COPPER(II) AND NICKEL(II) COMPLEXES OF
2-ALKOXYPHENOLS

A Thesis presented to the University of Surrey for the
degree of Doctor of Philosophy in the Faculty of Science.

by

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Summary

New copper(II) and nickel(II) complexes with 2-alkoxyphenols have been prepared.

The visible spectra of the copper(II) complexes indicated a quasi-tetrahedral stereochemistry for two of them, and a distorted octahedral stereochemistry for the remainder. Magnetic susceptibilities for most of the copper(II) complexes have been determined over the range of temperature 80-300 K, and the anhydrous complexes showed a variable degree of antiferromagnetic interaction. No unambiguous theoretical interpretation of the magnetic data as a function of the degree of aggregation was achieved, but in the case of bis(2-methoxyphenolato)copper(II), which has a quasi-tetrahedral stereochemistry as indicated by its visible spectrum, the very existence of antiferromagnetism pointed to a polymeric linear chain structure.

Unequivocal infra-red evidence for the participation of the alkoxy group in coordination was not found, but the spectra of some of the nickel(II) complexes showed tentative evidence of methoxy group coordination. Because of the uncertainty of the bonding role of the alkoxy group, the number of possible structures for the complexes was increased.

The visible spectra and magnetic properties of the nickel(II) complexes were consistent with an octahedral stereochemistry. A comparison of the copper(II) and nickel(II) series of complexes is given.
Acknowledgements

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The encouragement and criticism given by Dr. J.I. Bullock during the course of this research has been greatly appreciated.
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1. **Introduction**
1.1. **Historical Introduction**

Although a great deal of attention has been given to complexes of copper(II) with ligands of the following type:

\[
\begin{array}{c}
\text{X} \quad \overset{5}{\underset{b}{\text{C}}}, \quad \overset{4}{\underset{2}{\text{R'}}}, \quad \overset{6}{\underset{2}{\text{R''}}}, \quad \overset{7}{\underset{2}{\text{OH}}}
\end{array}
\]

(where X is -CHO, \(1\); \(\overset{1}{\text{C}} = \overset{2}{\text{N}}\), \(2\); \(\overset{1}{\text{C}} = \overset{2}{\text{R}}\), \(3\); \(-\text{NH}_2\), \(4\); etc.); no work has been done with 2-alkoxyphenols. A cobalt(II) complex with guaiacol, \(X = -\text{OMe}\), has been previously reported by Cotton and Holm.\(^5\) Unfortunately, the described method of preparation failed when attempted in these laboratories. This has been rectified in light of the experience gained with the copper(II) system.

1.2. **Factors controlling the choice of ligand and method of preparation**

For complexation to occur the 2-alkoxyphenol has to be ionized. This was accomplished by reaction with alkali. It is well known that phenols are susceptible to oxidation by air in neutral and alkaline solution,\(^6\) for example, an aqueous solution of sodium 2-methoxyphenolate slowly darkens on standing in the atmosphere. The tendency for an aqueous solution of a sodium or potassium 2-alkoxyphenolate to undergo aerial oxidation can be substantially reduced, if electron-withdrawing substituents such as -\(\text{NO}_2\) and -CHO are introduced into the 4-position. Providing the sodium or potassium 2-alkoxyphenolate solution was stable, the introduction of copper(II)
into the system was never found to catalyse oxidation. The reaction of copper(II) with 2-alkoxyphenols can be written as:

\[ 2ML + \text{Cu}^{2+} \rightarrow \text{CuL}_2 + 2M^+ , \]

where ML is the potassium or sodium salt of the 2-alkoxyphenol. A water milieu was always employed, and the copper(II) salt solution always added to the solution of the ionized ligand. If, however, sodium or potassium hydroxide was added to a solution containing a 2:1 mole ratio of ligand and copper(II), complex formation did not occur, instead basic copper(II) compounds were precipitated. This does not imply that the problem of basic copper(II) compound formation cannot arise in the former case, indeed it does if the 2-alkoxyphenol is a sufficiently weak acid, since the degree of base hydrolysis increases with the decreased acidity of the 2-alkoxyphenol. The problem of unfavourable base hydrolysis can be controlled to some extent by using concentrated solutions and an excess of free ligand. The work of Dolique and Mestres illustrates this point well. These workers studied the system copper(II)-phenol, \( X = H \).

In all the complex preparations described in this thesis a molar bias has been applied. Ideally we react LH (2 mole) and MOH (2 mole) with copper(II) (1 mole), in practice a bias has been applied as follows:

\[ \text{LH} \gg \text{MOH} \gg \text{Copper(II)}. \]

The molar bias has ranged from 3% to 10%.

With one exception, the complexes that have been
prepared cannot be washed once filtered. Washing with water, aqueous-organic, or organic solvents led to decomposition with the formation of basic copper(II) materials. Therefore in order to achieve a satisfactory level of complex purity, particular attention has had to be paid to preparative conditions.

**Ligands**

The ligands which we have considered are listed below.

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1.3. **Reason for undertaking this research work**

Copper(II) compounds and metallic copper are widely employed as fungicides. At the present time the search for suitable fungicides for the protection of wood is still being actively pursued. The xylem cells of trees contain lignin, one of the oldest natural organic polymeric materials on the evolutionary scale. The occurrence of the structural entity

![Chemical Structure](image)

in lignin and the current interest in the development of copper based fungicides for wood, led us to investigate the systems described in this thesis.

1.4. **Nickel(II) complexes of 2-alkoxyphenols**

In order to extend our knowledge of the reactions of these ligands with the first-row transition metal ions, the reactions of 2-alkoxyphenols with nickel(II) were investigated.

Precisely the same considerations as discussed above under the heading, 'Factors controlling the choice of ligand and preparative method', hold.
2. Physical Methods Employed in Structure Determination
2.1. **Infra-red Spectroscopy**

Prout et al.\(^8\) have unequivocally shown by X-ray crystallographic analysis that the methoxy group in diaquobis(methoxyacetato)copper(II) is coordinated to copper(II) through oxygen. Similarly, Orioli and Di Vaira\(^9\) have shown that the methoxy group in dibromo-[1-(o-methoxyphenyl)-2,6-diazaocatane]nickel(II) is involved in coordination.

Little has been done to establish the participation of an alkoxy group in coordination from consideration of infra-red spectroscopy. Some effort has been made in this area by Butcher\(^{10}\) who considered complexes of nickel(II) with ortho-methoxyaniline, and by Watt and Drummond\(^{11}\) who studied the di-iodo(N-methyl-ortho-methoxyaniline)palladium(II) complex. The former worker looked at the 1200-1300 cm\(^{-1}\) region of the infra-red spectrum, which contains the aryl-oxygen stretching vibration, whilst the latter considered the palladium-oxygen stretching region.

Examination of the part of the infra-red spectrum associated with copper(II)-, and nickel(II)- oxygen vibrations was not attempted, since the complexes already contained a copper(II)-, and nickel(II)- phenolic oxygen bond.

The aryl-oxygen stretching mode for methoxy-, and ethoxy-aromatic compounds occurs at about 1250 cm\(^{-1}\).\(^{12,13}\)

![Chemical structure](https://example.com/structure.png)

However, in the case of substituted 2-methoxy, and 2-ethoxy-phenols this region is complex,\(^{13}\) principally because the
aryl-phenolic oxygen stretching mode also occurs here.

The aliphatic-oxygen stretching mode appears in the range $1050-1000 \text{ cm}^{-1}$, and for all the complexes and ligands described in this work, unambiguous band assignment was possible.

The participation of an alkoxy group in coordination:

\[
\text{O} \quad \text{Cu(II)}/2 \\
\text{Y}
\]

with the resultant drainage of electrons from the ethereal oxygen, would be expected to lead to a weakening of the aryl-, and aliphatic-oxygen bonds. Hence a lowering of the stretching frequencies for these bonds might be taken as a criterion of coordination. However, there are difficulties in selecting a suitable reference for measuring the shift to lower frequencies. The free-ligand is unsuitable since it has to be ionized for complexation, and this in itself might produce the desired shift in frequency. Consequently, wherever possible, the spectrum of a complex was compared with that of the alkali metal salt of the ligand, and with the free ligand.
2.2. Magnetism

Copper(II)

The magnetic behaviour of copper(II), which has a $3d^9$ electron configuration with one unpaired 3d electron, has been extensively studied.

Magnetically, the complexes of copper(II) can be divided into two main classes. Firstly there are those which possess an essentially temperature independent magnetic moment of about 1.9 B.M., of which about 0.2 B.M. arises from spin-orbit coupling, in which the copper(II) centres can be considered to act independently of one another. However, at very low temperatures weak magnetic exchange may be observed. The second class comprises complexes for which the magnetic moment is close to, or below, the spin-only value of 1.73 B.M. at room temperature, and which have markedly temperature dependent moments. When this is the case the complex is said to possess a subnormal magnetic moment. (14) A subnormal magnetic moment is indicative of strong antiferromagnetic exchange between copper(II) centres. When encountered, information relating to the number (n) of interacting copper(II) centres, and to the magnitude of the antiferromagnetic exchange, can be obtained from a study of the dependence of the magnetic susceptibility on temperature. This is achieved by comparing the observed magnetic results to those predicted by theory. The theoretical treatment for copper(II) dealing with antiferromagnetic exchange between two or three centres within the same molecule (intramolecular antiferromagnetism) is well established, but in the case of exchange
between magnetic centres being transmitted essentially over the whole of the crystal (intermolecular antiferromagnetism) the theoretical work is less clear."(15)

Magnetic exchange between two centres i and j arises because of interaction between the magnetic dipoles. In most cases only the spin contribution to each dipole involved is considered, and the coupling is taken to be between the spin angular momentum vectors on the centres. The interaction energy is

$$-2J(S_i S_j),$$

where J is the exchange integral, with positive values indicating that the spins tend to align parallel to the same direction (ferromagnetic exchange), and negative ones that they tend to align antiparallel (antiferromagnetic exchange).

**Binuclear compounds**

In general, providing the interacting ions are identical and their ground terms are effectively S terms, the magnetic susceptibility of an isolated dimeric aggregate is given by;\(^{(16)}\)

$$\chi_{\text{m}} = \frac{Ng^2\beta^2}{3kT} \sum_{S'} S'(S'+1)(2S'+1)\exp\left(-\frac{ES'}{kT}\right)$$

where \(N = \text{Avogadro's number.}\)

\(\chi_\text{N} = \text{temperature independent paramagnetic susceptibility.}\)

\(g = \text{Lande splitting factor.}\)

\(\beta = \text{Bohr magneton.}\)

\(k = \text{Boltzmann's constant.}\)

\(T = \text{temperature.}\)

\(S' = \text{quantum number specifying the total spin of the system.}\)

\(^*\text{See page 48.}\)
which can take values 0 to 2S in integral steps, S being the quantum number specifying the spin angular momentum of each ion.

\[ \text{ES'} \] = the energy of a level specified by \( S' \) in the absence of a magnetic field.

For a dimeric copper(II) aggregate, \( S = \frac{1}{2} \), and

\[
\kappa N_a = \frac{N g^2 \beta^2}{3kT} \times \frac{1}{1 + 1/3 \exp(2J/kT)} + N\alpha.
\]

This is the well known Bleaney and Bowers equation(17) which has been extensively applied to susceptibility data for numerous binuclear complexes in which antiferromagnetic exchange occurs, in for example, the acetates,(18) carboxylates,(19) 1:1 pyridine-N-oxide complexes,(20) bidentate and tridentate Schiff's base complexes.(21)

The theory has been extended by Earnshaw, Figgis and Lewis(22) to isolated n-meric (n=3 to 10) aggregates of equivalent electron spins with nearest neighbour exchange being considered. The resultant susceptibility expression is similar to that given in the dimeric instance, but incorporates the term \( \sum (S') \), which specifies the number of times a given \( S' \) value may occur. \( S' \) is the quantum number specifying the total spin of the system.

\[
\kappa_m = \frac{N g^2 \beta^2}{3kT} \sum_{S'} \frac{S'(S'+1)(2S'+1)s(S')\exp(-ES'/kT)}{\sum_{S'} (2S'+1)s(S')\exp(-ES'/kT)}
\]

This expression is valid so long as the spread of the energy levels of any state which is appreciably occupied is small compared with \( kT \). This condition arises because in the development of this equation use is made of the Van Vleck

\*See page 48.
susceptibility formula \(^{(23)}\) in which it is assumed that,

\[
kT \gg E_{i,m}^{(1)}H + E_{i,m}^{(2)}H^2 + \ldots \ldots \ldots \ldots ,
\]

where \(E_{i,m}^{(x)}\) is the \(x\)th order Zeeman coefficient for the energy of a level in a magnetic field, \(H\); \(i\) and \(m\) specify quantum numbers. Upon application of a magnetic field the energy spread for a state specified by \(S'\) is \((2S' + 1)g\beta H\). Importantly, as \(n\) becomes large a value of \(S'\) which is sufficient to give \((2S' + 1)g\beta H \approx kT\) may occur and invalidate the expression. However, if \(J\) is large the expression may still be valid since the energy of states with large \(S'\) should be thermally inaccessible: the energy of a level specified by \(S'\) is,

\[
ES' = -\frac{2J}{n}S'(S' + 1) \quad (22).
\]

In the present work there is interest in the theoretical interpretation of the magnetic susceptibility data for polymeric chain systems in which \(n\) tends to infinity. The theoretical problem has been tackled in two ways; firstly the spins have been treated as vectors (the Heisenberg approach \(^{(24)}\)), and secondly they have been considered as scalar quantities (the Ising approach \(^{(25)}\)). Of the two methods the first is more realistic, but does not yield explicit functions for the susceptibility, although Fisher and Bonner have performed a numerical analysis on this basis. \(^{(26)}\) On the other hand, the Ising approach does yield explicit functions.

The one-dimensional Ising model

The crystal is considered to be made up of a number of infinite chains of magnetic centres. Nearest neighbour
exchange occurs between magnetic centres in the same chain, but no interaction occurs between the chains. An axis of anisotropy, \( z \), is defined, along which the spins tend to align parallel or antiparallel. The susceptibility along such an axis is \( X_{/\|} \), and perpendicular to it, \( X_{\perp} \). In this work the result for the \( z \) direction is taken to hold for the perpendicular direction.

Each magnetic centre in the chain is assigned a scalar spin coordinate, \( \sigma \), which can take the value \( \pm 1 \). If \( \sigma = +1 \), this corresponds to the spin state with the spin in the direction of \( z \), then \( \sigma = -1 \) corresponds to the spin in the opposite direction.

\[
\begin{array}{c}
\uparrow \\
0 = +1 \\
\downarrow \\
0 = -1
\end{array}
\]

The interaction energy between two centres, \( i \) and \( j \) with respective spin coordinates \( \sigma_i \) and \( \sigma_j \) is defined as,

\[
E_{ij} = -J \sigma_i \sigma_j, \text{ if } i \text{ and } j \text{ are nearest neighbours, otherwise,}
\]

\[
E_{ij} = 0.
\]

\( J \) is a measure of the strength of the coupling. \( E_{ij} = -J \) if the nearest neighbours have the same spin, and \( E_{ij} = +J \) if they are unlike. \( J \) is negative for an antiferromagnetic.

In addition, a magnetic moment, \( m \), is assigned to each centre and the energy of interaction of the \( i \)th particle with an external magnetic field chosen to be,

\[
E_H = -mH \sigma_i.
\]
The problem is now one of statistical mechanics, and the following expression results,

\[ M = N_m \sinh \frac{eH}{kT} \left[ \exp\left(\frac{-4J}{kT}\right) + \sinh \frac{2eH}{kT} \right]^{-\frac{1}{2}}, \]

where \( M \) = magnetic moment per mole at \( T^0K \) in an external magnetic field \( H \). For copper(II), \( S = \frac{1}{2} \) and \( \mu = g\beta/2 \).

If \( mH/kT \) is \( \ll 0.1 \), which is the case for \( T \gg 5^0K \) and \( H = 6000 \) oersteds, then

\[ X_a = \frac{Ng^2\beta^2}{4kt} \left[ \exp\left(\frac{-4J}{kT}\right) + \left(\frac{g\beta H}{2kt}\right)^2 \right]^{-\frac{1}{2}}. \]

A field \( H \) of about 6000 oersteds was employed in the experimental determination of susceptibility, consequently \( \left(\frac{g\beta H}{2kt}\right)^2 \ll \exp\left(\frac{-4J}{kT}\right) \), and can be neglected. Allowing for temperature independent paramagnetism,

\[ X_a = \frac{Ng^2\beta^2}{4kt} \exp\left(\frac{2J}{kT}\right) + N_a. \quad (A). \]

The subscript \( // \) is dropped since we have assumed that the susceptibility is the same in the perpendicular direction as in the parallel direction.

An explicit function for \( X_\perp \) has been derived by Fisher. Adams et al. have utilized it with \( X_{//} \) in the form

\[ X(T) = \frac{1}{3}X_{//}(T) + \frac{2}{3}X_\perp(T), \]

for interpreting the powder magnetic data obtained for anhydrous copper(II) chloride. A computer programme written in Elliot 503 Algol was used to check this claim. Unfortunately no
reasonable agreement was found, neither was it found to satisfy the magnetic data obtained for the complexes described in this work.

Expression (A) has been applied with some success by Inoue, Emori and Kubo in interpreting the magnetic data for dichloro(1,2,4-triazole)copper(II) and copper(II) benzoate trihydrate.\(^{(31)}\) The crystal structures for both compounds have been determined, and the structural units in each case are infinite chains. In addition to the linear antiferromagnetic contribution to the susceptibility, an anomalous paramagnetic effect is observed at low temperature. Kobayashi et al. have also utilized the expression in considering copper(II) quinone complex salts,\(^{(32)}\) here an anomalous paramagnetic effect at low temperature was ascribed to the end effect and the odd or even number effect of spins in the chain.

Barraclough and Ng\(^{(28)}\) have proposed a theory based on expression (A) and applicable above the temperature of maximum susceptibility, \(T_{\text{max}}\), but below which a modification was required. The analysis was later criticized\(^{(30)}\) since \(T_{\text{max}}\) had been taken to be \(T_{\text{Néel}}\).\(^{(33)}\) For example, tetraamminecopper(II) sulphate monohydrate,\(^{(34)}\) a well established case of a complex displaying linear antiferromagnetism, displays a broad susceptibility maximum at about 3.5°K, but the Néel temperature is 0.37°K. This theoretical analysis has been applied to copper(II) oxalate by Dubicki et al.\(^{(35)}\)

Curve Fitting

In order to obtain an estimate of the interaction energy \(J\),
the parameter Na in (A) was set at $60 \times 10^{-6}$ cgsu. Using two sets of $X_a$ and $T$ values the equation was solved simultaneously for $g$ and $J$. $X_a$ for the remaining temperatures was then evaluated. Calculations were continued until the closest fit was obtained. Alternatively, the graphical method of Inoue et al. (31) could have been used.

The problem of obtaining the optimum value of $J$ from curve fitting procedures has been discussed by Hyde et al. (36) and Ginsberg et al. (37). The last group of workers put forward a method for evaluating the temperature independent paramagnetism of the complex (t.i.p.). This method is not general and requires the compound to contain a small percentage of a paramagnetic copper(II) impurity, so that at low temperatures the entire susceptibility can be considered to be due to the impurity and t.i.p. of the complex.

Mechanisms of magnetic exchange

Two mechanisms of magnetic exchange are recognized. (14)

Firstly, direct exchange between copper(II) centres, which is believed to be exemplified by copper(II) carboxylate complexes possessing a copper(II) acetate monohydrate structure, and secondly indirect exchange (superexchange) which occurs by way of some diamagnetic intermediary ligand atom $Z$, as is thought to be illustrated by copper(II) 1:1 pyridine-N-oxide complexes, (20) and tridentate Schiff's base complexes. (37)

The factors which affect the magnitude of exchange have been the subject of a great deal of discussion, (14, 38) and generally speaking the way in which the magnitude of exchange
is influenced can be summarized as follows. For both mechanisms the degree of interaction is dependent upon the magnitude of the relevant orbital overlap, and the greater this is, the greater the interaction. For the direct exchange mechanism the nature of the attached ligand is important. An electron donating ligand will increase the interaction, and vice versa.

In the case of superexchange occurring by way of Z, the magnitude of exchange is increased if the electron density on Z is increased, and vice versa. Furthermore an increase in electron density at the copper(II) centres will decrease the exchange through Z, and vice versa. (37, 39)

\[
\begin{array}{c}
Z \\
Cu(II) \quad Cu(II)
\end{array}
\]

The one-dimensional Ising model does not specify whether the nearest neighbour interactions are direct or indirect, and as far as the statistics of the problem are concerned it makes no difference to a first approximation. (40)

Nickel(II)

The magnetic moment for nickel(II) is more sensitive to stereochemistry than in the case of copper(II).

Moments for octahedral complexes (\(^{3}A_{2g}\) ground term) occur between 2.9 and 3.4 B.M., depending on the spin-orbit coupling contribution. The moment should be independent of temperature and of small departures from octahedral symmetry.

Tetrahedral nickel(II) with an orbitally degenerate \(^{3}T_{1}\) ground term should possess moments lying between 3.6 and 4.0 B.M.,
and decrease markedly with temperature. However, departure from tetrahedral symmetry or electron delocalization results in the moment becoming closer to the spin-only value and to vary less with temperature.

Square planar nickel(II) should be diamagnetic, however, if the square planar crystal field is very weak a paramagnetic complex may be produced. This appears to be the case for the anhydrous nickel(II) ortho-hydroxyarylcarbonyl compounds in hydrocarbon solvents. (41)

2.3. Visible Spectra

Copper(II)

In order to relate electronic properties to structure a background of information based on compounds of known crystal structure is necessary. Considerable effort has been made in this area by Hathaway and co-workers, who have concentrated their attention principally upon copper(II)-ammine and ethylenediamine complexes (42, 43, 44, 45, 46). Even with this background information the situation is still not clear, and this is particularly well exemplified by the work of Tomlinson et al. on the tetrammine copper(II) complexes. (47)

Of interest in this work are the stereochemical deductions which can be drawn from the study of the electronic spectra of copper(II) complexes when there is a local oxygen environment. Hathaway et al. have recently turned their attention to this area of copper(II) chemistry. (48)

The 3d9 electron configuration gives rise to only one free-ion term, 2D, which is ten-fold degenerate in spin and
One positron energy level diagram for Copper(II).

Octahedral Increasing tetragonal distortion
### Table 1

**Electronic Spectra - Powder Results**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Axial bond length (Å)</th>
<th>$d_{x^2-y^2} - d_{yz}$ (kK)</th>
<th>$d_{x^2-y^2} - d_{zx}$ (kK)</th>
<th>$d_{x^2-y^2} - d_{x^2}$ (kK)</th>
<th>$d_{x^2-y^2} - d_{xy}$ (kK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Egyptian blue(^1)</td>
<td>(7.56)</td>
<td>15.8</td>
<td>18.8</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>Meta-zeunerite(^2)</td>
<td>2.56</td>
<td>15.0</td>
<td>13.0</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>Cu(PhCO(_2))(_2) (3H_2O)</td>
<td>2.51</td>
<td>15.3</td>
<td>11.6</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>Diabeolite(^3)</td>
<td>2.39</td>
<td>14.6</td>
<td>10.9</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>CuSO(_4), 5H(_2O)</td>
<td>2.40</td>
<td>13.0</td>
<td>10.5</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>Kroehnkite(^4)</td>
<td>2.41</td>
<td>12.7</td>
<td>10.3</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>Cu(CHO(_2))(_2), (4H_2O)</td>
<td>2.36</td>
<td>13.2</td>
<td>9.2</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>Ba(_2)Cu(CHO(_2))(_6, 4H_2O)</td>
<td>2.18</td>
<td>13.3</td>
<td>8.4</td>
<td>10.6</td>
<td></td>
</tr>
</tbody>
</table>

Compiled from reference (48).

1. BaCuSi\(_4\)O\(_{10}\). Square planar coordination.
2. Cu(UO\(_2\))\(_2\)(AsO\(_4\))\(_2\) \(8H_2O\).
3. Pb\(_2\)Cu(OH)\(_4\)Cl\(_2\). Axial Cl bond length corrected to correspond to an axial Cu-0 bond.
4. Na\(_2\)Cu(SO\(_4\))\(_2\)\(2H_2O\).
orbit. All or part of the five-fold orbital degeneracy is removed upon the application of a crystal field, the precise extent being dependent upon the field symmetry.

CuO\(_6\) chromophore

Regular octahedral stereochemistry is not found for copper(II) and this may be attributed to the Jahn-Teller effect, however, crystal lattice packing forces and repulsions between neighbouring ligands may be responsible. The one positron energy level diagram for copper(II) in a normal tetragonal environment is given in Figure 1. The order of levels is dependent upon the degree of distortion. Table 1 summarizes the electronic data known for the CuO\(_6\) system, which was compiled from reference\(^{(48)}\). Copper(II) in diaboleite has D\(_{4h}\) symmetry whilst in kroehnkite, copper sulphate, benzoate and copper formate this is approximately the case. Dibarium copper(II) formate tetrahydrate has been discussed\(^{(49)}\) in terms of D\(_{2h}\) symmetry.

The results of Table 1 show a clear correlation between the degree of distortion and the energy of the d\(^2\)\(-\)d\(^2\) transition. Furthermore, for a copper(II) complex of unknown stereochemistry but having a local oxygen environment, the observation of a main peak (12.7 - 15.8 kK) and a low energy shoulder (10.3 - 12.9 kK) in its electronic spectrum may be taken as tentative evidence for the tetragonal CuO\(_6\) chromophore.

CuO\(_4\) chromophore

Regular tetrahedral complexes of copper(II) are not found,
<table>
<thead>
<tr>
<th>Compound</th>
<th>Electronic Spectrum ( NU)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cs}_2\text{CuCl}_4$</td>
<td>4.6</td>
<td>(53)</td>
</tr>
<tr>
<td>$\text{Cs}_2\text{CuBr}_4$</td>
<td>4.6</td>
<td>(53)</td>
</tr>
<tr>
<td>N-t-butyl copper(III)</td>
<td>8.5 sh</td>
<td>(51)</td>
</tr>
<tr>
<td>N-isopropyl copper(II)</td>
<td>8.5 sh</td>
<td>(51)</td>
</tr>
<tr>
<td>N-isopropylsalicylideneamino)</td>
<td>13.6 sh 21.0°</td>
<td>(51)</td>
</tr>
</tbody>
</table>

+ Charge transfer for bis(N-t-butylsalicylideneamino) copper(II)

* Abbreviation for bis(N-t-butylsalicylideneamino) copper(III)
Splitting of the $^2D$ spectroscopic term of Copper(II) in a crystal field of $D_{2d}$ symmetry. (ref. 51)
this may be ascribed to the operation of the Jahn-Teller effect. On the other hand, spin-orbit coupling may produce sufficient splitting of the $T_2$ ground term to overshadow the Jahn-Teller effect, and this appears to be the case in $\text{Cs}_2\text{CuCl}_4$.\(^{(23)}\) Distortional influences can be minimised if copper(II) is substituted into a tetrahedral lattice. The spectrum of copper(II) substituted into ZnO has been recorded,\(^{(50)}\) and at room temperature a single broad band at 5.8 kK is observed. Table 2 summarizes the electronic data for copper(II) complexes with approximate tetrahedral stereochemistry. Figgis et al. have discussed the assignment of the spectral data for the Schiff's base complexes in terms of $D_{2d}$ symmetry\(^{(51)}\) (Figure 2), similarly, Hatfield and Piper have done so for $\text{Cs}_2\text{CuCl}_4$,\(^{(52)}\) and Karipides and Piper for $\text{Cs}_2\text{CuBr}_4$.\(^{(53)}\) On the basis of this data the appearance of d-d transitions in the range 5.0 - 13.6 kK may be taken as evidence for a distorted tetrahedral $\text{CuO}_4$ environment.

Bis(salicylaldehydato)copper(II) and bis(acetylacetonato)copper(II) are examples of the planar $\text{CuO}_4$ chromophore. Using the solid state reflectance spectra of these compounds as a reference, Graddon and Mockler have proposed a planar stereochemistry for the anhydrous ortho-hydroxyarylcarbonyl copper(II) complexes.\(^{(54)}\) In the solid state these spectra are characterised by high intensity bands in the ultra-violet region, the tail of which overlaps a broad absorption envelope in the visible region, extending from 20.0 - 14.0 kK. This partial obscuring of the visible region does not occur in the case of the synthetic silicate $\text{BaCuSi}_4\text{O}_{10}$, Egyptian Blue, which
Energy as a function of crystal field parameter $\Delta_0$ for the 3d$^8$ system nickel(II). Energies are in kK and the $^1S$ state of the free ion is not shown.
is an example of a square planar CuO₄ system. Clark and Burns have studied the electronic spectrum of this material in detail, and the absorption maxima data is given in Table 1.

In conclusion, this section has attempted to show that a set of criteria can be established for distinguishing between the tetragonal CuO₆, distorted tetrahedral CuO₄, and planar CuO₄ chromophores.

Nickel(II)

In this section emphasis is placed primarily on the use of electronic spectra as a guide to stereochemistry rather than upon detailed interpretation.

Six coordinate complexes

The energy level diagram for nickel(II) in an octahedral crystal field as a function of the crystal field parameter $\Delta \omega (\Delta \omega = E(e_g) - E(t_{2g}))$ is given in Figure 3. Six coordinate complexes usually exhibit a simple spectrum involving spin-allowed transitions to the $^3T_{2g}$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ states, occurring with low intensities in the ranges 7.0 - 13.0 kK, 11.0 - 20.0 kK and 19.0 - 27.0 kK respectively. In addition, absorption bands arising from spin-forbidden transitions, $\Delta S \gg 1$, may arise. The origin of spin-forbidden transitions has been discussed by Dunn, and Ballhausen and Griffith have considered this subject in depth. A transition between a state $^2S+1X$ and $^2S'+1Y$ is made allowed by the admixture into $^2S+1X$ of a state $^2S'+1Z$ with the same
### Table 3

**Diffuse Reflectance Data**

(kK)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$3A_{2g} - 3T_{2g}$</th>
<th>$3A_{2g} - 3T_{1g}(F)$</th>
<th>$3A_{2g} - 1E_g$</th>
<th>$3A_{2g} - 1T_{2g}$</th>
<th>$3A_{2g} - 1A_{1g}$</th>
<th>$3A_{2g} - 3T_{1g}(F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiBr$_2$</td>
<td>6.8</td>
<td>11.8</td>
<td>10.2</td>
<td>17.5</td>
<td>20.3</td>
<td>20.6</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>7.2</td>
<td>11.5</td>
<td>12.4</td>
<td>19.2</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>NiF$_2$</td>
<td>7.5</td>
<td>12.0</td>
<td>12.8</td>
<td>21.2</td>
<td>23.2</td>
<td>24.0</td>
</tr>
<tr>
<td>Ni(H$_2$O)$_6$$^{+2}$</td>
<td>8.5</td>
<td>13.5</td>
<td>15.4</td>
<td>18.4</td>
<td>22.0</td>
<td>25.3</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>8.6</td>
<td>14.0</td>
<td>15.5</td>
<td>21.2</td>
<td>24.0</td>
<td>25.7</td>
</tr>
<tr>
<td>NiOHBr</td>
<td>6.9</td>
<td>11.5</td>
<td>12.8</td>
<td>19.0</td>
<td>21.5</td>
<td>23.7</td>
</tr>
<tr>
<td>NiOCl</td>
<td>7.2</td>
<td>12.0</td>
<td>13.0</td>
<td>19.5</td>
<td>22.8</td>
<td>23.8</td>
</tr>
<tr>
<td>Ni$_2$(OH)$_3$Cl</td>
<td>7.7</td>
<td>12.6</td>
<td>13.7</td>
<td>20.0</td>
<td>22.5</td>
<td>24.8</td>
</tr>
<tr>
<td>Ni$_2$(OH)$_3$F</td>
<td>8.1</td>
<td>13.7</td>
<td>14.5</td>
<td>21.0</td>
<td>23.0</td>
<td>25.5</td>
</tr>
</tbody>
</table>

Data compiled from reference (59).

See also (50) and references therein contained.

Spin forbidden transitions were assigned using the criterion that they are weaker in intensity than spin allowed transitions.
spin as $2S' + 1Y$ under the influence of spin-orbit coupling energy, or by the admixture of $2S' + 1W$ into $2S' + 1Y$. The transition is now allowed, but the intensity is proportional to the square of the coefficient of admixture. This coefficient is dependent on the proximity of these states, and if close large intensities can result.

Figure 3 shows that the $1E_g$ state arising from the $1D$ state is close to the $3T_{1g}(F)$ state for $\Delta \omega = 7.0 - 9.0$ kK. For six-coordinate complexes possessing crystal field parameters of this size the transition to $3T_{1g}(F)$ appears as a well defined doublet. This has been considered to be due to the spin-forbidden transition $3A_{2g} - 1E_g$ arising from the spin-orbit coupling interaction between the $1E_g$ and $3T_{1g}(F)$ states. Jørgensen supports this interpretation and has investigated the variation in position of this band as function of $\Delta \omega$.\(^{(58)}\) However, Liehr and Ballhausen hold the view that the double-peaked absorption band arises from the spin-orbit fine structure of the $3T_{1g}(F)$ state, the spread of which is too large for vibrational bridging.\(^{(23)}\)

Table 3 summarizes the diffuse reflectance electronic data for weak field nickel(II) compounds having octahedral and distorted octahedral coordination polyhedra. The table was compiled from the work of Ludi and Feitknecht,\(^{(59)}\) in which they satisfactorily interpreted the data for nickel bromide, chloride, fluoride, and hydroxide using the expression derived by Griffith for the energy of the two $3T_{1g}$ states, namely.\(^{(57)}\)

$$E(3T_{1g}) = \frac{1}{4}(15B - \Delta \omega) + \frac{1}{4}(225B^2 - 18B\Delta \omega + \Delta \omega^2)^{\frac{3}{2}},$$

where $E(3A_{2g}) = -2\Delta \omega$, 
and B is the Racah parameter for the nickel(II) ion in the complex. From Figure 3 \( \Delta \) is given by the energy separation between \( ^3A_{2g} \) and \( ^3T_{2g} \). One interesting point to emerge from the work of Ludi and Feitknecht was that for compounds in which there was moderate or strong distortion no additional state splitting was observed. This was in contrast to the results for the corresponding cobalt(II) compounds. For a \( D_{4h} \) ligand field the \( ^3T_{2g} \) and \( ^3T_{1g}(F) \) states of an octahedral complex split into \( ^3B_{2g} + ^3E_g \) and \( ^3A_{2g} + ^3E_g \) states. This splitting has been observed by Goodgame et al.\(^{60}\) for the complexes of nickel(II) with heterocyclic amines. The spectra are generally characterised by four absorption bands in the range 7.0 - 17.0 kK.

Four coordinate complexes

Cotton and Wilkinson\(^{61}\) have discussed the spectral features of tetrahedral nickel(II) complexes. In general they display a multiple band near 16.0 kK assignable to the \( ^3T_1(F) - ^3T_1(P) \) transition with weak bands on the low and high energy sides assigned as spin forbidden transitions to components of the \(^1D\) and \(^1G\) states respectively. A near infra-red band at about 8 kK is assigned to the \( ^3T_1(F) - ^3A_2 \) transition, but the \( ^3T_1(F) \) to \( ^3T_2(F) \) transition occurring in the range 3 - 4 kK can rarely be unambiguously assigned as this region can contain vibrational bands due to C-H fundamentals as well as O-H bands due to any moisture. In contrast to octahedral complexes, tetrahedral compounds display
relatively high intensity bands (62) and it has been shewn that the difference is of the order of $10^2$. Furthermore, the intensity of the $3T_1(F) - 3T_1(F)$ transition has been shewn to be 10-20 times more intense than the $3T_1(F) - 3A_2$ transition. (62)

Planar complexes of nickel(II) can readily be distinguished from octahedral and tetrahedral compounds in as much as no electronic transition occurs below 10.0 kK. The lowest energy band is commonly attributed to the $b_{2g}(d_{xy}) - b_{1g}(d_{x^2-y^2})$ transition, however, Lever (50) has questioned the validity of this assignment and also generally considers the factors which influence band assignment.

The lowest energy band in planar nickel(II) complexes increases in energy approximately in the sequence,

$$NiS_4 < NiN_2O_2 ~ NiN_2X_2 ~ NiO_4 < NiP_2X_2 < NiN_4$$

In the case of the square complex $bis(2,2,6,6$-tetramethyl-3,5-heptanediono)nickel(II) (63) and the diamagnetic square form of $bis(3$-phenyl-2,4-pentanediono)nickel(II) (64) the lowest energy band occurs at 18.69 kK.
3. **Experimental**
## Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>M.Pt. (°C)</th>
<th>M.Pt. (Literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 methoxy-4-formylphenol</td>
<td>B.D.H.</td>
<td>80.5-81</td>
<td>77-79, 81-82</td>
</tr>
<tr>
<td>Potassium 2-methoxy-4-nitrophenolate</td>
<td>(65)⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-methoxyphenol</td>
<td>B.D.H.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-ethoxy-4-formylphenol</td>
<td>Eastman.</td>
<td>75.5-76.5</td>
<td>76-78</td>
</tr>
<tr>
<td>2,6-dimethoxy-4-formylphenol</td>
<td>Koch-Light.</td>
<td>107-109</td>
<td>113</td>
</tr>
<tr>
<td>m-hydroxybenzaldehyde</td>
<td>B.D.H.</td>
<td>102.5-103</td>
<td>103-4, 108</td>
</tr>
<tr>
<td>p-hydroxybenzaldehyde</td>
<td>B.D.H.</td>
<td>115-116</td>
<td>115-116</td>
</tr>
<tr>
<td>2-hydroxy-5-nitrotoluene</td>
<td>(66)</td>
<td>94-94.5²</td>
<td>96 anhydrous</td>
</tr>
<tr>
<td>2-ethoxyphenol</td>
<td>Eastman.</td>
<td>-¹</td>
<td></td>
</tr>
<tr>
<td>2,6-dimethoxyphenol</td>
<td>Eastman.</td>
<td>-¹</td>
<td></td>
</tr>
</tbody>
</table>

1. Used directly as supplied by the manufacturer.

2. Satisfactory microanalytical figures obtained.


4. Obtained by prolonged base hydrolysis of 3,4-dimethoxynitrobenzene. Its infra-red spectrum did not show the presence of potassium silicate.
3.1. **Ligands and Reagents**

The purity of the ligands was checked before use and some were recrystallized (see Table 4.). All other reagents were of A.R. quality. Standard I.N. potassium and sodium hydroxide solutions were obtained from B.D.H.

The use of cumbersome systematic names will be avoided. The following abbreviations based on the trivial names of the ligands (parentheses) will be used.

<table>
<thead>
<tr>
<th>Systematic Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methoxy-4-formylphenolato</td>
<td>V. (vanillinato)</td>
</tr>
<tr>
<td>2-methoxy-4-nitrophenolato</td>
<td>N. (4-nitroguaiacolato)</td>
</tr>
<tr>
<td>2-methoxyphenolato</td>
<td>G. (guaiacolato)</td>
</tr>
<tr>
<td>2-ethoxy-4-formylphenolato</td>
<td>B. (bourbonalato)</td>
</tr>
<tr>
<td>2,6-dimethoxy-4-formylphenolato</td>
<td>S. (syringaldehydato)</td>
</tr>
</tbody>
</table>

3.2. **Metal Analysis**

Copper(II) was determined volumetrically using EDTA and Fast Sulphon Black F as the indicator. This indicator was found to be specific in its colour action towards copper(II) in ammoniacal solution and its end-point sharp and stable. \(^{(67,68)}\)

The organic matter in 0.1 gm. samples was removed by heating with a mixture of concentrated nitric acid (8 ml.), perchloric acid (4 ml.), and concentrated sulphuric acid (2 ml.). It was absolutely essential that evaporation of the fuming mixture was completed to dryness. The optimum working pH for the indicator was 11, and if acid was still present after the
FIGURE 4.
Schematic Diagram of Thermobalance.
Furnace arrangement for controlled atmosphere work.

FIGURE 5.
organic matter was removed sufficient ammonium salts remained in solution to set up an adverse buffer action.

Nickel(II) was determined gravimetrically using dimethylglyoxime. The organic matter in 0.1-0.15 gm. samples was removed by heating with concentrated nitric acid (8 ml.), perchloric acid (6 ml.), and concentrated sulphuric acid (2 ml.).

3.3. Microanalysis

The majority of microanalyses were performed by Dr. A. Bernhardt (5251 Elbach uber Engelskirchen, West Germany), and the remainder (marked asterisk in Table 5) with a Perkin-Elmer 240 Elemental Analyser. Under optimum running conditions the absolute accuracy of this machine with respect to carbon, hydrogen and nitrogen determinations was ± 0.3%. All anhydrous samples were analysed by Dr. A. Bernhardt, and quantitatively dried prior to analysis.

3.4. Stanton Thermobalance

Lukaszewski and Redfern, Coats and Redfern have reviewed the subject of thermal analysis. Figure 4 is a detailed schematic diagram of the thermobalance and no further comment as to its mode of operation will be given here. The machine (type HT-D) employed in this work was sensitive to ± 0.1 mg., and the maximum temperature attainable was 1400°C. The furnace set-up in Figure 4 was not employed and instead the arrangement shown in Figure 5 adopted. This enabled work
to be carried out in a controlled atmosphere by either pumping gas upward through the furnace sheath (inlet volume rate, 400 ml./min.; outlet, 200 ml./min.), or by passing gas downward (inlet volume rate, 400 ml./min.). Nitrogen was the only artificial atmosphere employed. The gas was dried by bubbling it through concentrated sulphuric acid and then with an anhydrous magnesium perchlorate column. The temperatures at the furnace wall and at the base of the crucible were recorded by means of platinum, 13% rhodium/platinum thermocouples, and at the latter point this was done to an accuracy of ± 3°C. Platinum crucibles were always used except when macroscale work was undertaken, and in these circumstances aluminium foil crucibles were employed.

When dealing with a new hydrated complex compound the thermobalance was found to be an extremely useful tool: firstly, it was possible to determine that the drying conditions adopted in the preparation of the compound, yielded a material which was stable when exposed to the atmosphere at room temperature; secondly, the degree of hydration was accurately determined; thirdly, the thermal stability of the anhydrous compound was appraised; and fourthly, the machine was used for the macroscale preparation of the anhydrous complex.

In this study the following routine preliminary operations were carried out when dealing with a new hydrated complex. The complex was dried in vacuo over anhydrous calcium chloride. A small sample was taken (~100 mg.) and its behaviour, over a period of 1-2 hours, observed on the thermobalance at room temperature under normal atmospheric
conditions. This was then repeated under an atmosphere of dry nitrogen. If the mass-gain/loss base line was constant under both conditions then this method of drying was satisfactory. However, if there was a mass increase (moisture uptake) with time for the air run, and a mass decrease (moisture release) with time under dry nitrogen, then the drying procedure initially selected was unsuitable. In such cases, and in those in which the complex was unstable under dry nitrogen conditions alone, air drying was employed.

The buoyancy correction for the crucible used, under the conditions employed, was determined. This correction was especially large when dry nitrogen was passed downward through the furnace. As a general rule small samples (100-150 mg.), finely divided and loosely packed, were used and a heating rate of about 2°C/min. applied. After each run the infra-red spectrum of the material was recorded to check that the mass loss was due to the removal of water.

Macroscale preparations of anhydrous complexes were always performed with dry nitrogen passing downward through the furnace, which was operated isothermally on reduced power (only possible for temperatures below 200°C). This method of preparation was satisfactory only if the anhydrous complex was thermally stable, and if the rate of loss of water was greater than 0.1 mg./min., otherwise vacuum assisted conditions were considered. Once dehydration was completed the product was cooled to room temperature on the machine with dry nitrogen flowing through the system.
Silica 2mm. diffuse reflectance cell, 'Scientific Supplies', modified type 2I.
3.5. Infra-red and Visible Spectra

Infra-red mull spectra were obtained on a Unicam SP.200, and Grubb Parsons (model MK2E2), 'Spectromaster', spectrophotometers. Sodium chloride windows were employed for the former instrument, and potassium bromide windows with the latter. With potassium bromide windows the Grubb Parsons machine gave unsatisfactory results below 500 cm$^{-1}$, since it was operated at a high gain setting. This was obviated by using matted polythene plates, matted to reduce interference fringe bands, with the gain at the normal setting. Hygroscopic compounds were mull in a dry-bag filled with dry nitrogen.

Visible diffuse reflectance spectra were recorded on a Unicam SP.700 spectrophotometer using lithium fluoride as the reference. The normal cell supplied with the instrument was satisfactorily used for samples which were moderately hygroscopic, provided it was packed in a dry-bag and the seams sealed. For very hygroscopic materials the cell shown in Figure 6(3), which was sealed under vacuum, was used. Spectra were recorded at liquid nitrogen temperature using the attachment previously described by Butcher. (10)

3.6. Magnetic Measurements

Molar magnetic susceptibilities, $X_M$, were determined by the Gouy method, and

$$X_M = \left(\frac{k_v + B_w}{W}\right) \cdot M,$$
where $k =$ volume susceptibility of air.

$v =$ volume of the specimen.

$\dot{w} =$ force exerted on the specimen by the magnetic field.

$W =$ weight of the specimen.

$M =$ molecular weight of the compound calculated on the basis that there is one paramagnetic metal ion per molecule.

$B =$ constant involving the dimensions of the specimen and the magnetic field.

$B$ was determined by calibration with tris(ethylenediamine) nickel(II) thiosulphate. In order to calculate $X_a$, the magnetic susceptibility per gramme atom of the paramagnetic metal ion, $X_M$ was corrected for the diamagnetic contribution of all atoms, including that of the paramagnetic metal ion, by using the corrective values given by Lewis and Wilkins.\(^{72}\) The t.i.p. correction was not included. The effective magnetic moment of the paramagnetic metal ion at the temperature of measurement was calculated from the equation;

$$\mu_{\text{eff}} = 2.84(X_a.T)^{\frac{1}{2}}.B.M.$$  

For the measurement of magnetic susceptibility over a range of temperature (~80-300°K) the Gouy balance system devised by Earnshaw was used. Earnshaw has described and discussed the merits of this particular system in detail.\(^{73}\) The apparatus was calibrated with nickel chloride solutions.\(^{74}\) As measurements were made in an atmosphere of dry nitrogen the equation for the molar magnetic susceptibility reduces to,

$$X_M = \frac{2.g.l.w.M.}{W.H^2}$$
where $g$ = acceleration due to gravity at the place of measurement.

$l$ = length of specimen.

$H$ = magnetic field calibration value for the length of specimen, $l$.

The susceptibility notation used in this work is now reviewed. The following terms are defined:

$\chi_M$ = the observed molar magnetic susceptibility, calculated on the basis of one paramagnetic metal ion per 'molecule'.

$\chi_a$ = the magnetic susceptibility per gramme atom of the paramagnetic metal ion.

$\chi_m = n,\chi_a$, for an $n$-meric aggregate of identical paramagnetic metal ions.

Hygroscopic compounds were handled in several ways. For large quantities of material the Gouy tube was packed in a glove-bag filled with dry nitrogen. When quantities were small and the compound moderately hygroscopic the miniature 'pig' (Figure 6(2)) was used, which could be connected directly to the Gouy tube or via a short length of polythene tubing. The 'pig' and its contents were heated in a vacuum drying pistol, to remove last traces of moisture, immediately before connection. For extremely moisture sensitive compounds the apparatus shown in Figure 6(3) was employed. The compound was dehydrated in bulb B, and with the apparatus still under vacuum, packed into the Gouy tube, which was sealed off.
3.7. **Mass Spectra**

Mass spectra were obtained on an A.E.I. MS.12 machine. The standard direct insertion lock was used to introduce solid samples directly into the ion source region.
3.8. Analytical Results

The analysis figures for the prepared complexes are catalogued in Table 5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found %</th>
<th>Required %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>CuV₄₂H₂O</td>
<td>47.68</td>
<td>4.85</td>
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<tr>
<td>CuN₂₄H₂O</td>
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<td>-</td>
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<tr>
<td>CuN₂³</td>
<td>41.94</td>
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</tr>
<tr>
<td>CuG₄</td>
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<td>CuB₂₂H₂O</td>
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</tr>
<tr>
<td>CuB₂₅</td>
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</tr>
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<td>CuS₂₃H₂O</td>
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<td>CuS₂₆</td>
<td>50.63</td>
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</table>

<table>
<thead>
<tr>
<th>Found %</th>
<th>Required %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
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<tr>
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<tr>
<td>NiG₂₁₀</td>
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</tr>
<tr>
<td>NiS₂₃H₂O</td>
<td>45.33</td>
</tr>
<tr>
<td>NiS₂₁¹</td>
<td>51.26</td>
</tr>
</tbody>
</table>

* Analysed with a Perkin-Elmer 240 Elemental Analyser. The percentage deviation for duplicate analyses was always well within the specified accuracy of the machine (Section 3.3.). /continued....
Drying conditions and % drying loss prior to analysis

1. 2mm., 80°C; 1.40%.
2. Difficult to microanalyse for C, H and N since the compound readily partially dehydrates when subjected to slight mechanical pressure and mild desiccation.
3. Dried 75°C.
4. 2mm., room temperature 0.00%.
5. 2mm., 90°C; 1.77%.
6. 2mm., 85°C; 2.47%.
7. 2mm., 100°C; 1.82%.
8. 760mm., 81°C; 2.31%.
9. 2mm., 136°C; 2.26%
10. High Vacuum, 80°C; 0.00%
11. High vacuum, 114°C; 7.94%

All lower hydrate and anhydrous compounds were prepared directly from the pure, fully hydrated compound, except for Cu₆₂.
Mass Loss: 1.0 mg.

**CuV_2\cdot2H_2O \rightarrow CuV_2.**

**FIGURE 7.**

Run conditions:
Pt-crucible.
Initial heating rate 2°C/hr.
Chart speed 6"/hour.
Dry N\textsubscript{2} atmosphere, down
400ml./min.
Sample wt. = 0.0596gm.

Thermocouple output in millivolts:

- 1.0
- 0.5

91°C

Time →

Apparent mass gain due to buoyancy effects.
3.9. Preparation of Complexes

Drying in vacuo was performed over anhydrous calcium chloride. The yields of the complexes were essentially quantitative.

\[ \text{Cu} \text{V} \text{R}_2 \cdot \text{H}_2 \text{O} \]

2-methoxy-4-formylphenol, vanillin (6.30 gm., 0.0414 mole), was added to water (750 ml.) containing sodium hydroxide (40.5 ml., 1.0N., 0.0405 mole) and sodium acetate trihydrate (0.4 gm.). The mixture was vigorously stirred and the solution filtered. Copper sulphate pentahydrate solution (4.67 gm., 0.0187 mole) in water (200 ml.) was added dropwise to the filtrate which was stirred. The yellow-green microcrystalline complex was filtered off and dried in vacuo.

\[ \text{CuV}_2 \]

This was prepared by dehydration of CuV\(_2\) \(\cdot\) 2H\(_2\)O on a Stanton Thermobalance under an atmosphere of dry nitrogen. The thermogram for the isothermal dehydration process is given in Figure 7.

\[ \text{CuN}_2 \cdot \text{H}_2 \text{O} \]

Potassium 2-methoxy-4-nitrophenolate (7.35 gm., 0.0355 mole) and sodium acetate trihydrate (0.4 gm.) were dissolved in water (300 ml.). To the stirred solution was added dropwise a solution of copper sulphate pentahydrate
(3.98 gm., 0.0159 mole) in water (250 ml.). The bright yellow complex which separated from solution was filtered off (Whatman 542 filter paper), washed with water (~250 ml.) until the washings were free of sulphate ions, and air dried for two months. When ground or subjected to mild desiccation the complex partially dehydrated giving a brown material.

**CuN**

Prepared by 'isothermal' dehydration (58-86°C) of CuN$_2$,4H$_2$O on a Stanton Thermobalance under an atmosphere of dry nitrogen. The thermogram showed no evidence for the existence of an intermediate hydrate.

Although the instrument was set for isothermal working on reduced power, its design did not allow satisfactory control below about 90°C.

**CuG**

2-methoxyphenol, guaiacol (2.00 gm., 0.0161 mole), was added to a stirred aqueous solution of sodium hydroxide (14.51 ml., 1.N., 0.01451 mole, diluted to 90 ml.). The ligand slowly dissolved and the solution became darker in colour with time due to oxidation. Copper sulphate pentahydrate solution (1.63 gm., 0.00653 mole) in water (90 ml.) was added dropwise to the stirred solution. The light-brown material which separated from solution was filtered off, press dried between filter paper, and dried in vacuo.
2-ethoxy-4-formylphenol, bourbonal (3.00 gm., 0.0181 mole), was added to water (750 ml.) containing sodium hydroxide (17.18 ml., 1N., 0.01718 mole) and sodium acetate trihydrate (0.4 gm.). After vigorous stirring the solution was filtered and copper sulphate pentahydrate solution (2.04 gm., 0.00817 mole) in water (200 ml.) added dropwise to the stirred filtrate. An orange coloured microcrystalline solid separated from solution. This was filtered off, sucked dry for three hours, and finally dried in vacuo.

This was obtained directly from CuB₂,2H₂O by isothermal dehydration (94°C) on a Stanton Thermobalance under an atmosphere of dry nitrogen. Last traces of moisture were removed by heating in vacuo at 90°C, 2 mm.

2,6-dimethoxy-4-formylphenol, syringaldehyde (1.0012 gm., 0.005492 mole), was added to water (240 ml.) containing sodium hydroxide (5.32 ml., 1N., 0.00532 mole) which was vigorously stirred. The solution was filtered and copper sulphate pentahydrate solution (0.6444 gm., 0.002580 mole) in water (60 ml.) added to the stirred filtrate. The buff coloured solid which separated from solution was filtered off, sucked dry for three hours, and dried in vacuo.
Isothermal dehydration (87-92°C) of CuS₂,3H₂O on a Stanton Thermobalance under an atmosphere of dry nitrogen produced CuS₂. The thermogram showed no evidence for there being an intermediate hydrate. Last traces of moisture were removed by heating in vacuo at 85°C, 2 mm.

NiV₂,2H₂O

2-methoxy-4-formylphenol, vanillin (3.00 gm., 0.0197 mole), was added to a stirred aqueous solution of sodium hydroxide (18.7 ml., 1 N., 0.0187 mole, diluted to 750 ml.). The solution was filtered and a solution of nickel nitrate hexahydrate (2.59 gm., 0.00891 mole) in water (200 ml.) added dropwise to the stirred filtrate. On standing overnight a bright green microcrystalline solid separated from solution. This was filtered off, sucked dry for three hours, and dried in vacuo.

The Stanton Thermobalance was not used for the preparation of NiV₂ from NiV₂,2H₂O, since the rate of dehydration was too slow. Dehydration of NiV₂,2H₂O was accomplished by heating in vacuo at 100°C, 2 mm.

NiN₂,4H₂C

Potassium 2-methoxy-4-nitrophenolate (3.00 gm., 0.0145 mole) was dissolved in water (720 ml.). Nickel nitrate
Conditions:
Dry N₂ atmosphere, downflow 400ml./min.
Air run temperatures given in parentheses.
Sample wt. = 0.1141 gm.
hexahydrate (2.05 gm., 0.00705 mole) in water (96 ml.) was added dropwise with efficient stirring. On standing overnight a yellow solid separated from solution. This was filtered off, sucked dry for three hours, and air dried for three weeks.

Ni\textsubscript{2}N\textsubscript{2},2H\textsubscript{2}O

This compound was best prepared by 'isothermal' dehydration (44-81°C) of Ni\textsubscript{2}N\textsubscript{2},4H\textsubscript{2}O under an atmosphere of dry nitrogen on a Stanton Thermobalance (Figure 8), or alternatively by heating in air at 81°C.

Ni\textsubscript{2}

Obtained by heating Ni\textsubscript{2}N\textsubscript{2},4H\textsubscript{2}O or Ni\textsubscript{2}N\textsubscript{2},2H\textsubscript{2}O in vacuo at 136°C, 2 mm.

Ni\textsubscript{2}G\textsubscript{2},2H\textsubscript{2}O

2-methoxyphenol, guaiacol (2.10 gm., 0.0169 mole), was dissolved in water (60 ml.) containing sodium hydroxide (1.53 ml., 1.1N., 0.0153 mole). To this was added, slowly, and with efficient mixing a solution of nickel nitrate hexahydrate (2.11 gm., 0.00725 mole) in water (60 ml.). A light-grey solid separated from solution, which was filtered off, press dried between filter paper, and dried in vacuo. The dry product was treated with hexane, to remove free ligand impurity, and dried in vacuo.
NiG₂

Prepared by dehydrating NiG₂,2H₂O isothermally (87°C) on a Stanton Thermobalance under an atmosphere of dry nitrogen.

NiS₂,3H₂O

2,6-dimethoxy-4-formylphenol, syringaldehyde (1.2500 gm., 0.006860 mole), was added to a well stirred aqueous solution of sodium hydroxide (6.66 ml., 1.N., 0.00666 mole, diluted to 300 ml.). The solution was filtered and a solution of nickel nitrate hexahydrate (0.9380 gm., 0.003225 mole) in water (80 ml.) added dropwise to the stirred filtrate. After standing for five hours a light-green solid separated from solution, which was filtered off, sucked dry for two hours, and dried in vacuo.

NiS₂

NiS₂ was prepared by dehydrating NiS₂,3H₂O in the apparatus shown in Figure 6(3) at 114°C under high vacuum. The compound was extremely hygroscopic and immediately rehydrated on exposure to the atmosphere. Thermogravimetric analysis (t.g.a.) of NiS₂,3H₂O failed to show the existence of intermediate hydrates.

Table 6 catalogues the complexes along with their colours.

Sodium 2-methoxy-4-formylphenolate

2-methoxy-4-formylphenol, vanillin (0.5 gm.), was dissolved in a minimum volume of sodium hydroxide (2.N.). A clear
yellow solution resulted, from which, on vigorous shaking, the sodium salt separated. The sodium salt was filtered off, washed with a small quantity of water, and dried in vacuo.

**Sodium 2-ethoxy-4-formylphenolate**

2-ethoxy-4-formylphenol, bourbonal (0.5 gm.), was dissolved in a minimum volume of warm ethanol. Sodium hydroxide (0.75 ml., 4 N.) was added, whereupon the sodium salt separated from solution. It was filtered off, washed with ethanol and ether, and dried in vacuo.

**Sodium 2,6-dimethoxy-4-formylphenolate**

2,6-dimethoxy-4-formylphenol, syringaldehyde (0.2025 gm.), was dissolved in a minimum quantity of warm ethanol. Sodium hydroxide (1.10 ml., 1 N.) was added, and on cooling the sodium salt crystallized from solution. It was filtered off, washed with absolute ethanol and ether, and dried in vacuo.

---

**TABLE 6**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuV₂,2H₂O</td>
<td>Yellow-green</td>
</tr>
<tr>
<td>CuV₂</td>
<td>Brown</td>
</tr>
<tr>
<td>CuN₂,4H₂O</td>
<td>Yellow</td>
</tr>
<tr>
<td>CuN₂</td>
<td>Brown</td>
</tr>
<tr>
<td>CuG₂</td>
<td>Light-brown</td>
</tr>
<tr>
<td>CuB₂,2H₂O</td>
<td>Orange</td>
</tr>
<tr>
<td>CuB₂</td>
<td>Brown</td>
</tr>
<tr>
<td>CuS₂,3H₂O</td>
<td>Buff</td>
</tr>
<tr>
<td>CuS₂</td>
<td>Brown</td>
</tr>
<tr>
<td>NiV₂,2H₂O</td>
<td>Green</td>
</tr>
<tr>
<td>NiV₂</td>
<td>Yellow</td>
</tr>
<tr>
<td>NiN₂,4H₂O</td>
<td>Yellow</td>
</tr>
<tr>
<td>NiN₂,2H₂O</td>
<td>Yellow</td>
</tr>
<tr>
<td>NiG₂</td>
<td>Brown</td>
</tr>
<tr>
<td>NiG₂,2H₂O</td>
<td>Light-grey</td>
</tr>
<tr>
<td>NiG₂</td>
<td>Yellow</td>
</tr>
<tr>
<td>NiS₂,3H₂O</td>
<td>Light-green</td>
</tr>
<tr>
<td>NiS₂</td>
<td>Orange</td>
</tr>
</tbody>
</table>
4. Copper(II) Complexes. Results and Discussion
FIGURE 9.
Infra-red absorption in the range 9.00 - 10.00 microns (\(\text{III} - 1000 \text{ cm}^{-1}\)) for the copper(II) complexes

Notes:

(1) Transmittance increases in the direction

(2) The scale, \[ \begin{array}{c}
\text{I} \hline
\text{I} \hline
\text{I} \hline
\end{array} \]
, is linear in microns and covers the range 9.00 to 10.00, reading from left to right.

(3) Specific band positions are given in units of reciprocal wavelength (\(\text{cm}^{-1}\)).

(4) *, see Appendix 2.
FIGURE 10.

Infra-red absorption in the range 7.50 - 8.50
microns (I333 - II76 cm$^{-1}$) for the copper(II)
complexes.

Notes.

(I) Transmittance increases in the direction

(2) The scale, is linear in microns
and covers the range 7.50 to 8.50, reading from
left to right.

(3) The I250 cm$^{-1}$ reference line is shown. See Table 9.

(4) *, see Appendix 2.
FIGURE II.

Infra-red absorption in the range 2.50-3.50 microns.

- **CuH₂₄H₂O**: 3509 cm⁻¹, 3367 cm⁻¹
- **CuB₂₂H₂O**: 2.50 - 3.50
- **CuV₂₂H₂O**: 3436 cm⁻¹
- **CuS₂₂H₂O**: 2.50 - 3.50
4.1. **The Infra-red Spectra**

Figures 9 and 10 show the infra-red absorption for the copper(II) complexes in the range $1111-1000 \text{ cm}^{-1}$ and $1333-1176 \text{ cm}^{-1}$. The latter region contains the aryl-ethereal oxygen stretching mode (about $1250 \text{ cm}^{-1}$, see Section 2.1.) and the former the aliphatic-oxygen stretching mode ($1050-1000 \text{ cm}^{-1}$, see Section 2.1.) for the 2-ethoxy-, and 2-methoxyphenols.

In Figure 9 there can be little doubt concerning the assignment of the indicated absorption band(s) to the aliphatic-oxygen stretching mode. Only in the case of the copper(II) complexes with 2-ethoxy-4-formylphenol ($\text{Cu}_2\text{B}_2\text{H}_2\text{O}$ and $\text{CuB}_2$) is the situation less clear. From Figure 10 it is apparent that any attempt to attribute one particular band to the aryl-ethereal oxygen stretching vibration would be unwise on account of the complexity of the spectra. It is not possible to decide with any certainty the role of the alkoxy group as infra-red data for compounds in which an alkoxy group is known to coordinate is not available. None-the-less, a comparison of the spectra of the free ligand, its alkali metal salt, and the corresponding complexes in the $1000-1111 \text{ cm}^{-1}$ region, which is given here, may point to the non-involvement of the alkoxy group in coordination.

Figure 11 compares the region of the infra-red spectrum associated with the O-H stretching mode (at about three microns) for the hydrated copper(II) complexes. Of particular interest is the infra-red absorption of the complex, $\text{CuN}_2\text{H}_2\text{O}_4$. Two distinct bands occur at $3509$ and $3367 \text{ cm}^{-1}$, accompanied by a split $1650 \text{ cm}^{-1}$ band assignable to the
FIGURE I2.

CuV₂₂H₂O  —— UV bands: 22.0sh.(1.06); 25.5br.(1.28); 27.2(22.6)
CuN₂₂H₂O  ——  ~23.0(1.69); 31.0(1.85).
CuS₂₂H₂O  ——  ~22.0br-sh.(0.59); ~24.0br.(0.64); ~26.0(1.69).

sh. = shoulder.
br. = broad.
FIGURE 14.

CuV₂, CuN₂, CuB₂, CuS₂
H-O-H bending vibration. This points to the presence of two types of bonded water molecule within the complex. The similarity in profile of the 3509 cm\(^{-1}\) band to the 3436 cm\(^{-1}\) band of CuV\(_2\),2H\(_2\)O is to be noted, and in both instances the water molecules giving rise to these absorptions do not appear to be involved in appreciable hydrogen-bonding. In contrast, the broad absorption profiles of CuB\(_2\),2H\(_2\)O and CuS\(_2\),3H\(_2\)O shows the presence of hydrogen-bonded water.

4.2. The Diffuse Reflectance Spectra

In Section 2.3, a set of criteria to distinguish different stereochemistries was presented. Figure 12 shows the diffuse reflectance spectra obtained for CuV\(_2\),2H\(_2\)O, CuN\(_2\),4H\(_2\)O and CuS\(_2\),3H\(_2\)O at room temperature. The complexes display a main absorption band at 13.8-14.3 kK (1 kK = 1000 cm\(^{-1}\)) and a low energy shoulder at 10.1-11.7 kK, which points to the presence of the tetragonal CuO\(_6\) chromophore (section 2.3 and Table 1). The main absorption band in the spectrum of CuS\(_2\),3H\(_2\)O shows extensive asymmetry on its low frequency side, but resolution of this into component bands was not observed when the spectrum was recorded at liquid nitrogen temperature (14.0 kK (0.32) and 10.3 kK (0.23)). The figures in the inner set of parentheses refer to the absorbance on the arbitrary, 0-2, Unicam SP.700 scale.

The diffuse reflectance spectra of CuB\(_2\),2H\(_2\)O (recorded at liquid nitrogen temperature) and CuG\(_2\) (room temperature) are shown in Figure 13. Absorption bands ascribed to charge
transfer occur respectively at \( \sim 21 \text{ kK} \ (1.1) \) and \( \sim 23 \text{ kK} \ (0.75) \). In contrast to the spectra in Figure 12, the most striking feature is the low energy at which absorption occurs in the visible region. The presence of three bands below 12 kK in each case points to a quasi-tetrahedral stereochemistry (section 2.3, Table 2). If correct, these are rare examples of the quasi-tetrahedral CuO\(_4\) chromophore. The resolution of the CuG\(_2\) spectrum is improved at liquid nitrogen temperature, the bands occurring at \( \sim 24 \text{ kK} \ (0.75) \), 11.5 kK (0.43), 8.6 kK sh. (0.53) and 7.5 kK (0.61).

Figure 14 shows the diffuse reflectance spectra of CuV\(_2\), CuN\(_2\), CuB\(_2\) and CuS\(_2\) recorded at room temperature. All are brown (Table 6) on account of the tailing-off of strong ultra-violet bands into the visible region. The spectra are distinguished from those in Figure 12 in that absorption in the visible region is much more intense. The tailing-off of the strong ultra-violet bands into the visible region may account for this. Furthermore, d-d transition absorption bands may be swamped, resulting in a single broad absorption envelope being observed. This appears to be the case for CuV\(_2\) and CuN\(_2\), but for CuB\(_2\) and CuS\(_2\) the existence of two absorption bands is clearly seen at 14.6 kK (1.18), 11.4 kK sh. (0.95); and 12.5 kK (0.93), 10.6 kK sh. (0.78) respectively. This indicates the presence of the tetragonal CuO\(_6\) chromophore (section 2.3 and Table 1), which may also be tentatively inferred for the CuV\(_2\) and CuN\(_2\) complexes. The extent of absorption in the visible region for the complexes in Figure 14 is \( \sim 8-16 \text{ kK} \), and
consequently the presence of the planar \( \text{CuO}_4 \) chromophore is unlikely. (Section 2.3., extent of absorption envelope for the planar \( \text{CuO}_4 \) chromophore is 14-20 \( \text{MK} \).)

4.3. The Magnetic Properties

The effective magnetic moments of the copper(II) complexes at room temperature are given in Table 7. The hydrated complexes have normal moments (-1.9 B.M.) commonly observed for compounds having magnetically isolated copper(II) ions, whereas those for the anhydrous compounds are considerably smaller indicating spin interaction between the copper(II) ions. Magnetic susceptibilities for the anhydrous complexes, \( \text{CuB}_2 \cdot 2\text{H}_2\text{O} \) and \( \text{CuV}_2 \cdot 2\text{H}_2\text{O} \) were recorded over the temperature range 80-300\( \text{°K} \). Table 8 summarises this magnetic data, and with the exception of \( \text{CuG}_2 \) and \( \text{CuB}_2 \) the Curie-Weiss Law is obeyed. The small Weiss constants for \( \text{CuB}_2 \cdot 2\text{H}_2\text{O} \) and \( \text{CuV}_2 \cdot 2\text{H}_2\text{O} \) (\( \theta \approx 20 \) and \( \approx 12\text{°K} \) respectively) coupled with the small variation in magnetic moment (-1.9-1.8 B.M.), confirms the absence of significant magnetic exchange. Similarly, although \( \text{CuS}_2 \) possesses a low moment, the small Weiss constant indicates no substantial magnetic exchange. The data in Table 8 is meaningful only in a relative sense, since the Gouy balance system was operated at the limits of its sensitivity, and the hygroscopic compounds were always contaminated with a small amount of hydrated compound. Magnetic field dependence was checked at room temperature. The variation of reciprocal magnetic susceptibility with temperature for the anhydrous compounds, along with the calculated one-dimensional Ising
Table 7

Effective Magnetic Moments (B.M.) at Room Temperature

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. Wt.</th>
<th>D.M.C. x 10^6 (^1) (c.g.s. units)</th>
<th>(T^\circ K)</th>
<th>(\mu_{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuV(_2), 2H(_2)O</td>
<td>401.85</td>
<td>196.9</td>
<td>299</td>
<td>1.92</td>
</tr>
<tr>
<td>CuN(_2), 4H(_2)O</td>
<td>471.86</td>
<td>238.1</td>
<td>295</td>
<td>1.89</td>
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<tr>
<td>CuB(_2), 2H(_2)O</td>
<td>429.91</td>
<td>220.6</td>
<td>297</td>
<td>1.92</td>
</tr>
<tr>
<td>CuS(_2), 3H(_2)O</td>
<td>479.92</td>
<td>242.8</td>
<td>292</td>
<td>1.95</td>
</tr>
<tr>
<td>CuV(_2)</td>
<td>365.32</td>
<td>170.9</td>
<td>295</td>
<td>1.74</td>
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<tr>
<td>CuN(_2)</td>
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</tr>
<tr>
<td>CuG(_2)</td>
<td>309.80</td>
<td>162.4</td>
<td>291</td>
<td>1.65</td>
</tr>
<tr>
<td>CuB(_2)</td>
<td>393.88</td>
<td>194.6</td>
<td>299</td>
<td>1.61</td>
</tr>
<tr>
<td>CuS(_2)</td>
<td>425.88</td>
<td>203.8</td>
<td>300</td>
<td>1.58</td>
</tr>
</tbody>
</table>

\(^1\) D.M.C. = diamagnetic correction, ref. (72).
<table>
<thead>
<tr>
<th></th>
<th>Relative Magnetic Susceptibilities (Xa in c.g.s. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CuV₂</strong></td>
<td></td>
</tr>
<tr>
<td>T₀K</td>
<td>302.0 265.9 229.4 194.4 157.0 120.0 88.0</td>
</tr>
<tr>
<td>10⁶Xa</td>
<td>1328 1457 1608 1818 2076 2411 2820</td>
</tr>
<tr>
<td>g calc.</td>
<td>2.22. 2J = -39.3 cm⁻¹(I)</td>
</tr>
<tr>
<td>μ₀eff B.M.</td>
<td>1.80 1.77 1.73 1.69 1.62 1.53 1.42</td>
</tr>
<tr>
<td><strong>CuN₂</strong></td>
<td></td>
</tr>
<tr>
<td>T₀K</td>
<td>300.0 265.5 228.3 193.5 156.9 118.5 90.1 86.3</td>
</tr>
<tr>
<td>10⁶Xa</td>
<td>1153 1282 1443 1615 1861 2232 2664</td>
</tr>
<tr>
<td>g calc.</td>
<td>1.98. 2J = -27.2 cm⁻¹(I)</td>
</tr>
<tr>
<td>μ₀eff B.M.</td>
<td>1.67 1.66 1.63 1.59 1.54 1.46 1.39 1.39.</td>
</tr>
<tr>
<td><strong>CuG₂</strong></td>
<td></td>
</tr>
<tr>
<td>T₀K</td>
<td>299.1 262.5 225.9 190.1 153.5 117.0 85.8 83.5.</td>
</tr>
<tr>
<td>10⁶Xa</td>
<td>1125 1163 1247 1302 1280 1158 - 930.2.</td>
</tr>
<tr>
<td>g calc.</td>
<td>2.51. 2J = -1243 cm⁻¹(I)</td>
</tr>
<tr>
<td>μ₀eff B.M.</td>
<td>1.65 1.57 1.51 1.41 1.26 1.05 - 0.79.</td>
</tr>
<tr>
<td><strong>CuB₂</strong></td>
<td></td>
</tr>
<tr>
<td>T₀K</td>
<td>300.3 263.5 228.1 192.3 154.8 117.5 84.8</td>
</tr>
<tr>
<td>10⁶Xa</td>
<td>1027 1092 1141 1198 1198 1059 774.</td>
</tr>
<tr>
<td>g calc.</td>
<td>2.41. 2J = -125.1 cm⁻¹(I)</td>
</tr>
<tr>
<td>μ₀eff B.M.</td>
<td>1.58 1.52 1.45 1.36 1.22 1.00 0.73.</td>
</tr>
</tbody>
</table>

/continued...
\textbf{Table 8 (contd.)}

\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{CuS}_2^k & \textbf{T}^0K & 300.2 & 265.4 & 230.1 & 193.7 & 156.8 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{10}^6\textbf{Xa} & 1171 & 1294 & 1493 & 1723 & 2015 & 2522 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{10}^6\textbf{Xa calc.} & 1171 & 1307 & 1483 & 1725 & 2075 & 2604 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{\mu}_{\text{eff}} & \text{B.M.} & 1.68 & 1.66 & 1.66 & 1.64 & 1.60 & 1.56 & 1.53 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{CuV}_{2,2H_2O} & \textbf{T}^0K & 302.0 & 266.0 & 230.0 & 194.5 & 157.5 & 120.0 & 86.3 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{10}^6\textbf{Xa} & 1494 & 1674 & 1935 & 2263 & 2735 & 3498 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{\mu}_{\text{eff}} & \text{B.M.} & 1.91 & 1.90 & 1.89 & 1.88 & 1.86 & 1.84 & 1.82 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{CuB}_{2,2H_2O} & \textbf{T}^0K & 299.5 & 264.8 & 230.4 & 193.1 & 156.8 & 119.5 & 87.5 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{10}^6\textbf{Xa} & 1563 & 1718 & 1924 & 2286 & 2801 & 3576 \text{ (Da) = Dimeric aggregate} \\
\hline
\textbf{\mu}_{\text{eff}} & \text{B.M.} & 1.94 & 1.92 & 1.89 & 1.89 & 1.88 & 1.86 & 1.79 \text{ (Da) = Dimeric aggregate} \\
\hline
\end{tabular}

\textit{(I) = Ising.}

\textit{(Da) = Dimeric aggregate.}
CuB₂: observed, calculated Θ.

CuV₂: observed, calculated Δ.

CuN₂: observed, calculated Θ.

CuS₂: observed, calculated X.

Temperature, °K.
\[ \text{\( \bullet = \text{Cu} \)} \]

16(1) monomeric-bidentate.

\[ \text{CuB}_2, \text{H}_2\text{O} \]

16(2) polymeric-monodentate.

\[ \text{\( + 'lattice' \) H}_2\text{O} \]

16(3) polymeric-monodentate.

- H\(_2\)O

16(4) CuB\(_2\), \text{H}_2\text{O}

\[ \text{monomeric-monodentate.} \]

16(5) CuB\(_2\), \text{H}_2\text{O}

\[ \text{monomeric-bidentate.} \]

16(6) CuB\(_2\), \text{H}_2\text{O}

\[ \text{polymeric-bidentate.} \]

16(7) dimeric-bidentate.

\[ \text{\( \bullet = \text{Cu} \)} \]

16(8) polymeric-bidentate.
$\text{CuN}_2 \cdot 4 \text{H}_2\text{O} \quad (82)$

monomeric-bidentate.

polymeric-monodentate.

$\text{polymeric-monodentate.}$

$\text{polymeric-monodentate.}$

$\text{polymeric-monodentate.}$
variation, equation (A), Section 2.2., is shown in Figure 15. Clearly CuG$_2$ and CuB$_2$ display 'strong' antiferromagnetic interaction, whilst for the remaining anhydrous compounds it is weaker. Using the Weiss constant as a guide to the magnitude of interaction, it appears to increase in the order,

$$\text{CuV}_2 (\theta = 102^\circ K) \succ \text{CuN}_2 (\theta = 68^\circ K) \succ \text{CuS}_2 (\theta = 30^\circ K).$$

4.4. Discussion

In the absence of detailed X-ray crystallographic information any discussion can only be of a general nature. The ligands may be monodentate (coordinating through phenolic oxygen) or bidentate and chelating (coordinating through the alkoxy and phenolic oxygen). As shown, the infra-red investigation provided no unambiguous evidence in support of either a monodentate or bidentate-chelating coordinating action. (In this discussion 'bidentate' means 'bidentate and chelating', unless otherwise stated.)

The anhydrous CuG$_2$ complex (no hydrated form was obtained) provides the best starting point for discussion. The visible spectrum showed copper(II) to be in a quasi-tetrahedral environment. Two reasonable structures are possible, Figure 16(1) and 16(2). 16(1) is monomeric with the ligand bidentate, whilst 16(2) is polymeric with the ligand monodentate. In view of the antiferromagnetic interaction displayed by this complex, structure 16(2) is assigned.

The visible spectrum of CuB$_2$·2H$_2$O also indicated a quasi-tetrahedral environment for copper(II). On this basis possible
structures are 16(3), 16(4), and 16(5). If 16(3) is correct, then the absence of significant magnetic exchange could be due to the presence of an asymmetric phenolic oxygen bridging network. The long Cu–O bond, and/or large Cu–Cu distance would prevent magnetic exchange. Dehydration might produce 16(6) in which the copper(II) stereochemistry is planar within the chain, and the bridging symmetric. The shortening of the long Cu–O bond, and/or reduction in the Cu–Cu separation associated with symmetric bridging, could account for the appearance of magnetic exchange in CuB2. Axial perturbation from oxygen atoms in adjacent chains, giving a tetragonal CuO6 environment, could also account for the observed visible spectrum. If the structure of CuB2·2H2O is based on 16(4) and 16(5), then in order to account for the antiferromagnetism of CuB2, these structures would be expected to undergo rearrangement on dehydration with the formation of bonding links between copper(II) ions so that magnetic exchange can take place. The nature of CuB2 will then be dependent on the juxtaposition of the monomeric molecules within the crystal lattice, and perhaps the most readily visualized dehydration process for 16(4) is to the linear polymeric structure 16(6). If the monomeric CuB2·2H2O molecules of 16(5) are suitably positioned within the crystal lattice, then removal of water may be accompanied by a twisting of the chelate rings into the same plane, followed by dimerization 16(7) or polymerization 16(8) of the planar molecules, with the intermolecular Cu–O linkage between them providing a means for magnetic exchange between copper(II) ions.
The NN' - ethylenediamine(salicylaldimine) copper(II) complex is dimeric in the solid state with a similar bonding link, 16(9), between the monomers as in 16(7) and 16(8). Lewis and Walton showed, however, that this linkage did not give rise to any significant magnetic exchange between the copper(II) ions, and suggested that this might be due to the length of the intermolecular Cu—O bond (2.41Å) or the Cu—O—Cu bond angle.

It is to be noted that if substantial rearrangement does take place on dehydration, then the magnetic properties of CuB 2 may well be dependent on the method of dehydration. This has been found for copper benzoate trihydrate.

Of particular interest was a theoretical interpretation of the observed dependence of magnetic susceptibility on temperature which would differentiate structures 16(6) and 16(8) from structure 16(7) for CuB 2. As seen in Table 8 and Figure 15, the magnetic data for CuB 2 can be interpreted in terms of the infinite one-dimensional Ising expression, but it can also be explained by the expression for a dimeric aggregate of interacting copper(II) ions (Table 8, section 2.2.; Appendix 1.), therefore differentiation is not possible on this basis. Similarly for CuG 2, but the dimeric aggregate equation does not give as good an explanation of the magnetic data (Table 8). The calculated Ising g-values for CuB 2 and CuG 2 are rather high. For copper(II) compounds g-values usually fall in the range 2.10-2.40.

CuV 2,2H 2O, CuN 2,4H 2O and CuS 2,3H 2O have diffuse reflectance spectra which are indicative of a CuO 6 tetragonal environment.

Possible structures starting from this standpoint are 16(10),
and the ease with which it readily partially dehydrates favours structures 16(11) and 16(12) for which the presence of 'lattice' water, as with CuS$_2$·3H$_2$O, is required. The dehydrated complexes show a variable degree of antiferromagnetic interaction, and if derived from 16(11), it would be expected to arise from the interaction of planar molecules bonded as in 16(7) and 16(8). If the hydrated complexes are based on structure 16(12), then the observed normal room temperature magnetic moments could be explained if an asymmetric phenolic oxygen bridging network, 16(13), existed (see discussion on CuB$_2$·2H$_2$O). Dehydration of 16(12) with the formation of a symmetric bridging network (see discussion on CuB$_2$·2H$_2$O) could explain the appearance of magnetic exchange. The observed visible spectra can be accounted for if axial Cu—O bonds exist between the chains, 16(14). A structural and magnetic analogy is provided by CuCl$_2$·2H$_2$O and CuCl$_2$. (80,15) So far no comment has been made concerning the stereochemistry about the phenolic oxygen atom in polymeric structures where the ligand is monodentate.

In structures such as 16(6), 16(12) and 16(14) it would probably be approximately trigonal planar with the benzene rings of the ligands twisted by some angle $\phi$ with respect to the Cu—O–Cu plane so as to minimise steric interaction (16(15)). Examples of such twisting are afforded by di-$\mu$-(pyridine N-oxide)-bis(di-chlorocopper(II)), $\phi = 70.0^\circ$, and polybis($\mu$-(2-picoline N-oxide)-chlorocopper(II)di-$\mu$-chloro-)diaquocopper(II), $\phi = 88.8^\circ$. (81)

CuV$_2$, CuN$_2$ and CuS$_2$ have structures based on 16(14), then the

\[ \text{More precisely trigonal monopyramidal for 16(6) and 16(14), probably with the phenolic oxygen sp}^2 \text{ hybridised and the unhybridised p orbital taking part in the long inter-chain bond.} \]
slight decrease in antiferromagnetic interaction in going from 
\( \text{Cu}_2 \text{V}_2 \) to \( \text{Cu}_2 \text{N}_2 \) can be ascribed to the greater electron withdrawing power of \(-\text{NO}_2\) over \(-\text{CHO}\). Steric interaction between the ligands would be expected to increase in \( \text{Cu}_2 \text{S}_2 \) and this could be alleviated by increasing \( \phi \) and/or increasing the Cu–O bond lengths and Cu–Cu distance. The observed decreased magnetic interaction is best accounted for by the latter. Good curve fitting was achieved with the one-dimensional Ising expression (Table 8 and Figure 15), but it can only be considered as tentative evidence in favour of 16(14) (see Appendix 1.).

Attempts to complex copper(II) with 2-ethoxyphenol yielded products contaminated with copper hydroxide, whilst the rapid aerial oxidation of 2,6-dimethoxyphenol on treatment with alkali, which is greatly enhanced when copper(II) ions are introduced, prevented its complexation.

To clarify the structural situation attempts were made to react copper(II) with 4-hydroxy-, and 3-hydroxybenzaldehyde. No complexes were obtained. If the 2-alkoxyphenols are chelates in their coordinating action then this is understandable, but not conclusive, since in structures such as 16(2), 16(3), and 16(12), although the alkoxy group is non-coordinating, its importance may lie in other roles, e.g. in the formation of a quasi-chelate species in solution prior to the separation of the solid. The failure of 2-hydroxy-5-nitrotoluene to complex can similarly be considered.

A mass spectroscopic investigation of \( \text{Cu}_2 \text{V}_2,2\text{H}_2\text{O}, \)
\( \text{Cu}_2 \text{N}_2,4\text{H}_2\text{O}, \text{Cu}_2 \text{S}_2,3\text{H}_2\text{O}, \text{Cu}_2 \text{B}_2,2\text{H}_2\text{O} \) and \( \text{CuG}_2 \) was undertaken. All
complexes other than the latter dehydrated in the source region and decomposed with the expulsion of organic fragments. The spectrum of CuG₂ (source temperature 222°C) showed the presence of copper containing species in the vapour state. The highest mass peak occurred at 311 mass units, accompanied by one at 309 mass units. The ratio of the peak height of the latter to the former was 3:2, which is correct for the presence of Cu⁶³ and Cu⁶⁵ isotopes. The 311 mass peak corresponds to Cu⁶³G₂, and the fact that a mass spectrum is obtained shows that the Cu–O bond(s) possesses substantial covalent character. The detection of only a monomer species, CuG₂, does not favour structure 16(1) over 16(2), since results for the vapour state cannot be automatically taken to hold for the solid state.
5. **Nickel(II) Complexes. Results, Discussion, and Comparison with Copper(II)**
**Figure 17.**

Infra-red absorption in the range 9.00 - 10.00 microns (III - 1000 cm\(^{-1}\)) for the nickel(II) complexes.

**Notes.**

(1) Transmittance increases in the direction 

(2) The scale, \(---\), is linear in microns and covers the range 9.00 to 10.00, reading from left to right.

(3) Specific band positions are given in units of reciprocal wavelength (cm\(^{-1}\)).

(4) *, see Appendix 2.
FIGURE 18.

Infra-red absorption in the range 7.50 - 8.50 microns (1333 - 1176 cm⁻¹) for the nickel(II) complexes.

Notes.

(1) Transmittance increases in the direction

(2) The scale, , is linear in microns and covers the range 7.50 to 8.50, reading from left to right.

(3) The 1250 cm⁻¹ reference line is shown. See Table 9.

(4) *, see Appendix 2.
FIGURE 19.
Infra-red absorption in the range 2.50-3.50 microns.
5.1. The Infra-red Spectra

As with the copper(II) complexes the 1111-1000 cm\(^{-1}\) and 1333-1176 cm\(^{-1}\) regions of the infra-red spectrum were examined in an attempt to decide upon the bonding role of the 2-methoxy group in the nickel(II) complexes (see Figures 17 and 18 respectively). The aliphatic-oxygen stretching mode gives rise to an absorption band(s) at 1000-1050 cm\(^{-1}\), and a band for the aryl-ethereal oxygen stretching vibration occurs at about 1250 cm\(^{-1}\) (see Section 2.1.) for the 2-methoxyphenols.

Comparison of Figure 17 and Figure 9 shows that the absorption pattern is not different from that for the corresponding copper(II) compounds. However, for the nickel(II) complexes of 2-methoxy-4-formylphenol (HV) and 2-methoxy-4-nitrophenol (HN) the absorption band associated with the aliphatic-oxygen stretching mode is shifted to lower frequencies relative to the band position for the corresponding copper(II) complexes. Furthermore, the shift is to frequencies lower than those observed for the ligands and their alkali metal salts (Appendix 2). This is tentative evidence for methoxy group coordination (Section 2.1.). No significant change in band position was found for the remaining nickel(II) compounds compared with the copper(II) counterparts.

In Figure 18 no distinct difference in the absorption pattern for the nickel(II) and corresponding copper(II) complexes was observed in the range 1333-1176 cm\(^{-1}\). For the same reasons as given in Section 2.1. and 4.1. no attempt at band assignment is made. The absorption band positions for the copper(II) and
Table 9.
Infra-red absorption in the range 1333-1176 cm⁻¹
(7.50-8.50 microns) for the Copper(II) and Nickel(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bands cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuV₂₂H₂O.</td>
<td>1337 1316sh.s, 1307s, 1263m, 1230s, 1205w, 1190sh.w.</td>
</tr>
<tr>
<td>NiV₂₂H₂O.</td>
<td>1326sh.s, 1312s, 1271s, 1233s, 1200m.</td>
</tr>
<tr>
<td>CuV₂.</td>
<td>1333sh.s, 1299sh.s, 1274s, 1259sh.s, 1225s, 1200sh.m.</td>
</tr>
<tr>
<td>NiV₂.</td>
<td>1330sh.s, 1285s, 1253s, 1220s, 1198sh.s.</td>
</tr>
<tr>
<td>HV.</td>
<td>1299s, 1266s, 1250sh.m, 1199m.</td>
</tr>
<tr>
<td>NaV.</td>
<td>1321s, 1309s, 1279m, 1256m, 1236sh.m, 1224m, 1202sh.m, 1192m.</td>
</tr>
<tr>
<td>CuN₂₄H₂O.</td>
<td>1332m, 1295s, 1247w, 1222s, 1179w.</td>
</tr>
<tr>
<td>NiN₂₄H₂O.</td>
<td>1332s, 1305sh.s, 1290s, 1284sh.s, 1247m, 1217s, 1178m.</td>
</tr>
<tr>
<td>NiN₂₂H₂O.</td>
<td>1330s, 1307sh.s 1290s, 1282sh.s, 1247m, 1218s, 1179m.</td>
</tr>
<tr>
<td>CuN₂.</td>
<td>1271s, 1214m, 1179w.</td>
</tr>
<tr>
<td>NiN₂.</td>
<td>1332m, 1285s, 1205m, 1175m.</td>
</tr>
<tr>
<td>HN.</td>
<td>1333s, 1302m, 1266s, 1247sh.s, 1242s, 1193s.</td>
</tr>
<tr>
<td>KN.</td>
<td>1333s, 1299s, 1280s, 1242s, 1217s, 1200sh.s, 1186s.</td>
</tr>
<tr>
<td>CuB₂₂H₂O.</td>
<td>1330m, 1304s, 1267sh.m, 1261m, 1230m, 1221sh.m, 1176sh.w.</td>
</tr>
<tr>
<td>CuB₂.</td>
<td>1332s - 1318s, 1312sh.s, 1267s, 1256sh.s, 1222s, 1196sh.s.</td>
</tr>
<tr>
<td>HB.</td>
<td>1289sh.s, 1276s, 1253s, 1193m.</td>
</tr>
<tr>
<td>NaB.</td>
<td>1328v, 1305s, 1259s, 1230s, 1200sh.w.</td>
</tr>
</tbody>
</table>

/Continued.../
Table 9 (contd.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavenumbers (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiG₂, 2H₂O</td>
<td>1318m, 1284s, 1261s, 1215s, 1172s.</td>
</tr>
<tr>
<td>NiG₂</td>
<td>1321s, 1299sh.m, 1285s, 1263s, 1258sh.s, 1220sh.m, 1212s, 1172s.</td>
</tr>
<tr>
<td>CuG₂</td>
<td>1321m, 1285s, 1280s, 1263s, 1253s, 1218sh.s, 1211s, 1176s.</td>
</tr>
<tr>
<td>Hg</td>
<td>1300m, 1261s, 1222s, 1206s.</td>
</tr>
<tr>
<td>CuS₂, 3H₂O</td>
<td>1321s, 1269w, 1230w, 1198w.</td>
</tr>
<tr>
<td>NiS₂, 3H₂O</td>
<td>1333sh.s, 1325s, 1274w, 1229m, 1198w.</td>
</tr>
<tr>
<td>CuS₂</td>
<td>1323s, 1276w, 1250w, 1222w, 1183w.</td>
</tr>
<tr>
<td>NiS₂</td>
<td>1326s, 1319sh.s, 1276m, 1258sh.m, 1221m, 1189w.</td>
</tr>
<tr>
<td>HS</td>
<td>1328s, 1274w, 1252s, 1220sh.w, 1206s, 1188w, 1181w.</td>
</tr>
<tr>
<td>NaS</td>
<td>1323m, 1284m, 1215m, 1190sh.w, 1185m.</td>
</tr>
</tbody>
</table>

k Appendix 2.

Qualitative indication of band intensity; s = strong, m = medium, w = weak.
sh. = shoulder.
nickel(II) complexes in this range are catalogued in Table 9.

Figure 19 shows the infra-red absorption for the hydrated nickel(II) complexes in the O-H stretching region at about three microns. Like CuN₂₄H₂O, NiN₂₄H₂O displays an interesting absorption profile in this region, the sharp high frequency bands at 3552 and 3484 cm⁻¹, and the broad band centred at 3195 cm⁻¹ indicating water molecules of two types in the compound (compare CuN₂₄H₂O, Section 4.1.). Thermogravimetric analysis established the presence of two types of water molecule (Figure 8), but rather surprisingly the infra-red spectrum of NiN₂₂H₂O is almost identical to that of NiN₂₄H₂O.

Consequently, the assignment of two classes of water molecule in CuN₂₄H₂O on the basis of the infra-red evidence alone, can only be tentative. The remaining hydrates display broad absorption bands in the three micron region characteristic of hydrogen-bonded water. (75)

5.2. The Diffuse Reflectance Spectra and Magnetism

The spectral data for the nickel(II) complexes is collected in Table 10 and the spectra shown in Figure 20. In light of the discussion given in Section 2.3. on six coordinate nickel(II) complexes, these spectra are consistent with an octahedral stereochemistry (weak ligand field). It is doubtful whether the low energy absorption band in the spectrum of NiS₂⁻₅kK, Figure 20) arises from a d-d transition. The V₁ band can be assigned to the ³A₂g(F) - ³T₂g(F) transition and the split or asymmetric V₂ band to the ³A₂g(F) - ³T₁g(F) transition. Possible
<table>
<thead>
<tr>
<th>Compound</th>
<th>$V_1$</th>
<th>$V_2$</th>
<th>Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiG$_2$·2H$_2$O</td>
<td>8.7</td>
<td>13.6sh., 15.2</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>8.65</td>
<td>13.6sh., 15.3</td>
<td>24.6-25.6sh.</td>
</tr>
<tr>
<td>NiG$_2$</td>
<td>7.3</td>
<td>12.4, 14.0sh.</td>
<td>21.6sh., 23.6</td>
</tr>
<tr>
<td>NiV$_2$·2H$_2$O</td>
<td>7.8</td>
<td>13.2, 14.2sh.</td>
<td>21.2sh., 24.0sh.</td>
</tr>
<tr>
<td>NiV$_2$</td>
<td>8.0</td>
<td>13.4, 14.2sh.</td>
<td>21.05, 21.8sh.</td>
</tr>
<tr>
<td>NiN$_2$·4H$_2$O</td>
<td>8.7</td>
<td>13.6, 15.0</td>
<td>19.4sh.</td>
</tr>
<tr>
<td></td>
<td>9.2</td>
<td>13.5, 15.6</td>
<td>19.2sh., 20.4sh.</td>
</tr>
<tr>
<td>NiN$_2$·2H$_2$O</td>
<td>9.2</td>
<td>13.0, 15.0</td>
<td>19.0sh.</td>
</tr>
<tr>
<td>NiN$_2$</td>
<td>9.4</td>
<td>13.3, 15.7</td>
<td>19.4sh.</td>
</tr>
<tr>
<td>NiS$_2$·3H$_2$O</td>
<td>9.0</td>
<td>12.5, 15.0</td>
<td>21.6sh., 23.1sh.</td>
</tr>
<tr>
<td>NiS$_2$</td>
<td>9.3</td>
<td>12.6, 15.3</td>
<td>21.35, 22.85</td>
</tr>
<tr>
<td>NiS$_2$</td>
<td>7.4</td>
<td>12.3</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>12.5</td>
<td>19.4sh.</td>
</tr>
</tbody>
</table>

RT = room temperature spectrum.
NT = liquid nitrogen temperature spectrum, sh = shoulder.

$^\times$ Intense bands.
A = Ni(NO$_3$)$_2$, 2H$_2$O
B = Ni(NO$_3$)$_2$.
Table 11

Effective Magnetic Moments (B.M.) at Room Temperature

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. Wt.</th>
<th>D.M.C. x 10^6 \textsuperscript{1} (c.g.s. units)</th>
<th>T^\textsuperscript{0}\textsuperscript{K}</th>
<th>( \mu_{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiG\textsubscript{2}.2H\textsubscript{2}O</td>
<td>341.00</td>
<td>188.4</td>
<td>295</td>
<td>3.21</td>
</tr>
<tr>
<td>NiG\textsubscript{2}</td>
<td>304.97</td>
<td>162.4</td>
<td>297</td>
<td>3.20</td>
</tr>
<tr>
<td>NiV\textsubscript{2}.2H\textsubscript{2}O</td>
<td>397.02</td>
<td>196.9</td>
<td>289</td>
<td>3.25</td>
</tr>
<tr>
<td>NiV\textsubscript{2}</td>
<td>360.99</td>
<td>170.9</td>
<td>293</td>
<td>3.24</td>
</tr>
<tr>
<td>NiN\textsubscript{2}.4H\textsubscript{2}O</td>
<td>467.03</td>
<td>238.1</td>
<td>292</td>
<td>3.22</td>
</tr>
<tr>
<td>NiN\textsubscript{2}.2H\textsubscript{2}O</td>
<td>431.00</td>
<td>212.1</td>
<td>292</td>
<td>3.28</td>
</tr>
<tr>
<td>NiN\textsubscript{2}</td>
<td>394.97</td>
<td>186.1</td>
<td>292</td>
<td>3.38</td>
</tr>
<tr>
<td>NiS\textsubscript{2}.3H\textsubscript{2}O</td>
<td>475.09</td>
<td>242.8</td>
<td>294</td>
<td>3.25</td>
</tr>
<tr>
<td>NiS\textsubscript{2}</td>
<td>421.05</td>
<td>203.8</td>
<td>290</td>
<td>3.29</td>
</tr>
</tbody>
</table>

\textsuperscript{1} D.M.C. = diamagnetic correction, ref. (72).
$O = Ni$

$2I(1)$

$2I(2)$

$2I(3)$

$2I(4)$
causes for this splitting and asymmetry were considered in Section 2.3. The substantial lowering of ligand field strength, as indicated by the position of $V_1$ ($V_1\text{oct.} = \Delta_0$, Section 2.3.), in the NiG, NiN, and NiS complexes, is to be noted.

Supporting evidence for the assignment of octahedral stereochemistry comes from the effective magnetic moments at room temperature (Table II). The magnetic moments fall within the range normally observed for octahedral nickel(II), 2.9 - 3.4 B.M.

5.3. Discussion and Comparison

Unlike copper(II), nickel(II) produces octahedral hydrated and anhydrous complexes with 2-methoxyphenol. Furthermore, nickel(II) fails to yield a pure complex with 2-ethoxy-4-formylphenol.

The hydrated copper(II) complexes of HV, HN, and HS were assigned a distorted octahedral stereochemistry on the basis of their visible spectra, and in addition, this stereochemistry was tentatively inferred for the anhydrous complexes. A parallelism can be drawn with the nickel(II) complexes of these ligands, but here the evidence for an octahedral environment in the hydrated and anhydrous complexes is more definite.

In contrast to copper(II), there is tentative evidence for methoxy group coordination in the nickel(II) complexes of 2-methoxy-4-nitrophenol and 2-methoxy-4-formylphenol (Section 5.1.). A possible structure, if this is correct, for the hydrated complexes of these ligands is Figure 21(1), with the addition of 'lattice' water for NiN, $\text{NiN}_2 \cdot 4\text{H}_2\text{O}$. To account for the observed effective magnetic moments and visible spectra of the anhydrous
compounds \( \text{NiV}_2 \) and \( \text{NiN}_2 \), dehydration must be accompanied by polymerization. A possible structure is \( \text{2I}(2) \). To attempt to explain the large reduction in ligand field strength which accompanies the complete dehydration of \( \text{NiN}_2,4\text{H}_2\text{O} \), compared with the smaller reduction in ligand field strength observed on dehydrating \( \text{NiV}_2,2\text{H}_2\text{O} \), would be unwise, especially in the absence of detailed structural information.

In the remaining nickel(II) complexes the ligands may well be bidentate and chelating (see Section 4.4.), and if so, the same considerations as given above apply. However, if the ligands are monodentate (see Section 4.4.) then a structure based on \( \text{2I}(3) \) is possible for the hydrates (plus 'lattice' water in the case of \( \text{NiS}_2,3\text{H}_2\text{O} \)). Dehydration with the formation of inter-chain axial Ni-0 bonds would account for the observed visible spectra\(^{(83)}\) and magnetic properties of the anhydrous complexes \( \text{2I}(4) \). As each phenolic oxygen atom is shared between three nickel(II) ions in \( \text{2I}(4) \) (in structure \( \text{2I}(2) \) the unspecified oxygen atom involved in the intermolecular linkage is shared between two nickel(II) ions) this might account for the reduction in ligand field strength, since the availability of lone pair electrons to the nickel(II) ions should be reduced.

A similar structural argument holds for the nickel(II) complexes of 2-methoxy-4-formylphenol and 2-methoxy-4-nitrophenol if the ligands are monodentate, but the problem of the small change in ligand field strength in going from \( \text{NiV}_2,2\text{H}_2\text{O} \) to \( \text{NiV}_2 \), as compared with the large decrease in ligand field strength observed on the complete dehydration of the other nickel(II) complexes, would again be difficult to reconcile.
5.4. Concluding Remarks

The crux of the structural problem has been whether or not there is alkoxy group coordination. CuV₂,2H₂O, CuV₂, CuB₂,2H₂O, CuB₂ and NiV₂,2H₂O are microcrystalline, and if suitable single crystals could be obtained, an X-ray crystallographic examination would resolve the structural problem. A structure determination coupled with a single crystal magnetic anisotropy study would be immensely helpful in trying to understand the magnetic exchange found in the anhydrous CuV₂ and CuB₂ complexes.
6. Appendices
6.1. Appendix 1. Magnetism

No reasonable interpretation of the magnetic data for CuB₂ and CuG₂ was achieved using the results of Earnshaw et al. (n=10). However, this data could be satisfactorily considered in terms of the magnetic susceptibility expression for a dimeric aggregate of interacting copper(II) ions, viz.,

\[ \chi_a = \frac{N \alpha^2 B^2}{3kT} \times \frac{1}{1 + \frac{1}{3} \exp \left( \frac{2J}{kT} \right)} + N \alpha \]  

(See section 2.2.)

The following curve fitting procedure was adopted. Using the observed temperature of maximum susceptibility, 2J was evaluated; 2J = 8/5Tmax. \( g \) was calculated from the magnetic susceptibility equation using \( \chi_{a, \text{max.}} \), Tmax., 2Jcalc., and \( N \alpha = 60 \times 10^{-6} \) c.g.s. units. If satisfactory curve fitting with these values was not obtained, \( g \) was varied. (See section 4.3.).

Reference was made in Section 2.2. to the fact that Adams et al. had utilized the one-dimensional Ising expressions for the parallel and perpendicular susceptibility of an infinite chain of interacting copper(II) ions for interpreting the magnetic data of anhydrous cupric chloride, viz.,

\[ \chi(T) = \frac{1}{3} \chi_{11}(T) + \frac{2}{3} \chi_{1}(T) \]  

(B) powder

The expression for \( \chi_{1} \) in reference (30) is wrong. It should be

\[ \chi_{1}(T) = \frac{N \alpha^2 B^2}{8 |J|} \left( \tanh \left( \frac{J}{kT} \right) + \frac{|J|}{kT} \right) \text{sech}^2 \left( \frac{J}{kT} \right) \]

Sinn has confirmed this. (84) Using the literature magnetic
data (85, 86) for anhydrous cupric chloride (observed temperature of maximum magnetic susceptibility is 69°K) reasonable curve fitting was achieved using expression (B), \( g = 2.13; \) \( 2J = -110.0 \) cm\(^{-1}; \) temperature range considered, 20-300°K; percentage deviation from literature data \( \pm 5.5\%\). The magnetic susceptibility data for CuB\(_2\), and CuG\(_2\) could not be fitted to equation (B), but the data for CuV\(_2\), CuN\(_2\), and CuS\(_2\) was satisfactorily fitted. The calculated \( g' \) and \( J' \) values are compared with those using only the parallel expression, \( g \) and \( J \) (Table 8).

<table>
<thead>
<tr>
<th></th>
<th>( g' )</th>
<th>( 2J' ) cm(^{-1} )</th>
<th>( g )</th>
<th>( 2J ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuV(_2)</td>
<td>2.13</td>
<td>-88.0</td>
<td>2.22</td>
<td>-39.3</td>
</tr>
<tr>
<td>CuN(_2)</td>
<td>1.96</td>
<td>-72.0</td>
<td>1.98</td>
<td>-27.2</td>
</tr>
<tr>
<td>CuS(_2)</td>
<td>1.96</td>
<td>-30.0</td>
<td>1.94</td>
<td>-12.4</td>
</tr>
</tbody>
</table>

Only with additional magnetic data extending below the temperature of maximum susceptibility might differentiation between these two approaches be achieved, but as shown for CuB\(_2\) and CuG\(_2\), any structural deduction based on the criterion of reasonable curve fitting must be tentative. Logically, theoretical discussions of magnetic data should follow an X-ray structure determination and a single crystal magnetic anisotropy study (see tetraammine-copper(II) sulphate monohydrate\((3\frac{1}{2})\)).

Computer curve fitting procedure for equation (B).

Equation (B) was solved for \( g \) using an experimentally observed value of \( \chi_a \) at temperature \( T \), usually the lowest temperature at which measurements were made, \( N \alpha = 60 \times 10^{-6} \) c.g.s.
units, and an arbitrarily chosen value for J. $X_a$ was then calculated using $g$-calculated and J, at various values of T. This represented one cycle of the programme, which was then repeated for a whole series of J values. The computed and observed magnetic susceptibilities were manually compared.

(Units: for J in cm$^{-1}$, $k = 0.69499$, $N^2 = 0.26072$)

All band positions reported in this thesis were taken from the spectra recorded on the Grubb Parsons spectrophotometer. Nujol bands were used for internal calibration, and the assignment of these bands confirmed by comparison with the spectra obtained using hexachlorobutadiene as the mulling agent.

The sodium salts of HV, HS, and HB could not be obtained pure because of contamination with the free acid or solvent, and sodium carbonate. Although the sodium salts of HV and HS are formulated as NaV and NaS they are in fact solvated (infra-red spectroscopy). In the case of NaV it was found that on standing under absolute ethanol overnight the infra-red spectrum was unchanged except for the appearance of a secondary peak at 1032 cm$^{-1}$, but if ground under absolute ethanol, dehydration occurred, accompanied by a considerable simplification of the spectrum. A single band now appeared at 1032 cm$^{-1}$ in the region 1000-1050 cm$^{-1}$.

The weak sharp infra-red absorption band observed for KN at 3559 cm$^{-1}$ was initially attributed to a small amount of potassium hydroxide impurity (H-O stretching vibration$^{(19)}$), but a combined t.g.a. and infra-red study showed that this band originated from water of hydration. The weak 3559 cm$^{-1}$ and 1658 cm$^{-1}$ (H-O-H bending vibration) absorption bands observed in the hydrated compound were absent in the anhydrous compound.

(Required for KN$_2$O: H$_2$O 8.0%; Found 7.6%)
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