen atoms of the chelating bidentate aOeu ligand {r(Cu···N(1)] = 193.5 pm; r[Cu···N(4)] = 194.0 pm} and the chlorine atoms {r[Cu···Cl(1)] = 227.9 pm; r[Cu···Cl(2)] = 231.4 pm}; the axial position is occupied by a more remote chlorine atom centrosymmetrically related to Cl(2) {r[Cu···Cl(2)′] = 295.7 pm}.

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*To receive any correspondence.

Table 4 Geometries of the aOeu ligand in $[Cu(aOeu)Cl_2]_2$ and in $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$

Bond distances/pm			Bond angles/°		
Bond	Mono-complex	Bis-complex	Angle	Mono-complex	Bis-complex
C(1)—N(1)	130(2)	120(5)	N(1)—C(1)—N(2)	123(1)	128(4)
C(1)—N(2)	132(2)	138(5)	N(1)—C(1)—N(3)	122(1)	123(4)
C(1)—N(3)	137(2)	135(5)	N(2)—C(1)—N(3)	115(2)	109(4)
C(2)—N(3)	136(2)	154(5)	C(1)—N(3)—C(2)	126(1)	126(4)
C(2)—N(4)	128(2)	121(5)	N(3)—C(2)—N(4)	124(1)	121(4)
C(2)—O(1)	134(2)	126(5)	N(3)—C(2)—O(1)	110(1)	105(3)
C(3)—O(1)	144(2)	150(5)	N(4)—C(2)—O(1)	126(1)	133(4)
C(3)—C(4)	151(2)	153(7)	C(2)—O(1)—C(3)	117(1)	114(3)
			O(1)—C(3)—C(4)	107(1)	106(4)

Table 7 Significant features of the molecular geometries of aOeu, bg, edbg, and clge co-ordinated to copper(II)

	Free molecule			Co-ordinated to copper(II)		
Ligand	Average $r(C{\cdots}N_{br})$/pm	Average $r(C{\cdots}N_{ter})$/pm[a]	Ratio	Average $r(C{\cdots}N_{br})$/pm	Average $r(C{\cdots}N_{ter})$/pm[a]	Ratio
aOeu				136.5	132.0	1.035
bg[b,c]	135.2	136.8	0.988	137.4	134.2	1.024
edbg[d]				141.0	137.2	1.028
clge[e,f]	135.2	134.0	1.009	137.0	131.5	1.042

[a] This average does not include those contacts formally defined as double bonds between carbon and terminal imine groups. [b] S. R. Ernst and R. W. Cagle, *Acta Crystallogr., Sect. B*, 1977, **33**, 235. [c] Ref. 12. [d] N. R. Kunchur and M. Mathew, *J. Chem. Soc., Chem. Commun.*, 1966, 86. [e] M. J. Begley, P. Hubberstey, and C. H. M. Moore, *J. Chem. Res.*, 1985, (*S*) 180; (*M*) 4035. [f] Ref. 2.

The co-ordination polyhedron around the Cu^{2+} ion in the cationic fragment (Figure 5), which consists of a planar arrangement of a centrosymmetric bis(aOeu)-copper(II) complex hydrogen-bonded to two water molecules, can be described as either a square plane comprising the four imine nitrogen atoms of the two chelating aOeu ligands $\{r[Cu{\cdots}N(1)] = 203$ pm; $r[Cu{\cdots}N(4)] = 202$ pm$\}$ or an axially distorted octahedron, the axial positions above and below the CuN_4 chromophore being occupied by the terminal amine nitrogen atoms of two $\{[Cu(aOeu)_2]^{2+}{\cdot}2H_2O\}$ fragments in adjacent ribbons $\{r[Cu{\cdots}N(2)'] = 311$ pm$\}$. Evidence for a Cu···N(2)′ bonding interaction arises from the location and electronic structure of the ligand.

The molecular geometries of the aOeu ligand in the two complexes are summarised in Table 4. Although very little significance can be ascribed to that in $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$, that in $[Cu(aOeu)Cl_2]_2$ is accurately known. The ligand is effectively planar and chelates the Cu^{2+} ion adopting the di-imine tautomeric form (**5**). Its geometry (Table 4) is consistent with sp^2 hybridization of the skeletal atoms, excluding those of the OEt fragment, and the presence of a delocalized π system.

The co-ordination geometry of aOeu is comparable with those of co-ordinated biguanide (bg) and ethylenediaminebiguanide (edbg), all three ligands forming $\overline{\text{Cu}-\text{NH}=\text{C(R)}-\text{NH}-\text{C(R)}=\text{N}}\text{H}$ chelate rings. The formation of bridging C—NH—C fragments on co-ordination, C=N—C bridges existing in the free molecules, also occurs for 1-carbamoylguanidine (clge). It leads to changes in the π-electron density which are manifest in shorter terminal than bridging C—N bonds. Comparison of data for aOeu, bg, edbg, and clge co-ordinated to copper(II) is effected in Table 7.

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Table 1: Comparison of the products of the reaction between cnge and copper(II) chloride in refluxing ethanol

Table 2: Final positional parameters for $[Cu(aOeu)Cl_2]_2$

Table 3: Final thermal parameters for $[Cu(aOeu)Cl_2]_2$

Table 5: Intermolecular contacts of less than 330 pm; hydrogen-bond and electrostatic interactions for $[Cu(aOeu)Cl_2]_2$

Table 6: Planarities of the aOeu ligand and of the ligating atoms in $[Cu(aOeu)Cl_2]_2$

Table 8: Final positional parameters for $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$

Table 9: Final thermal parameters for $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$

Table 10: Bond distances and angles for $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$

Table 11: Planarity of the $\{[Cu(aOeu)_2]2H_2O\}$ fragment and of the aOeu ligand in $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$

Table 12: Intermolecular contacts of less than 330 pm; hydrogen-bond and electrostatic interactions for $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$

Appendices: Observed and calculated structure factors for $[Cu(aOeu)Cl_2]_2$ and $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$

Figures 2 and 3: Projections of the structure of $[Cu(aOeu)Cl_2]_2$ onto the (001) and (100) planes

Figure 4: Projection of the structure of $[Cu(aOeu)_2]Cl_2{\cdot}2H_2O$ onto the (001) plane

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