'Mono and Binuclear Complexes Of Schiff-Base Macrocyclic and Related Ligands: Synthetic and Structural Studies'.

A Thesis Submitted for the Degree of Doctor of Philosophy by Brian Paul Murphy, B.Sc.

Faculty of Science
The Open University, Milton Keynes. November 1984

Date of submission: 5 October 1984.
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I dedicate this volume to my parents,
Alan, Julie, Adrian and
especially to Brenda.
DECLARATION

The work described in this thesis was carried out in the Department of Chemistry, The Queen's University of Belfast on behalf of the Open University, Milton Keynes, between October 1981 and September 1984. The work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

B. P. Murphy.
November 1984.
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Labor Omnia Vincit Improbus

(Virgil: Georgics)
# CONTENTS

<table>
<thead>
<tr>
<th>ABSTRACT</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>CHAPTER 1 - REVIEW</td>
<td></td>
</tr>
<tr>
<td>A Brief History</td>
<td>4</td>
</tr>
<tr>
<td>The Macrocyclic Effect</td>
<td>8</td>
</tr>
<tr>
<td>Synthesis</td>
<td>10</td>
</tr>
<tr>
<td>Transmetallation</td>
<td>13</td>
</tr>
<tr>
<td>Ligand-versus-Metal Effects</td>
<td>14</td>
</tr>
<tr>
<td>Polyether Macrocycles</td>
<td>17</td>
</tr>
<tr>
<td>Polyaza Macrocycles</td>
<td>23</td>
</tr>
<tr>
<td>Schiff-base Macrocycles</td>
<td>25</td>
</tr>
<tr>
<td>Macrocycles from DAP and Related Dicarbonyls</td>
<td>32</td>
</tr>
<tr>
<td>[1 + 1] Macrocycles</td>
<td>34</td>
</tr>
<tr>
<td>[2 + 2] Macrocycles</td>
<td>34</td>
</tr>
<tr>
<td>Thiocyanate: an ambidentate ligand</td>
<td>60</td>
</tr>
<tr>
<td>Binunclearity in Nature</td>
<td>66</td>
</tr>
<tr>
<td>Type 1 Copper</td>
<td>66</td>
</tr>
<tr>
<td>Type 2 Copper</td>
<td>66</td>
</tr>
<tr>
<td>Type 3 Copper</td>
<td>67</td>
</tr>
<tr>
<td>Haemocyanin</td>
<td>67</td>
</tr>
<tr>
<td>Tyrosinase</td>
<td>68</td>
</tr>
<tr>
<td>Laccase</td>
<td>68</td>
</tr>
<tr>
<td>Ceruloplasmin</td>
<td>68</td>
</tr>
<tr>
<td>Ascorbate Oxidase</td>
<td>69</td>
</tr>
<tr>
<td>Cytochrome-c-Oxidase</td>
<td>69</td>
</tr>
<tr>
<td>Superoxide Dismutase</td>
<td>70</td>
</tr>
<tr>
<td>Haemerythrin</td>
<td>70</td>
</tr>
</tbody>
</table>
Complexes of Q .................................................. 184
Template Synthesis .............................................. 185
Transmetallations ................................................ 186
X-ray Structure of [CuQ₁][BPh₄]₂ ............................ 200
Complexes of the Acyclic Ligands ............................. 205
Copper Complexes of the α-diimine Ligands .................. 214
The Cu (I) Complexes of btz, bt and bo ....................... 215
X-ray Structure of [Cu(btz)₂][BPh₄] ......................... 215
X-ray Structure of [Cu₂(bt)₄][ClO₄]₂ ........................... 218
The Cu (II) Complexes of biz and bi ........................... 227
Oxidation Studies of a Binuclear Cu (I) Complex ............. 234
GENERAL CONCLUSIONS ........................................... 240
APPENDIX .......................................................... 244
    Intramolecular Antiferromagnetism ......................... 245
    Electron Spin Resonance Spectroscopy ....................... 245
    Measurements of Gas Uptake .................................. 250
REFERENCES ...................................................... 251
ABSTRACT

Template condensation of the diketones, 2,6-diacyetylpyridine and 2,5-diformyl-furan with a series of diprimary amines has yielded a range of binucleating macrocyclic ligands with potential internuclear separation between $\sim7.5$ and $3\AA$. The cations used to generate the $(2+2)$ condensation product include $\text{Gp (II)}$ metal ions, $\text{Pb}^{2+}$ and $\text{Ag}^+$. Complexes of these ions and of first transition series ions, obtained by transmetallation, have been structurally characterized using electronic, infrared, n.m.r and e.s.r spectroscopy. In a few cases X-ray crystallographic structure determination has been carried out (collaboration with Dr MGB Drew at the University of Reading).

Mononuclear complexes could be made either with the large and flexible ligands or with the smallest ligands; in one case as the result of a ring-opening reaction. Binuclear transition metal complexes were obtained with all the macrocycles studied.

The degree of spin-spin interaction between the metal centres in the paramagnetic binuclear complexes varied with internuclear distance and the nature and disposition of the bridging ligand, if present.

Some simple substrate oxidations have been studied using the $\text{diCu (I)}$ complex of a 30-membered $\text{N}_6\text{O}_4$ macrocycle as catalyst.; $\text{diCu(I)}$ complexes of related acyclic ligands have been prepared and examined to discover whether they might also have potentially useful catalyst - properties.

The binuclear chemistry of Cu (I) has also been studied in complexes of a heterocyclic $\alpha$-diimine ligand where an unusual mode of coordination has been shown to exist.
INTRODUCTION

There are many important biological catalysts whose function is attributed to the occurrence of metal ions in pairs; haemocyanin (Cu ... Cu), cytochrome-c-oxidase (Cu ... Fe) and haemerythrin (Fe ... Fe) represent some of the natural examples. Consequently, there is considerable chemical interest in synthetic models; binucleating ligands which are capable of binding metal ions in pairs.

This project set out to prepare a range of binucleating ligands differing in potential metal-metal separation and in the number, nature and disposition of donor atoms. Ligands prepared include the following macrocyclic and related acyclic ligands:
The α-diimine ligands illustrated below which were included in the work also (surprisingly) gave binuclear derivatives in a few instances.

\[
\begin{align*}
&\text{X} = S : b^1z, \\
&\text{NH} : 'biz', \\
&\text{N} \\
\end{align*}
\]

\[
\begin{align*}
&\text{X} = S : b^1, \\
&\text{NH} : 'bi', \\
&\text{O} : 'bo' \\
\end{align*}
\]

All the macrocyclic and related acyclic ligands gave binuclear derivatives with first transitions series ions. With the largest 28-membered \(N_6\) macrocycles \(33N\) and \(33NMe\), the paramagnetic metal centres exerted only a weak 'through-space' interaction. In the smaller \(N_6\) ligands \(H\) and \(P\), metal centres are often connected through a 3-atom ligand bridge such as thiocyanate. The binuclear lead complex of the ligands however shows one short 'N-only' thiocyanate bridge. In \(Q\), because of the non-coordinating nature of the furan oxygen; the two metal centres are arranged in an East-West rather than North-South orientation. This results in a short (~3 - 3.5\(\AA\)) internuclear distance with resulting strong interaction operating through one or two-atom ligand bridges. The furan-based acyclic ligands \(J\), \(EDAAF\) and \(PDAAF\) have similarly short internuclear distances \(J\) values for the di-Cu (II) complexes, cover a range from \(ca -10\) for \(33N\) to \(ca -300cm^2\) for \(Q\).

A binuclear Cu (I) complex has been investigated for suitability as an oxidation catalyst.

The work described in Chapters 2 and 3 is proceeded in Chapter 1 by a review of relevant literature, covering particularly the area of Schiff-base macrocycles.
CHAPTER 1 - REVIEW
A BRIEF HISTORY

Over the last two decades the coordination chemistry of macrocyclic compounds has grown rapidly. The literature output of this branch of chemistry has developed from the few scattered reports that existed prior to 1960, to the current prolific state. Ironically, macrocyclic complexes, despite their former rarity, have been around for a very long time. In fact, they could be said to be almost as old as life itself for nature has put together metal ion and cyclic ligand in haem-proteins, chlorophyll and vitamin B₁₂ - which any green plant or multicelled organism needs. Metal complexes of the macrocycle phthalocyanin have been studied for over 40 years because they have found important uses as commercial dyes, optical and electrical materials and catalysts.

A major reason for the recent interest has been the realization that metal ions encapsulated in macrocycles could have novel and potentially useful properties - a discovery made several billions of years ago by the process of natural selection. Synthetic inorganic chemists are now trying to reproduce in vitro Nature's chemical successes by modelling biological systems.

The earliest relevant studies on coordination compounds of the synthetic macrocycles emerged from New-Zealand (Curtis) and the U.S.A (Thompson and Busch), almost simultaneously. Curtis, in 1960, described the macrocyclic product (I) - Fig.1 produced in the reaction between tris - (ethylenediamine) nickel (II) perchlorate and acetone. The generality of this reaction was subsequently demonstrated by the discovery of a range of cyclocondensations between ketones and short linear \( \omega \)-diamines. Meanwhile, Thompson and Busch carried out the first deliberate synthesis of a new macrocyclic ligand (2) - Fig.1.
In 1967 Pederson introduced a new class of macrocycle of which (3) - Fig.2 is a typical example. These cyclic polyethers became known as "crown" compounds. Their capacity to form stable complexes with the transition metals was somewhat limited but this was compensated for to some degree by their interesting ability to form isolable crystalline complexes of the alkali and alkaline earth metal ions and also by their ability to encapsulate small non-metallic molecules or ions. Lehn et al made a major advance in synthesizing the cryptands. These macropolycyclic ligands were an extension of the 2-dimensional crowns into three dimensions by joining bridgehead nitrogens with polyether strands (4) - Fig.2. Such ligands could totally encapsulate a metal ion that fits in a three-dimensional cavity and in doing so form an inclusion complex or cryptate. Elegant synthetic work by Lehn and co-workers extended the macrobicyclic ligand series to the purpose-built macrotri- and tetracycles e.g. (5) - Fig.2.
A final example of sophisticated ligand design is an illustration of the progress made in the field over the last 20 years. Busch et al are currently studying totally synthetic iron and cobalt-containing complexes that reversibly bind oxygen at room temperature. This type of macrocycle has been dubbed laccunar (from Latin meaning hollow or gap). The design incorporates a "dry-cave" bounded by bulky hydrophobic groups on one side of the iron complex, the other being blocked by monodentate ligand or solvent. It is the built-in 'dry-cave' which permits the oxygen to bind but not oxidize the Fe(II), thus taking the science one step closer to replicating the unique $O_2$-binding function of haem-Fe.

Apart from the chemical properties of macrocyclic complexes, spin-offs from macrocyclic chemistry have included organic synthesis in the presence of metal ions and rationalization of the unusual behaviour of
the haem-proteins and other metalloproteins. Synthetically, 'tunable' environments of the macrocyclic type also bear relevance to areas of metal-ion catalysis. Biochemistry itself is all about catalysis on a major scale, and Nature's armies of bugs are the best chemists of all. It is therefore clear that modelling biochemistry is an important objective for the inorganic chemist.

Fig. 3
THE MACROCYCLIC EFFECT

From the very earliest studies it was realised that macrocyclic ligands could impart unusual properties to their complexes. Examples include slow rates of formation and dissociation of the complex, high ligand field strengths and large stability constants for macrocyclic complexes when compared with the corresponding open-chain ligands. The term 'macrocyclic effect' was coined in recognition of these properties. It is a collective term incorporating both kinetic and thermodynamic components.

The kinetic effects have been illustrated by Cabiness and Margerum, in a study of the comparative rates of dissociation and formation of copper (II) complexes of, for example, macrocycle \( L^1 \) versus the open-chain analogue \( L^2 \), Fig. 4.

\[
\text{FORMATION: } \text{Cu}^{2+}(\text{aq}) + L \xrightarrow{K_f} \text{CuL}^{2+}
\]
\[
\text{DISSOCIATION: } \text{CuL}^{2+} + n\text{H}^+ \xrightarrow{K_d} \text{Cu}^{2+}(\text{aq}) + L^1\text{H}_n^{n+}
\]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( K_f ) ( (\text{M}^{-1} \text{s}^{-1}) )</th>
<th>( K_d ) ( (\text{s}^{-1}) )</th>
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<tr>
<td>( L^1 )</td>
<td>( 5.8 \times 10^2 )</td>
<td>( 3.6 \times 10^{-7} )</td>
</tr>
<tr>
<td>( L^2 )</td>
<td>( 2.9 \times 10^4 )</td>
<td>( 4.1 )</td>
</tr>
</tbody>
</table>

Fig. 4
Although the rate of formation is somewhat retarded the open-chain ligand $L^2$ dissociates ca $10^7$ times faster than $L^1$. If the mechanism of the dissociation is envisaged as an "unwrapping" process whereby each nitrogen donor, starting at one end, is "unfastened" in sequence and immediately replaced by a solvent molecule then, after four such replacements the linear tetra-amine will have dissociated. This sequence, however, is not possible in the case of coordinated macrocycle $L^1$ where the terminal nitrogen does not exist. Dissociation of $L^1$ is thought to require an initial folding of the macrocycle before the breaking of the first bond $^{19}$.

The enhanced thermodynamic stability is not merely due to an increased chelate effect. Hinz and Margerum $^{22,23}$, in a thermodynamic study of the above $L^1/L^2$ system with Ni (II), suggested that $\Delta H^0$ for complexation of the macrocycle is more negative than for the corresponding linear ligand because the open-chain requires a greater degree of solvation in its uncomplexed state. This associated solvent ($H_2O$) must be displaced on complex formation. Recent studies by Clay et al $^{24}$ on similar cyclic and non-cyclic copper complexes relate the thermodynamic origins of the macrocyclic effect to ligand solvation rather than any significant difference in metal-ligand interaction. Paoletti et al $^{21}$ and Kodama and Kimura $^{25,26}$ concluded that entropy contributions were the dominant factors determining the observed stabilities. Paoletti et al $^{27-29}$ later concluded, from enthalpy measurements, that both enthalpy and entropy must contribute.

The entropy contribution will be favourable since cyclic ligands do not lose configurational entropy on coordination to the same extent as non-cyclic ligands. The enthalpy effect depends upon ligand solvation, the match between metal ion size and the macrocyclic 'hole' $^{27,30}$ and on the stereochemical preferences of the metal. The enthalpy term may therefore be favourable or unfavourable in comparison.
to the open-chain. An extension of the macrocyclic effect - the 'cryptate effect' is used to describe the analogous enhanced stability of complexes of the polyether cryptands.

SYNTHESIS

The synthetic routes to macrocyclic ligands fall into two main categories. The first; direct synthesis by conventional organic chemistry and the second; synthesis in situ involving cyclization in the presence of a metal ion - known as 'template' synthesis. It should be noted that new macrocycles may also be prepared by the modification of a parent macrocycle, previously synthesized by one of the above procedures. Many macrocycles may be made by both methods.

Direct synthesis has been extensively employed in the preparation of cyclic tetramines, crowns and cryptands. The two latter classes of macrocycles are discussed in more detail later.

Yields for directly synthesized macrocycles are frequently very low because of competing intermolecular polymerization reactions. This problem is usually controlled by completing the final ring-closure step under conditions of high dilution. Several cyclic amines have been prepared in high yield by direct synthetic routes. A typical example is the preparation of L^3 ('cyclam'), Fig.5, which is achieved in 80% yield.

Fig.5
When good yields can be achieved, the ease of purification and characterization of the free ligand is a positive advantage. In addition, comparisons of the various spectra of free ligand are useful in the interpretation of subsequent metal-complex spectra. Perhaps the forte of such an approach is the generality of the process which is limited, in principle, only by the nature of the reactants; unlike the template process (see below) which is much more metal-ion specific.

Cyclic polyethers excepted, the template or in situ synthesis, is the most frequently used method of forming macrocycles. While many macrocyclic ligands can be prepared by both procedures the in situ techniques have provided many other macrocycles that would not have been possible otherwise. Addition of a metal ion before the macrocyclic ring-closing step can result in a dramatic improvement in yield.

Several factors govern the efficacy of a metal ion as a template; these are:

1. Metal ion size.
2. Electronic configuration.
3. Size of macrocycle to be formed.
4. The number and nature of donors in the macrocycle.
5. The possible conformations available to the coordinated macrocycle.

Such factors give rise to the coordination template effects. These effects are broadly classified as either kinetic or thermodynamic.

Kinetic: The kinetic template effect is operative if the steric course of a series of stepwise reactions is controlled by the metal ion. The effect has been studied by Busch et al. \(^{36-38}\). The formation of (8) - Fig.6, illustrates this point. Ring-closure proceeds via, first, a slow step (i) involving attack at one coordinated mercaptide. The second mercaptide and halide are now orientated (7) such that, (ii) a rapid ring-closure step can occur. Comparative reaction with benzyl bromide showed only two slow consecutive steps \(^{38}\).
Thermodynamic: A metal ion may promote the formation of a macrocycle by removing it from equilibrium as a macrocyclic – metal complex (either soluble or insoluble). When this is the case the thermodynamic template effect is in operation.

The template effect should not be confused with the macrocyclic effect. It deals with the intervention of a metal ion in a reaction between organic components to form the macrocycle. The macrocyclic effect is concerned with the stability of the product of reaction between preformed macrocycle and metal ion.

Most template syntheses probably involve the kinetic template effect, although it is not always possible to distinguish between these effects. The 'edge' that the template synthesis has over the direct method is that it has allowed the easy isolation of many macrocycles which are unstable as the free ligand by forming the stable complex.
TRANSMETALLATION

Since not all metal ions are effective as templates for all macrocycles, the accessibility of new metal complexes was, in the early days, somewhat limited. However, transmetallation, a process whereby one metal ion, typically the template ion, is replaced by another, different metal ion via an exchange process in solution, has been used by Nelson et al.\(^\text{39}\), Fig.7. The kinetic lability of the complexed template ion provides the key to subsequent transmetallated derivatives which become possible when a short-lived, liberated macrocycle is 'captured' and stabilized by coordination to the second, new metal ion, before decomposition occurs.

\[ \text{Fig.7} \]
LIGAND-VERSUS-METAL EFFECTS

A common thread connecting many of the observations in this thesis is the role played by ligand/metal requirements in the synthesis and chemistry of the complexes. This next section concentrates on this interplay.

The design of any complex must include consideration of several factors:

(1) The stability of the complex: This will be dependent upon

(a) the relative strength of the donor-acceptor interactions, cf Pearson's hard/soft acid/base theory. E.g. in the generalized template synthesis of Fig.8. When $X = S$ the 'soft' Ag(I) ion is effective as a template, whereas when $X = O$ the 'hard' Mg$^{2+}$ ion will template the reaction.

(b) Chelate effects: Metal chelate complexes are more stable than their unidentate analogues and 5 and 6-membered rings are by far the most common.

(2) Geometrical consequences: Factors influencing the geometric arrangement of donors around a metal include;

(a) The shape and flexibility of the ligand.

(b) The nature of the donor atoms e.g. nitrogens are primary, secondary, tertiary amine, imino, azo. Each type of nitrogen will have a characteristic spatial distribution of electrons e.g. amines - $sp^3$ and imines - $sp^2$. Therefore, coordination of different types of donor can enforce different conformations of the ligand.

(c) Stereochemical dictates of metal ion: The stereochemical preference of a metal ion may impose a particular conformation on
Fig. 9
the ligand. E.g. 4 - coordinate complexes may have tetrahedral or square planar arrangement of donors; 6 - coordinate octahedral or trigonal prism; 5 - coordinate square pyramidal or trigonal bipyramidal e.g., Fig.9. The tetrahedral di-Cu(I) sites of (9) - Fig.9 leave the macrocycle in a planar conformation while the square planar di-Cu(II) sites of (10) require the same macrocycle to be bent.

(d) Size of metal ion: This factor is of obvious importance in macrocyclic chemistry e.g. rigid molecules which are too small to encircle the metal ion can be accommodated in structures where the metal lies above the plane of the macrocycle or as a molecular sandwich e.g., Fig.10. The Ca(II) ion (Pauling radius $0.99\text{Å}$) fits neatly into the macrocycle (11) while the larger Sr(II) ion (Pauling radius $1.13\text{Å}$) must sit outside the macrocyclic plane (12).

The principles outlined above will be encountered many times in the course of this review.
Attention has already been given to the pioneering work of Pederson on the synthetic macrocyclic polyether 'crowns'. A typical synthetic reaction is given below; it involves a condensation reaction between a bis-phenol and a dichloride, Fig.11.

The yields are strongly dependent on the nature of $M^+$ implying a template role for the cation. In the above example substantial improvements in yield are obtained on progressing along the series of cations: $M^+ = n$-Bu$_4$N$^+$, Na$^+$, K$^+$, the rationale being that while K$^+$ fits into the cavity comfortably, Na$^+$ is too small and n-Bu$_4$N$^+$ too large.

The ability of the 'crowns' to form stable complexes of alkali and alkaline earth metal ions is a reflection of the nature of the donors, namely, the relatively non-polarizable, or 'hard', oxygen donors. Some mixed donor molecules have also been produced containing sulphur and nitrogen donors.

The momentum of the research in this branch of macrocyclic chemistry was maintained not only by the hitherto undivined area of alkali metal coordination chemistry but also by applications concerning the biological role of Li$^+$, Na$^+$ and K$^+$ cations, for example, in an effective treatment of psychiatric disorders with lithium salts, the Na$^+$ - K$^+$ 'pump' etc.
TYPE 1

TYPE 2

TYPE 3

TYPE 4

Fig. 12
There are basically four types of crown complexes as evidenced by crystal structures. Illustrations in, Fig12.

Type:-

1. Metal fits cavity of crown.

2. Large cation sitting above plane of crown.

3. Small cation wrapped by crown e.g. the 'tennis-ball seam' or, forms binuclear complexes.

4. Not all potential donors are used.

The most spectacular property of the crowns is their ability to solubilize salts in organic solvents. For example, KMnO₄ can be made to dissolve in benzene by addition of perhydrodibenzo [18]-crown. Solubilization of potassium hydroxide in aromatic hydrocarbons yields a 0.2M basic solution. The strong basicity of these solutions is attributed to the presence of 'naked' hydroxide ion, which is unprotected by solvation in attack upon substrate. Many synthetic applications of the use of 'naked' anions (anion activation) have already been realized.

Early research into the chemistry of the 3-dimensional macropoly-cyclic cryptands has been dominated by Lehn and Weiss. The various topologies of such ligands are given in Fig.13; Z represent a bridgehead atom.
A, defines a 2-dimensional cavity such as occurs in the crowns, already discussed. The macrocycles of higher cyclic order are the cryptands: B, -[2] cryptand; C, -[3] cryptand; D, -spherical and E, -[4] cryptand. The cryptands B, C, D and E are capable of forming inclusion complexes or cryptates in which the substrate is contained within the 3-dimensional cavity.

The macrocyclic effect is particularly strong with cryptates and so it has been given a special name - the cryptate effect. Selectivity for alkali and alkaline earth metals is pronounced and can be related to the match between cavity size of the ligand and the metallic diameter.

The macrotricyclic ligands of type D, the spheroidal [3] -cryptand, have been shown to be able to bind, in addition to metal ions, cationic, anionic, and molecular species such as NH₄⁺, Cl⁻, and H₂O. Binding of Cl⁻ by an array of zwitterionic hydrogen bonds has been observed also for cryptand B, Fig. 14. Anion coordination chemistry has been reviewed by J-M Lehn.

Cryptate solutions exhibit the same anion activation effects as do the crown ethers but the activation is even more pronounced, for example, cryptate solutions can be prepared containing substantial concentrations of solvated electrons. Protection of the cation within a polycyclic ligand has also led to the preparation of stable crystals containing the alkali metal anions.

The macrotricyclic, cylindrical ligands, type C, formed from two macrocyclic units linked by two bridges, have been designed in the face-to-face fashion in anticipation of their binuclear chemistry. They are capable of binding more than one metal; one into each end of the 'cylinder'. The topology of these macrocycles, as of any binucleating ligand presents two interesting possibilities:
Fig. 14

(a) Metal --- metal distance can be controlled by varying the length of the bridges and -
(b) Asymmetrical 'cylinders', can be synthesized therefore opening up the fields of heterometallic and mixed valence chemistry.

The binuclear copper (I) and copper (II) complexes, prepared by Lehn, and structurally defined by Weiss, are considered as models for the type 3 copper proteins such as haemocyanin (discussed later).

The synthesis of closely related macrocycles displaying interesting geometries has recently been achieved. These compounds, known as the catenanes, include novelties like knotted and linked rings and the mobius strip. As early as 1961 they were discussed in a theoretical article on chemical topology. The Mobius strip macrocycle, a one-sided, one-edged 'isomer' of a cylinder, with a single $180^\circ$ twist about its long axis, was reported by Walba et al.
The first metallocatenane was that produced by J-P Sauvage et al., of a highly stable Cu(I) complex of a catenand of two interlocking crown polyether-type ligands. The high stability is reflected in the observation that this complex could not be electrochemically demetallated. The topology of the ligand, shown in Fig.15, highly favours tetrahedral geometry around the metal complex. The enforced mutuality of the two cyclic moieties prevents dissociation of either, hence producing the high degree of stability of its complexes.

Fig.15
The work of Busch et al. exemplifies the approach of purposeful ligand design. They have shown that for a given metal ion there is an ideal macrocycle ring size for which there are abnormally strong metal-donor bonds and high $D_Q$ values. Rings that fit specific metals produce extreme immobilization resulting in the observation of rare oxidation states. Variation of the macrocyclic structure keeping both fixed stereochemistry and constant donors (four nitrogens) has then allowed redox potentials to be varied over wide ranges (2V). \(^{30}\)

The stabilization of unusually high oxidation states of transition metals (Ni (III) and Cu (III)) has been achieved with macrocycles such as L and L, Fig.16.

While Busch et al. demonstrated that progressive unsaturation and/or alkylation made attainment of Ni (III) more difficult, Fabrizzi found that ring expansion from L to L had similar effects.

**Fig.16**
Fig. 17
Studies on the closely related amide macrocycle \( L \) have revealed unusually low potential, \( E^0 \), for the \( M(III)/M(II) \) couple (\( M = Ni, Cu \)) \(^{98,99} \). More recently, Kimura and associates \(^{100} \) have reported facile \( E^0 \) (0.24 versus SCE) generation of \( Ni(III) \) from \( Ni(II) \) complexes of \( L \). Moreover, in air oxidations, the binding, activation and oxygen insertion (13 - Fig.17) via aromatic hydroxylation of substituent (\( R = CH_2C_6H_5 ; L \)) or solvent (benzene) is reported. These biomimetic properties have been traced to the special steric and electronic effects that are imposed by the two basal deprotonated amide (imide) groups and an axial nitrogen donor in the rigid square pyramidal structure.

Recent reports by Meyerstein \(^{101,102} \) have shown that saturated amino ligands, \( L \), are capable of stabilizing \( Ni(I) \) and \( Cu(I) \) to the extent that they do not pick up \( O_2 \) in aqueous solution.

Polyazamacrobicyclic ligands, or sepulchrates, have been developed by Sargeson \(^{103-105} \). The transition elements \( Cr \) ——— \( Zn \) have been encapsulated as illustrated in (14) - Fig.17

**SCHIFF-BASE MACROCYCLES**

The condensation reaction between amine and carbonyl to form a Schiff-base has been widely exploited in the synthesis of nitrogen-donor macrocycles. The mechanism is given in Fig.18. In the absence of a metal ion acid catalysis \(^{92} \) is often required to activate the \( C = O \).

In the metal-ion controlled reaction, the metal functions as an acid drawing electron density away from the coordinated carbonyl group, activating it towards nucleophilic attack by an incoming uncoordinated amine.
Fig 18
Self-condensation Products of O-aminobenzaldehyde

The propeller shaped tri- and tetradeinate ligands, TRI and TAAB, Fig.19, are obtained on condensation in the presence of Ni (II) 107-109. Selective crystallization of the perchlorate salts allowed the separation of two complexes. X-ray structural studies confirmed the mode of coordination of the tridentate TRI, as being the 'capped' structure in Fig.19, while both high-spin and low-spin forms of TAAB 111 were found to be planar. By comparison, the condensation in the presence of the Cu (II) produces planar quadridentate Cu(TAAB)(NO₃)₂ 107-111 and not Cu(TRI)²⁺ 113.

These observations may be rationalized by the stereochemical requirements of the Cu (II) and Ni (II) ions. The Jahn-Teller distorted Cu (II) ion will be expected to exert certain restrictions on the metal-ion controlled self-condensation and rearrangement reactions, when compared with a non-distorted species such as Ni (II). These restrictions presumably eliminate the possibility of formation of TRI on Cu (II) by making axial sites unavailable for coordination of intermediates in the macrocycle formation steps.

More generally Zn (II) 114, 115, 116, Fe (II) and Fe (III) 111, 118 form template complexes of TAAB, while Mn (II) 119 is ineffective as a template for either TRI or TAAB. The larger size of the Mn (II) ion may be responsible. Similarly Uranyl (VI), where the axial sites needed in TAAB are blocked by the oxygen atoms of UO₂²⁺, is an ineffective template and produces a non-cyclic product. However, on treatment with water the cyclic trisanhydratetramer 120 is produced. Presumably the in-plane radius of UO₂²⁺ is better suited to the cavity of the tetramer. Formation of the trimer, which would then only be possible using axial sites, is precluded by the presence of the axial O₂⁻ atoms.
Fig. 19

TRI

TAAB

\[ X = \text{NMe, S} \]

(15)

(16)
The complexes of TAAB are activated towards nucleophilic attack at the imine linkages. Alkoxides add across in the trans manner illustrated in (15) - Fig.19. Nucleophilic addition reactions with Cu (II) and Ni (II) TAAB complexes have been extended to include diolanions, amines and diamines e.g. \([O-(CH_2)_2-X-(CH_2)_2-O]^2+\) yields the square pyramidal 'basket' structure (16) - Fig.19. The fact that \([O-(CH_2)_5-O]^2-\), will not produce a 'basket' implies that coordination of X occurs before the addition reaction i.e. a template mechanism is operative.

The above discussion has outlined examples of how metal-ion size and geometrical preference can control the product obtained.

Jager-type Macrocycles

The so-called Jager macrocycles, produced by reaction between diamines and \(\beta\)-ketoiminato complexes of the type in, Fig.20, have recently gained fresh prominence because of the potential that some structurally modified derivatives have as models for biological systems. They are also examples of how ligand design can provide the means to modify the chemistry of a metal ion. A generalized synthetic scheme is given in Fig.20.
Busch et al. found that while attempting ring-closure reactions they could isolate two important families of ligand, from the same reaction pot. These ligands were the dimeric face-to-face macrocycles, (18) - Fig.21 and the monomeric lacunar macrocycles (17) - Fig.21. It was found that when the substituent on the bridgehead nitrogen, $R^2$, is methyl then pure monomer lacunar-type ligands were obtained. However, the corresponding complexes with $R^2 = H$ all form two isomeric species. In addition, when $R^1 < (\text{CH}_2)_10$ then two isomers are obtained even when $R^1 = \text{CH}_3$.

Much more interest has been shown in the lacunar complexes. Systematic variations of $R^1$, $R^2$ and $R^3$ have been manipulated to 'home-in' on a particular desired property of the final complex, e.g. dioxygen binding and/or substrate inclusion. From (17), - Fig.21, it can be seen that the nature of $R^1$ will dictate the 'head-room' available within the lacuna. Thus when $R^1 = (\text{CH}_2)_3$ and $R^2 = R^3 = \text{CH}_3$ a tight cavity exists which will not permit access of $O_2$ to the internal axial site and the Ni (II), Co (II) and Fe (II) complexes will not bind $O_2$ . If however $R^1 = \text{m-xylyl}$ then reversible $O_2$ binding is achieved for Co (II) and Fe (II) systems . The $O_2$-binding properties can be 'fine-tuned' by variation of $R^2$ and $R^3$. When $R^2 = C_6H_5$ and $R^3 = \text{CH}_2C_6H_5$, optimum binding by Fe (II) is achieved ($K_{O_2}^{235} = 0.55$, $K_{O_2}^{273} = 0.0025$).

By raising the ceiling of the lacuna it is theoretically possible to create room for the inclusion of substrate which is held close to bound dioxygen and then, hopefully, observe monooxygenase activity. Systems in which sizeable substrates such as dimethyl phenol, (19) - Fig.22, can approach the metal centre closely have potential as models for cytochrome P450, however, activity has not yet been achieved.
Macrocycles Derived From 2,6-DAP and Related Dicarbonyls

Condensation reactions between dicarbonyl compounds such as 2,6-diacylpyridine (DAP) and diprimary amines have played a central role in the synthesis of macrocyclic ligands. Usually the synthesis is performed in the presence of a metal ion which serves to direct the steric course of reaction preferentially towards cyclic rather than oligomeric/polymeric product; the kinetic template effect, and/or to remove the product from equilibrium by coordination; the thermodynamic template effect (see earlier discussion). The chosen size of the template ion can be further used to direct the condensation between one molecule of dicarbonyl and one molecule of diprimary amine or between two molecules of each reactant, thus forming [1 + 1], [2 + 2] or [4 + 4] macrocyclic products, respectively. This section will use this distinction between the macrocycles in the discussion of their coordination chemistry.

DAP has proved to be a particularly useful precursor dicarbonyl, with its strongly donating pyridine 'anchor' which serves to hold and activate the carbonyl towards nucleophilic attack.
### TABLE I

<table>
<thead>
<tr>
<th>Ligand</th>
<th>X</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>m</th>
<th>n</th>
<th>Template M&lt;sup&gt;2+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;sup&gt;9&lt;/sup&gt;L</td>
<td>N</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>3</td>
<td>3</td>
<td>Zn', Cu', Ni', Co', Mn</td>
</tr>
<tr>
<td>&lt;sup&gt;10&lt;/sup&gt;L</td>
<td>N</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3</td>
<td>3</td>
<td>Zn, Cu, Co&lt;sup&gt;'&lt;/sup&gt;.</td>
</tr>
<tr>
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<td>H</td>
<td>H</td>
<td>3</td>
<td>3</td>
<td>Zn.</td>
</tr>
<tr>
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<td>N</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>3</td>
<td>4</td>
<td>Zn, Cu, Ni.</td>
</tr>
<tr>
<td>&lt;sup&gt;13&lt;/sup&gt;L</td>
<td>P</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>3</td>
<td>3</td>
<td>Ni&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> ref. 147

---

16. 
L : R = H
17. 
L : R = CH<sub>2</sub>NMe<sub>2</sub>

Fig. 23
(1) \( [1 + 1] \) Macrocycles

(i) Tetradentate

The 14-membered tetradentate \( \text{"N}_4 \) ligand \( L_9 \), Fig. 23, was one of the earliest demonstrations of 'template effect'. It can be synthesized by the \textit{in situ} reaction of DAP with 3,3'-diaminodipropylamine in the presence of Ni (II), Cu (II), Mn (II), Co (II) and Zn (II)\(^{140-143}\).

Single crystal X-ray structure determinations show the macrocycle to be coordinated in the distorted square-planar fashion around the metal ions. Prince \textit{et al.}\(^{144}\) and Kepour and Stotter\(^{145}\) have extended the range of \( \text{"N}_4 \) macrocycles, \( L_L \). Table I summarizes the tetradentate analogues of \( L_9 \). It is interesting to note that the Co (III) derivative of \( L \) \( ^{10}_{\text{CoLCl}} \) \( \text{[ClO}_4\text{]}^{146} \), has been shown by X-ray structural analysis to contain a 3-membered chelate ring where the N-methyl carbon atom of \( R_2 \) has become deprotonated and is \( \sigma \)-bonded to the Co (III) ion. Fig. 24.

![Macrocycle structure](image)

**Fig. 24**

The Ni (II)\(^{148}\), Fe (II)\(^{149}\), Co (II) and Co (III)\(^{150}\), and Cu (II)\(^{151}\) complexes exist also for the meso form of \( L \) and Ni of \( L \).\(^{16,17,152}\)
(ii) Pentadentate

In 1964 Curry and Busch\textsuperscript{153} reported the \textit{in situ} synthesis of the 15-membered pentadentate ligand $L$, Fig.25, from DAP and 3,6-diazaoctane-1,8-diamine in the presence of iron (II). When, as a result of X-ray and other investigations\textsuperscript{154-156}, the complex was formulated as the 7-coordinate $\mu$-oxo-dimer $\left[\left(Fe\,^{18}\,^{15}L\,(C\,^{10}O\,^{4})\right)\left(C\,^{10}O\,^{4}\right)\right]_{2}\,H_{2}O$ with $L$ occupying the equatorial plane, it sparked-off a series of investigations into the structural elucidation of 7-coordinate geometry—a rarity, at the time, among transition metal complexes. It has since transpired, as a result of single crystal structural determinations on an extensive range of metal complexes of $L-\,^L$ that the 15-membered $L$ and L and 16-membered $L$ rings prefer to dispose their five donor atoms in a pentagonal planar arrangement about the central metal. 7-coordinate pentagonal bipyramidal geometries were thus demonstrated for Mg (II), Mn (II), Fe (III), Fe: (II), Zn (II), Cd (II) and Sn (IV), and 6-coordinate pentagonal pyramidal for Co (II), Ag (II), Cd (II), and Hg (II) complexes\textsuperscript{154,157-165}. Table II summarizes the metal ions effective in the templated synthesis of $L-\,^L$. Noticeable by their absence are Ni (II) and Cu (II). This may be due to the strong preference of these ions for square-based stereocchemistries (octahedral, tetragonal, square pyramidal, square planar) in which the bonding orbitals are disposed orthogonally. Calculations have shown\textsuperscript{166} that d and d ions attain a greater crystal field stabilization energy from octahedral rather than $D_{5h}$ symmetry. Although a few pentagonal bipyramidal complexes of these ions are known\textsuperscript{167,168} there is clear evidence at least for Ni (II), that this is an unstable stereochemistry relative to the octahedron (see below).
TABLE II

<table>
<thead>
<tr>
<th>Ligand</th>
<th>X</th>
<th>m</th>
<th>n</th>
<th>Template M</th>
</tr>
</thead>
<tbody>
<tr>
<td>L^{18}</td>
<td>NH</td>
<td>2</td>
<td>2</td>
<td>Mn, Fe, Zn, Co\textsuperscript{II}, Cd, Hg, Sn(IV), Pb.</td>
</tr>
<tr>
<td>L^{19}</td>
<td>NH</td>
<td>2</td>
<td>3</td>
<td>HgCd, Mg, La, Mn, Fe\textsuperscript{II,III}, Co, Ag, Zn.</td>
</tr>
<tr>
<td>L^{20}</td>
<td>NH</td>
<td>3</td>
<td>2</td>
<td>Mn, Ag, Cd, Hg, Sn(IV), Pb.</td>
</tr>
<tr>
<td>L^{21}</td>
<td>NH</td>
<td>3</td>
<td>2</td>
<td>Mn, Ag, Cd, Hg, Sn(IV), Pb.</td>
</tr>
<tr>
<td>L</td>
<td>O</td>
<td>2</td>
<td>2</td>
<td>Cd, Zn, Mg, Sr, Ba, Mn, Fe, Co\textsuperscript{II}, Ag, Pb.</td>
</tr>
</tbody>
</table>

Fig. 25
Ni (II) complexes of these ligands have been prepared by a trans-
metallation process from e.g. the dimeric $[\text{Ag L}_{19}]_2[\text{ClO}_4]_2$ in dry ROH
(R = CH$_3$ or C$_2$H$_5$). The resultant complex contains the new, more flexible
ligand L produced by the addition of ROH across one of the imine
linkages. In doing so this part of the macrocycle becomes saturated
and therefore is no longer in a planar conjugated relationship with the
pyridine ring and the remaining azomethine moiety. This confers the
necessary flexibility on the ligand to coordinate on an octahedron.

If the reaction is carried out under 'wet' conditions, hydrolysis
occurs to yield the octahedral complex of the ring opened ligand L
Fig.25. In support of this 'flexibility hypothesis', it is found that the
larger 17-membered macrocycle L, on transmetallation, occupies five
octahedral sites in Ni (II) without the addition of ROH.

Thus, in summary, L, L and L demonstrate how unusual geometry,
namely pentagonal bipyridal, can be imposed on a metal by the con-
formation of a ligand while the converse has been observed for the case
of the Ni (II) complexes. In this latter case a new conformation via
chemical modification is imposed on the ligand by the stereochemical
requirements of the metal ion.

A series of seven-coordinate, pentagonal bipyramidal, complexes of
the series Mn (II) - Zn (II) has been obtained using the open-chain
ligand L. Their structures are exemplified by the representative Cu (II)
complex which uses the primary amine groups as axial donors, the penta-
gonal plane comprising the remaining 'N$_3$X$_2$' donors (X = N for L)
Fig.26. The seven-coordinate Ni (II) complexes undergo a slow (4 days
at ambient temperature) isomerization to the octahedral $[\text{Ni L}]^{2+}$
Fig.26. L can be produced by the addition of one NH group across the
adjacent C = N bond.
An analogous series exists also for the open-chain ligand $L^2_6$ ($X = O$), Fig.26. In this case the Ni (II) complexes are stable since substitution of NH by ether oxygen preempts the isomerization described above. Returning to the pentadentate macrocycles further illustration of metal stereochemistry dictating ligand formation can be seen in the series of dicyano derivatives of $L^{18,19}$ and $L^{21}$. [$Fe L^{18,19} (CN)_2$] $XH_2O$ ($X = 0, 0.5,$ or $1$) are diamagnetic, while [$Fe L^{21} (CN)_2$] ·$H_2O$ is high spin ($\mu_{eff} = 5.09$ B.M.) at 293K falling to 3.37 BM at 93K. Mossbauer data of the latter derivative at 93K implies the metal ion exists in a 1:1 ratio of $S = 0 : S = 2$ spin states. Since $S = 0$ ground state is precluded in $D_{5h}$ symmetry the implication is that the CN⁻ ligands coordinate in a trans-octahedral fashion, requiring the expulsion of one donor, probably a secondary amine group of $L$ or $L'$ from the coordination sphere. This would produce a large CFSE advantage for a $t_{2g}$ $E_g^0$ system.

The hysteresis effects which accompany the $(S = 2) \rightarrow (S = 0)$ spin crossover may be produced by a lattice alteration accompanying a change in stereochemistry from $D_{5h}$ to $O_h$. 
TABLE III

<table>
<thead>
<tr>
<th>Ligand</th>
<th>R</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Template M(^+/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L^{27})</td>
<td>H</td>
<td>NH</td>
<td>(-[\text{CH}_2]_2)</td>
<td>(-[\text{CH}_2]_2)</td>
<td>Mn, Zn 172</td>
</tr>
<tr>
<td>(L^{28})</td>
<td>H</td>
<td>O</td>
<td>(-[\text{CH}_2]_2)</td>
<td>(-[\text{CH}_2]_2)</td>
<td>Mn, Zn, Mg 153, 172</td>
</tr>
<tr>
<td>(L^{29})</td>
<td>H</td>
<td>NH</td>
<td>(-[\text{CH}_2]_2)</td>
<td>(-[\text{CH}_2]_2)</td>
<td>Mn, Zn 172</td>
</tr>
<tr>
<td>(L^{30})</td>
<td>H</td>
<td>S</td>
<td>(-[\text{CH}_2]_2)</td>
<td>(-[\text{CH}_2]_2)</td>
<td>Mn, Zn 172</td>
</tr>
<tr>
<td>(L^{31,32})</td>
<td>Me</td>
<td>S</td>
<td>(-[\text{CH}_2]_a^m)</td>
<td>(-[\text{CH}_2]_a^m)</td>
<td>Ag, 165</td>
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<tr>
<td>(L^{33,34})</td>
<td>Me</td>
<td>S</td>
<td>(-[\text{CH}_2]_m^c)</td>
<td>(-[\text{CH}_2]_m^c)</td>
<td>R, Zn, Cd, Th (111) 175-177</td>
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<tr>
<td>(L^{35,36})</td>
<td>Me</td>
<td>P-Ph</td>
<td>(-[\text{CH}_2]_b^m)</td>
<td>(-[\text{CH}_2]_b^m)</td>
<td>Ag, Cd 174</td>
</tr>
</tbody>
</table>

a \(L : m = 2, n = 3\)  
b \(L : m = 3, n = 2\)  
c \(R = [\text{CH}_2]_2 : L^{33}\)  
32 \(L : m = 3, n = 2\)  
35 \(L : m = n = 3\)  
34 \(o-	ext{C}_6\text{H}_4 : L^{34}\)

Fig. 27
In the Cu (II) complexes of \( L^{32} - [CuL^{32}]^{2+}, [CuL^{32}(NCS)]^+ \) and \([CuL^{32}(NCS)_2]\) - two, one and neither macrocycle S-atoms atoms are involved in coordination, respectively, Fig.28. Similarly, the high-spin \( S = 2 [FeL^{32}Cl(MeOH)]^+ \) and low-spin \( S = 0 [FeL^{32}X]^+ (X = NCS^-, I^-) \) complexes reveal, respectively, coordination of one and two sulphur atoms situated at the apices of an octahedron, Fig.28.

Zn (II) complexes of the 'N\(_3\)S\(_2\)' macrocycles \( L^{33} \) and \( L^{34} \) are thought to be seven-coordinate with the ligand in the equatorial plane and axial halide ions. Other pentadentate analogues \( L^{27} - L^{30} \) of pyridyldiimine macrocycles are formed from Schiff-base condensations using 2,6-diformyl-
pyridine (DFP) and a series of diprimary amines using Mn (II), Zn (II) and Mg (II) as template ions.

Fenton and Cook found that by using a variety of alcohol solvents the macrocycles $L$ could be obtained by a metal-free condensation of DFP and diprimary amines ($X = 0$). In these ligands the ROH has added across the $C=N$ moiety in order to relieve angular strain, Fig. 29.

![Diagram of ligand structure](image)

$L_{37}: R = \text{Me}$

$L_{38}: R = \text{Et}$

$L_{39}: R = \text{n-Bu}$

Fig. 29

(111) Hexadentate

Condensation of 1, 4, 7, 10, 13-pentazatridecane in the presence of iron (II) chloride yields bronze crystals of the complex Fe ($L -H$) Cl$_2$, Fig. 30, potentially, hexadentate ligand $L$. The structure of the complex is unknown but could easily involve a dimeric oxygen-bridged
structure analogous to that already discussed for the pentadentate ligand \( \text{L} \).

The closely related ligands \( \text{L} \), with oxygen donors, have been reported by Fenton et al. Pb (II), the alkaline earth metals \( \text{Hg (II)} \), and Cd (II) have already been used as templates – summarized in Table IV, Fig. 31. The potential value of such macrocycles in the removal of the toxic metals Pb, Cd and Hg from the body has been pointed out.

Fenton's team has also demonstrated the ability of Ca (II), Sr (II), Ba (II) and Pb (II) to function as templates in the formation of macrocycles \( \text{L} \) and \( \text{L} \).
TABLE IV

<table>
<thead>
<tr>
<th>Ligand</th>
<th>R</th>
<th>M</th>
<th>Templates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L^1$</td>
<td>-(CH$_2$)$_2^-$</td>
<td>H</td>
<td>Ca, Sr, Ba, Pb, Cd, Hg</td>
</tr>
<tr>
<td>$L^2$</td>
<td>-(CH$_2$)$_2^-$</td>
<td>Me</td>
<td>Ca, Sr, Ba, Pb, Cd, Hg</td>
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<tr>
<td>$L^3$</td>
<td>o-C$_6$H$_4^-$</td>
<td>H</td>
<td>Ca, Sr, Ba, Pb</td>
</tr>
<tr>
<td>$L^4$</td>
<td>o-C$_6$H$_4^-$</td>
<td>Me</td>
<td>Sr</td>
</tr>
</tbody>
</table>

Fig. 31
[2 + 2] Macrocylikes

Whether \([1 + 1]\) or \([2 + 2]\) cyclic condensations occur is governed at least in part by the size of the metal ion used in the in situ template process. Thus, while Mn (II) - Zn (II) afford the 14-membered \(\text{N}_4\) \([1 + 1]\) macrocycle \(L\). In contrast the larger Ag (I) cation produces the binuclear complex \([\text{Ag}_2 \text{L}^4]^2\) \(K = \text{ClO}_4, \text{BPh}_4\) Fig. 32, in which \(L\) is the 28-membered macrocycle derived from the condensation of two molecules of DAP with two molecules of diprimary amine - \([2 + 2]\) condensation. The crystal structure shows each Ag (I) to be four-coordinate, bonded to the three nitrogens of one trimethine unit and to one secondary amine nitrogen. The Ag ...Ag separation is 6.0Å and no metal ...metal interaction is observed. It would seem likely, therefore, that it is the relatively large size of the Ag (I) ion which is responsible for directing the course of the reaction towards the \([2 + 2]\) rather than the \([1 + 1]\) product.

Application of this principle to other systems has resulted in the synthesis of \([2 + 2]\) macrocycle's of varying size and nature of donor and has resulted in both mononuclear and binuclear complexes. The alkaline earths have been particularly effective mononuclear templates in these systems.

The macrocyclic ligands about to be discussed are illustrated in, Fig. 32.

The Mononuclear Complexes

Ca (II), Sr (II), Ba (II) and Pb (II) are all effective as template ions in the synthesis of the macrocycles \(L\), \(L\) and \(L\). K(I) will also template \(L\). The metal ions Mg (II) and Mn (II) - Zn (II), Ag (I) and Cd (II) are all ineffective as templates for these \([2 + 2]\) macrocycles; a mononuclear Cd (II) complex of \(L\) is obtainable by transmetallation as can Na (I) and NH\(_4\) complexes. In the above examples the complexes usually contain one central metal ion, with
planar conjugated, 18-membered hexadentate macrocycles. Interestingly, the Ba (II) complexes of L and L are isolated with a ligand: metal ratio of 2:1, implying a sandwich structure containing 12-coordinated Ba. The various types of structures are illustrated in Fig.33, i.e. hexagonal bipyramid (21), hexagonal pyramid with 'vacant' axial position possibly occupied by a sterically active lone pair (22) and the 12-coordinate sandwich (23). The results have been rationalized in terms of:-

(1) The match/mismatch in size of the metal ion in relation to the macrocycle hole size and (2) the charge on the metal.

A comparison of the eight-coordinate diameters of the metal ions concerned with the macrocyclic cavity radius of 2.7Å for L, reveals a clear link between metal ion size and the stoichiometry of the complexes or effectiveness as a template. Ba (II) having the largest diameter of 2.84Å is too large to fit the macrocycle hole and consequently forms the sandwich structure (23) - Fig.33, with L and L. The metals Ca (II), Sr (II), Cd (II) and Pb (II) which form 1:1 stoichiometries with L, L and L have diameter of 2.24, 2.52, 2.20 and 2.58Å respectively, while those metals ineffective as templates, namely Mg (II) and the transition series Mn (II) - Zn (II) (8-coordinate diameters 1.80 - 1.92Å) are clearly too small to accommodate all six donors in a stable planar mononuclear arrangement and are too large to form binuclear complexes. However, the fact that K(I) with an eight-coordinate diameter of 3.02Å forms 1:1 complexes while Ba (II) (2.84Å) form 2:1 stoichiometry suggests this consideration alone is insufficient to account for the phenomenon, and that the smaller ionic charge associated with K(I) must also contribute.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>R</th>
<th>Ligand</th>
<th>R</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>47a</td>
<td>o-C₆H₄</td>
<td>a</td>
<td>48</td>
<td>o-C₆H₄</td>
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<td>o-C₆H₄</td>
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<td>49</td>
<td>(CH₂)₂⁻</td>
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<td>57b</td>
<td>CH₂CMe₂CH₂⁻</td>
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<td>59</td>
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<td>(CH₂)ₙ⁻</td>
</tr>
<tr>
<td>53b</td>
<td>(CH₂)₂N(CH₂Py)(CH₂)₂⁻</td>
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<tr>
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<td>(CH₂)₂N(CH₂NH₂)(CH₂)₂⁻</td>
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<tr>
<td>54</td>
<td>(CH₂)₃NH(CH₂)₃⁻</td>
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<tr>
<td>55</td>
<td>(CH₂)₂O(CH₂)₂O(CH₂)₂⁻</td>
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<td></td>
</tr>
<tr>
<td>56</td>
<td>CH₂CH(OH)⁻CH₂⁻</td>
<td></td>
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</table>

1 a R = H, otherwise R = Me

Fig. 32
Although, as discussed above, the macrocycle L\textsuperscript{47a} is too large to form stable first row transition metal complexes, it was found that on transmetallation using [Ba L\textsubscript{2}\textsuperscript{47a}][ClO\textsubscript{4}]\textsubscript{2} that a series of new mononuclear complexes could be isolated in 40-80% yield\textsuperscript{190} X-ray analysis on a representative Co (II) complex revealed that the inner ring of L\textsuperscript{47a} had contracted from 18- to 15-member atoms producing the new pentadentate macrocycle L\textsuperscript{63}.

The contraction can be visualized in two steps, Fig. 34.

(i) Nucleophilic addition of solvent MeOH across one C = N and (ii) Nucleophilic addition of newly formed secondary amine intramolecularly across the adjacent C = N. This second addition is facilitated further by the increased flexibility gained on conversion of a double into a single C-N bond. The process is an example of the entatic principle\textsuperscript{187} - activation energy of reaction involving metal centres is lowered if the centre is held in a strained or poised condition. Thus, it is the mis-
match in size between the 18-membered \( L \) cavity and the transition metal radius, which is responsible for this metal-induced ring contraction.

In 1970 Stotz and Stoufer reported the synthesis of the uncomplexed macrocycle \( L \) in the presence and absence of a template ion (Cu (II)). Since Schiff-base macrocycles are not usually stable in the uncomplexed state this was an unexpected result. A reinvestigation by Nelson et al shows that the macrocycle has rearranged to the form shown in, \( L \), Fig.35. Presumably this happens in three steps.

1. Imine to enamine tautomeric shift, introducing flexibility to relieve the steric interaction.
2. Rotation about C = N bond so as to allow,
3. nucleophilic attack forming the tricyclic system \( L \).

Fig.34
The small, innermost 12-membered ring and the unfavourable disposition of the pyridine nitrogens prevents coordination to a metal.

Treatment of macrocycle $L$ with Cu (II) leads to a metal ion induced ligand rearrangement. Thus the mononuclear complex of the new macrocycle $L$ was produced in which $L$ has rearranged from a tricyclic (7+12+7) to a tricyclic (15+6+3) system. The 15-membered ring formed as a result now has four nitrogen donors disposed in an approximate plane and can accommodate Cu (II) in a square pyramidal geometry, as evidenced by X-ray structural studies.

Sr (II) and Ba (II) will template the reaction between DAP and 1,3-diaminopropane in methanol producing the macrocyclic complexes of general formula $ML(Clo_4)_2$. This 20-membered macrocycle is a close relative of the 18-membered $L$. Both, on transmetallation form only binuclear Cu (II) complexes (discussed in the binuclear section).

If DAP and diethylenetriamine are reacted at room temperature, in the presence of the alkaline earth metal ions Mg (II) - Ba (II), mononuclear complexes $ML(Clo_4)_2$ are obtained, where $L$ is an open-chain product containing two terminal primary amine groups. Transmetallation at this stage leads to the seven-coordinate Mn (II) - Zn (II) complexes discussed previously.

\[ \text{Fig.36} \]
The open-chain complexes $[M \text{L}^2](\text{ClO}_4)_2 \ (M = \text{Ca} \text{ (II)}, \text{Sr} \text{ (II)}, \text{Ba} \text{ (II)})$ can be used as precursors to the ring-contracted product via a transamination mechanism. X-ray analysis of the Ba (II) complex subsequently revealed that this product contained the 18-membered di-imine, Fig.36, form and not the 24-membered tetraimine macrocycle $L^{53a}$. $L$ can be formed by addition of the secondary amine groups across neighbouring imine bonds with concomitant extrusion of two 5-membered imidazolidine rings. The failure of Mg (II) to facilitate ring-closure can be understood in terms of its 1.80Å, eight-coordinate diameter being too small for the macrocycle, even in its ring-contracted form.

The chemistry leading to the macrocycle $L^{51}$ closely shadows that described for $L^{53a}$ with the exception that ring-contractions cannot occur on replacing NH of $L^{53a}$ for the oxygen of $L^{51}$. Mg (II), Ca (II) or Ba (II) effect a template reaction producing the open-chain ligand $L^{26}$ (described earlier). Only the large Ba (II) ion of $[\text{BaL}^2]^2^+$ can be used a precursor to the transamminated macrocyclic product, $[\text{BaL}^{51}][\text{ClO}_4]^2 . \text{H}_2\text{O}^{197}$.

Quite recently the macrocycle $L^{56}$ has been observed to undergo analogous ring expansion and contraction controlled by the cavity size requirement of the template metal ion used $^{198}$. Thus, Pb (II) produces the 18-membered ring-contracted macrocycle, $L^{(24)}$—Fig.37, as confirmed by X-ray diffraction studies. Use of Ba (II) in the template reaction dictates that the macrocycle be expanded to its 20-membered isomer (25) (n.m.r. evidence) $^{198}$.

Macrocycle $L^{55}$, with both its trimethine 'ends' well separated by the ether linkages seems aptly equipped for binuclear chemistry. However, it does form stable mononuclear complexes with transition metals Fe (II) Co (II, III) and Cu (II). The ligand twists so that both trimethine entities are disposed mutually at right-angles. The ether oxygens are not used in coordination $^{199}$, Fig.38.
Fig. 37

Fig. 38

$M = \text{Fe}(11), \text{Co}(11), \text{Co}(111), \text{Cu}(11)$
The Fe (II), Cu (II), and Co (II) complexes are all low-spin and it is thought that it is the large C.F.S.E. stabilization, gained by adopting this geometry which is the overriding thermodynamic driving force.

The dipositive ions of Ca, Sr, Ba and Pb produce mononuclear complexes of L$_{\text{a,b}}$, by template methods analogous to those already described. More recently members of the lanthanide series have also been used to synthesize this and other members of a homologous series of the macrocycle.

The importance of the size of the template is illustrated by the failure of Mg (II) to produce macrocyclic products. In the case of Ba (II) 1:1 and 1:2 metal:macrocycle ratios are found. N.m.r and X-ray structural studies in accord with a structure involving eleven-coordinate Ba (II).

Recently mononuclear Cu (II) complexes of the pyrrole-based Schiff-base macrocycle L, L$_{\text{58,59 60}}$ and L have been obtained. X-ray structures show the Cu (II) to be in a square-plane using two imines and two deprotonated pyrrole nitrogens, thus rejecting two potentially coordinating imines, Fig.39.
BINUCLEAR COMPLEXES

As has already been noted, 2,6-DAP and 2,5-DFF will react, in the presence of large alkaline earth metal ions, to produce good yields of mononuclear complexes of \([2 + 2]\) macrocyclic products. Binuclear complexes can be achieved by replacement of the single template ion in a metathesis reaction with transition metal ions, particularly the stereochemically non-demanding Cu (II) ion.

Pyridine, Furan and Pyrrole-based Macrocycles

The ligands concerned are listed in, Fig.32. Template reactions producing \([2 + 2]\) condensations are not unique to the alkaline earth metal ions. I have already described template synthesis on Ag (I) producing a\([2 + 2]\) macrocycle, \(L^{54}\), in contrast to the\([1 + 1]\) product obtained with first row transition metals \(185\). \(L\) will not be discussed further in this chapter since it forms part of the subject matter of this thesis.

\(L\) is synthesized in a similar fashion producing a di-Ag (I) complex where each Ag (I) is thought to be four-coordinate using three nitrogens and one sulphur donor \(202\).

Di-Pb (II) complexes of \(L\) have also been prepared via template procedures \(137\).

Several comparisons can be drawn within this series of macrocycles. They all contain rigidly planar and powerfully chelating 'jaws' situated on the North-South axis as drawn. In each case tridentate moieties are linked by two flexible chains which may or may not furnish other potential donors.
Binuclear Cu (II) complexes have been isolated for all macrocycles. Each Cu (II) ion is bonded to one of the trimethine units and may (L¹, L²) or may not make use of other donors in the macrocycle. Each Cu (II) therefore has three donors at the three corners of an approximate square plane. Frequently the fourth site of each square-plane is simultaneously occupied by a single ligand behaving in a bridging manner intramolecularly between the two metal centres. By altering R, as in this series, it is possible to vary the inner macrocycle ring from 18 (L⁴⁹) to 30 (L⁵⁵) atoms. In this way we can synthesize macrocycles of increasing cavity size to accommodate a range of bridging substrate molecules. X-ray diffraction studies have revealed the existence of exogenous OH⁻, OMe⁻, N₃⁻ and imidazolate (im⁻) bridges, and a single case of an endogenous RO⁻ bridge.

The im⁻ bridges occur with the macrocycles L¹, L² and L₅⁵. As far as Cu (II) is concerned X-ray structures (L² and L₅⁵) confirms that the metal ion exists in the same coordination environment in each case (Cu ... Cu separations 5.87 and 5.99 Å respectively). Magnetic susceptibility measurements give J values of -21.2 cm⁻¹ and -21.0 cm⁻¹, respectively. The presence in both complexes of well-resolved seven-line e.s.r. spectra at the ΔM = 2 transition for DMSO/MeOH frozen solution confirms the occurrence of antiferromagnetic coupling and implies retention of the im⁻ bridge in solution.

It is noticeable that bridging im⁻ is only obtained where the inner macrocyclic ring contains 24 atoms or greater. The smaller 18 and 20-membered macrocycles L⁴⁹ and L⁵⁰ thus appear best suited for the accommodation of the smaller single-atom bridges e.g. OH⁻, OMe⁻, N₃⁻. This is borne out by the complexes of both these ligands, moreover such bridges may only be accommodated when the macrocycles fold so that the two trimethine planes intersect at angles appreciably less than 180°. The X-ray structure of [Cu₂L⁵⁰(OH)(H₂O)]³⁺ shows a Cu ... Cu separation
of 3.145 Å and the Cu — O(H) — Cu angle to be 110.3(7)°. Magnetic studies reveal antiferromagnetic interaction between the coppers: J values for bridging OH⁻ and OMe⁻ are -32 cm⁻¹ and -53 cm⁻¹ respectively, while e.s.r. data confirm the integrity, of the bridged structure in solution. It seems likely that the enhanced coupling for the OMe⁻ case is due to increased electron density on the bridging oxygen atom.

The suitability of the larger macrocycles for accommodation of larger substrates has already been examined. However, there comes a point when the increased flexibility, conferred by the introduction of more atoms to R (i.e. increasing ring size), allows the ring to fold in a concertina type manner and therefore accommodate also the single atom bridges. Thus L⁵⁵ (a 30-membered macrocycle) produces [Cu₂L (OH) (H₂O) (C₅H₄)]²⁺ with a Cu ...Cu separation 3.57 Å compared to 5.99 Å for the μ-im⁻ complex of the same macrocycle. The Cu—O(H)—Cu angle is 141.7(7)°. With J = -120 cm⁻¹, antiferromagnetic coupling is larger than in the analogous [Cu₂L (OH) (H₂O)]³⁺, where L⁵⁰ is a 20-membered macrocycle; Cu ...Cu separation 3.145 Å and Cu—O(H)—Cu angle 110.3(7)°. Given that the Cu (II) ions in each complex have the same coordination environment, the difference in coupling has been attributed to the increased Cu—O(H)—Cu angle observed for L⁵⁵, thus facilitating increased overlap of magnetically important orbitals.

The sole example to-date of an endogenous bridge in these macrocycles was recently described by Fenton and McKee. X-ray diffraction studies on [Cu₂(L — H) (MeCN) (H₂O)]³⁺ have shown each tetragonal Cu (II) to be bridged by one deprotonated ROH, Fig.40.

The complex incorporates several features of the oxidized haemocyranin (Hc) active site: Tetragonal Cu (II); Cu ...Cu separation 3.642 Å compared to ca 3.6 Å for Hc; and both contain a single endogenous OR⁻
and low magnetic susceptibility. The usefulness of this complex as a structural model for Hc and type 111 Cu proteins in general is therefore apparent.

The introduction of pendant donors to the macrocycle $L^{53b}$ has been briefly reported; di-Cu (II), Ni (II) and Co (II) complexes have been achieved.

Condensations of higher order, namely $[4 + 4]$, have recently been communicated. It was observed in the crystal structure of a Mn (II) derivative $L$. The 40-membered macrocycle is found wrapped around a tetra-Mn (II) core, Fig.41. Each endogenous R-O$^-$ is in contact with three Mn (II) ions. The structure of the core is reminiscent of the Fe-sulphur cubes of the naturally occurring ferredoxins. The synthesis of a complex where Fe is replaced for Mn and RS$^-$ for RO$^-$, if possible, will prove interesting.

The furan and pyrrole based macrocycles have been prepared and form binuclear Cu (II) and Co (II) complexes. In passing it should be noted that the smaller 18-membered macrocycle (R = (CH$_2$)$_2$, X = O) failed to form binuclear complexes.

Binuclear encapsulation of the transition metals by $L^{57a,57b}$ does not involve coordination of the furan oxygen atoms. Each metal is thus bound by only the two imines on one side of the macrocycle in an East-West relationship. As a result, these systems have the potential to bind two bridging substrates so as to obtain a coordination number of at least four. When necessary monodentate ligating groups have been used to achieve higher coordination numbers. Thus bridging substrates OR$^-$, R = H, Me, Et Pr$^+$ have been observed for a di-Cu (II) series of $L^{57a}$.

The di-$\mu$-hydroxo Cu (II) complex is the precursor to a number of di-bridged Cu (I) complexes, Cu$_2L^{57a}X_2$, X = Cl$^-$, Br$^-$, I$^-$, N$_3^-$, NCS$^-$, prepared simply by heating $[Cu_2L^{57a}(OH)_2]^2^+$ in the presence of NaX $^{205}$. 
This facile reduction has been traced to the preferred conformation of the macrocycle and therefore represents a further example of ligand-controlled chemistry. The most strain free configuration is achieved when the macrocycle is coordinating to a tetrahedral metal centre like Cu (I) rather than the square-based Cu (II). An alternative way to reduce strain occurs when the metal centres adopt a trigonal bipyramidal arrangement, e.g. as in $\text{Cu}_2 L (OR)_2 (\text{NCS})_2$, $R = \text{Me}, \text{Et}, \text{Pr}$. A series of tetrahedral and trigonal bipyramidal di-Co (II) exist for $L$ with numerous bridging substrates, $X^- = \text{OH}^-, \text{OMe}^-, \text{OPr}^-, \text{OBu}^+, \text{OPh}^-, \text{SEt}^-, \text{Cl}^-, \text{Br}^-$, $\text{N}_3^-$, $\text{NCS}^-$, $\text{NCSe}^-$. Again the $\text{NCS}^-$ and $\text{NCSe}^-$ derivatives will be treated subsequently. Antiferromagnetic exchange interactions have been noted for the di-Cu (II) and tetrahedral di-Co (II) complexes $\text{Cu}_2 L (\text{OMe})_2$. Like the mononuclear analogues ($R = (\text{CH}_2)_3$, etc.) the pyrrole NH becomes involved in coordination by deprotonation. Two potentially coordinative imines are ignored, see Fig.42.
The thiocyanate ion, $\text{NCS}^-$, represents the anionic component of the parent thiocyanic acid, said to exist as two tautomers - thiocyanic acid (26) and iso-thiocyanic acid (27) - Fig. 43. X-ray structural studies of the crystalline KSCN derivative suggest that the free ion is linear and exists as a hybrid of $S-C=\equiv N$ and $S=\equiv C-N^-$. For thiocyanate compounds in general, the stabilization of one canonical form in preference to another will depend on the chemical environment. Thus charge may be located formally at either end of the ion producing, as a consequence, its familiar ambidentate character. Similar studies on complexes containing coordinated NCS$^-$ have shown that this approximate linearity is maintained in most of its compounds. In addition, it has been observed that the $M-N-C$ angle is normally $180^\circ$ while the $M-S-C$ angle usually approaches $90^\circ$.

From the classical point of view the chemistry of the thiocyanate ion was interpreted as that of a halide-like point charge. In more recent years the emphasis of research has shifted to the study of its ambidentate bonding capabilities and the search for structure/physical property correlations.

As a versatile, ambidentate ligand, NCS$^-$ presents five basic bonding modes, Fig. 44.

$$H-S-C\equiv N \quad \longleftrightarrow \quad H-N=\equiv C=S$$

(26) \hspace{2cm} (27)
The terminal nitrogen and sulphur bonding modes (1) and (2) together with the 3-atom bridging configuration (3) are used in almost all of the known thiocyanate complexes. In stark contrast, coordination in a single-atom bridging fashion (4) and (5) between two metal ions has been rare and, until 1979, unknown. There are five examples of structurally defined complexes containing the N-only bridging mode (4) and one of the S-only bridging mode (5).

N-only bridging was first realised by Cotton in 1979 following the X-ray structural analysis of the mixed-valence metal-metal bonded anion $[\text{Re}_2(\text{NCS})_{10}]^-$ and subsequently by Reedijk in $[\text{Cd}_2(\text{NCS})_4(4\cdot t\text{-butyl}-1,2,4\text{-Triazole})]^{2-}$ (1982), by Nelson in $[\text{Co}_2\text{L}(\text{OE}_1)(\text{NCS})_3]$ (1983) by Tasker and Lindoy in $[\text{Ni}(\text{macrocycle})(\text{NCS})_2]_2$ (1983) and by Reedijk in a series of complexes $[\text{M}_3(1,2,4\text{ triazole})(\text{NCS})_6(\text{H}_2\text{O})_2]$ when $M = \text{Ni(N)_2Co (II), Mn (II)}$ (1984). The unique example to date of, S-only bridging remains that demonstrated by Nelson et al in $[\text{Cu}_2\text{L}(\text{SCN})_2]^{57a}$.
(1981). With the exception of Reedijk's Cd (II) polymer and Lindoy's Ni (II) dimer where crystal packing effects may operate, the occurrence of the single-atom bridging modes can be ascribed to an enforced close proximity of the metal centres which precludes formation of the 3-atom bridge (3)-Fig.44. Of particular relevance to this review is the fact in the cases of [Co₂L (OEt)(NCS)₃] and [Cu₂L (SCN)₂] it is the small macrocyclic cavity that is responsible for the small metal ... metal separations (3.116(4)Å and 2.796(8)Å respectively). The choice of nitrogen as the bridging atom in the di-Co (II) complex and sulphur in the di-Cu (I) is a reflection of the class 'a' or 'b' nature of the metals concerned, Fig.45. Analogous single-atom bridged selenocyanate, NCS⁻, derivatives are believed to exist in both cases.

Fig.45
Despite the small number of structurally defined examples of mode (4)—Fig.44, a simple physico-structural correlation based on infrared data is already emerging. I.r. spectroscopy of coordinated NCS\(^-\) has been extensively reviewed\(^{222}\). There are three normal vibrations for coordinated NCS\(^-\) - \(\nu_{\text{CN}}, \nu_{\text{CS}}\) and \(\delta_{\text{NCS}}\). Of these \(\nu_{\text{CN}}\) has been the most heavily studied because it is normally a strong absorption which falls around 2050 cm\(^{-1}\) - a part of the i.r. spectrum which is usually free of potentially interfering ligand vibrations. This is not the case for the weaker, lower energy \(\delta_{\text{NCS}}\) and particularly \(\nu_{\text{CS}}\) vibrations. The \(\nu_{\text{CN}}\) frequency and their structural assignments for the first row transition metals are summarized in, Fig.46.

Examination of Fig.46 shows that all types of coordination involving sulphur have overlapping regions (2, 3, 5). Terminal nitrogen bonding occurs at lower frequencies 2030 - 2080 cm\(^{-1}\). However, the most striking feature is that (with the exception of ref.218 for which no i.r. data is reported) all the known N-only bridging thiocyanates exhibit the \(\nu_{\text{CN}}\) absorption at frequencies below 2000 cm\(^{-1}\) (1885 cm\(^{-1}\) is the lowest recorded as expected for the high oxidation state in the complex) - well removed from the more familiar regions associated with NCS\(^-\). So low, infact, is \(\nu_{\text{CN}}\) in these complexes that when first encountered by Cotton et al\(^{223}\) in 1967 it was erroneously assigned as a \(\nu_{\text{C}=\text{O}}\) frequency of a carbonyl group, only to be corrected twelve years subsequently on the basis of an X-ray crystal structure\(^{215}\).

\[
\begin{array}{c}
\text{3} \\
\text{2} \\
\text{1} \\
\text{4} \\
\text{5}
\end{array}
\]

2200 2000 1800

Fig.46
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<th>Binuclear Site</th>
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<tr>
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<tr>
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<td>Ceruloplasmin</td>
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<td>Cu Cu</td>
<td>Ascorbate oxidase</td>
<td>oxidase,</td>
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<tr>
<td>Mo Mo</td>
<td>Nitrogenase</td>
<td>6-e reduction of $N_2 \rightarrow 2NH_3$.</td>
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</table>
BINUCLEARITY IN NATURE

There are many metalloproteins in which enzymic activity is dependant on the occurrence of a bimetallic active centre. The metals present may have an active or passive function. Table VI summarizes some of the binuclear active sites known.

As is readily apparent, even from a small group of proteins such as those in Table VI, the copper ion is involved in a wide range of biological processes. Very often a large but even number of Cu atoms are found per protein molecule. For the copper proteins copper is usually found as one of three types.

**TYPE 1 COPPER ("Blue-Copper Centres")**

These intensely blue (for Cu) species exist in an unusual non-planar (tetrahedral) coordination geometry comprising two thioether (cysteine and methionine) and two unsaturated nitrogen (histidine). They can be characterized by (i) an intense absorption near $600 \text{ mm (e} \approx 4000 \text{ M }^{-1} \text{ cm}^{-1}$), (ii) An E.S.R. spectrum with unusually small hyperfine coupling constants, $A_{11,1} \approx 100 \times 10^{-1} \text{ cm}^{-1}$ and (iii) high positive redox potential for the $\text{Cu}^{2+}/\text{Cu}^{+}$ couple, reflecting appreciable stability of the Cu (I) state. In addition n.m.r. studies reveal the active site to be relatively inaccessible to solvent molecules $^{226,227}$. Plastocyanin (M.W.10,500) and Azurin (M.W.16,000) are copper proteins which contain only type 1 Copper. They are found in plant chloroplasts and are an essential component of the photo-synthetic electron-transfer chain. X-ray structural studies of the active centre exist $^{241,244}$.

**TYPE 2 COPPER**

This copper centre is present in all blue multicopper oxidases. They have spectroscopic properties similar to simple Cu (II) complexes and exhibit normal E.S.R. spectra.
TYPE 3 COPPER (E.S.R. non-detectable)

This site is also present in all multicopper oxidases. It is characterized by; (i) the occurrence of two copper ions in close proximity; (ii) absence of an E.S.R. signal, which is a manifestation of strong antiferromagnetic coupling interactions. It can thus act as a two electron donor/receptor and is essential to the reduction of dioxygen. The type 3 site also exhibits an intense 330nm absorption $\lambda = 3000 - 5000 \text{M cm}^{-1}$.

In addition to types 1, 2 and 3 there are non-blue copper proteins. They exhibit properties similar to type 2 copper but differ significantly from one another with respect to prosthetic groups, quaternary structure and reactivity.

THE PROTEINS

Haemocyanin

Despite their name these oxygen carrying proteins do not contain a haeme group. They have very high molecular weights and are found in molluscs and anthropods. In the reduced Cu (I) state they are capable of binding one mol of dioxygen per pair of copper ions. The two Cu (I) ions are 3.4Å apart. Oxidation produces a change in both coordination and geometry to give two tetragonally coordinated type 3 Cu (II) ions ($\approx 3.6\AA$ separation) bridged by an endogenous $\text{RO}^-$ (probably from serine) and by exogenous dioxygen as $\mu-1,2$-peroxide, Fig.47.
TYROSINASE:

This is a type 3 active site protein with mixed functions. It will reversibly bind dioxygen, dismutate peroxide, catalyse the two-electron oxidation of o-diphenols to o-quinones (catecholase activity) and the monooxygenation of mono-phenol to o-diphenols (monooxygenase/cresolase activity). The active site is similar to haemocyanin; however, the oxidative functions of tyrosinase require an increased substrate accessibility to the metal centres.

LACCASE:

Extracted from the tree enzyme Rhus verniciferus, laccase, which contains only one of each type of Cu, is the simplest of the multicopper oxidases. It has a molecular weight of 110,000 and it catalyses the oxidation by dioxygen of diphenols and aromatic diamines. In the process dioxygen undergoes a four-electron reduction to water. The electrons are thought to enter at the type 1 copper site, causing oxidation of substrate. Reduction of O_2 to H_2O occurs at the type 3 centre in two-electron steps. In contrast to haemocyanin and tyrosinase, laccase binds dioxygen as a hydroperoxy species to only one of the copper centres. Interaction with a nearby type 2 centre is suspected, Fig. 48.

As it is water-soluble and easily purified it has proved to be particularly convenient in the study of the cooperative activities of each of the three types of copper.

CERULOPLASMIN:

Ceruloplasmin, another multicopper oxidase, is the major copper-containing protein of mammalian blood plasma. With a molecular weight of 134,000 it contains two type 1, one type 2 and four type 3 copper sites. It catalyses the four-electron reduction of O_2 to water. Its physiological role is thought to be the oxidation of Fe (II) and transport of copper for incorporation into the cytomchrome-c-oxidase.
active centre (see later)\(^{237}\). Wilson's disease which affects the liver, the nervous system, and mental stability, is caused by high copper concentration in the cell. Such high concentrations are associated with a genetically derived inability to synthesize apoceruloplasmin (i.e. without metal centre) so that transfer of copper to the protein cannot occur. Treatment involves injection of chelating agents such as penicillamine to form water soluble, excretable, copper complexes.

**ASCORBATE OXIDASE:**

This enzyme is yet another blue copper oxidase which occurs widely in plants. It contains eight copper ions per molecule – three type 1, one type 2 and four type 3. It has a molecular weight of 14,000. It catalyses the oxidation of ascorbic acid (vitamin C) to dehydro-ascorbic acid\(^{232}\).

**CYTOCHROME-C-OXIDASE:**

Cytochrome-c-oxidase is an example of a heteronuclear Cu/Fe enzyme\(^{239}\). It is the terminal enzyme of the electron transport chain in mitochondria, coupling the respiration process to oxidation by molecular oxygen. Four metal centres two iron and two copper ions are found in this enzyme which is difficult to study as it is anchored to the mitochondrial membrane. The enzyme functions by accepting electrons from ferrocytochrome c and then donating these electrons to dioxygen. The magnetic properties of the oxidized form lead to the conclusion that the active centre contains Fe (III)\(^{5}\), Cu (II)\(^{9}\) and high-spin Fe (III)... Cu (II) pair showing antiferromagnetic coupling\(^{-1}\)(J > -200 cm\(^{-1}\))\(^{239}\). Various candidates such as im\(^-\), SR\(^-\), OR\(^-\), OH\(^-\) have been considered as bridges between Fe and Cu, but the actual bridge remains to be elucidated.
SUPEROXIDE DISMUTASE:

This enzyme is a widespread copper protein which has the protective function of catalysing the disproportionation of the toxic superoxide ion, $O_2^-$:

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2.$$ 

Hydrogen peroxide is then scavenged by the enzyme catalase. Depending upon the source the enzyme is found to contain Cu - Zn, Fe - Zn or Mn - Zn couples. Most studies have concentrated on bovine erythrocyte superoxide dismutase. It has a molecular weight of 31,200 per subunit (2 subunits per molecule), and contains copper linked to zinc by an imidazolate to the tetrahedral zinc, Fig. 48. The role of the zinc appears to be structural in the formation and stabilization of the active site.

HAEMERYTHRIN:

Contrary to the name, haemerythrin is another of nature's non-haeme answers to the oxygen-carrying question, employed by several marine invertebrates. Each of its eight subunits contains two iron atoms capable of binding one molecule of dioxygen. In oxyhaemerythrin the irons are antiferromagnetically coupled ($J > 77 \text{ cm}^{-1}$). Structural studies of azidomet-derivatives have revealed the μ-oxo-bridged structure, Fig. 48. Accepted views are that oxyhaemerythrin has a similar structure in which $O_2$ takes the place of $N_3^-$. 

2Fe2S FERRODOXINS:

The larger 4Fe and 8Fe 8S ferrodoxins are excluded from this discussion. Adrenodoxin (M.W.13,000) is a 2Fe 2S ferredoxin derived from animal sources (from the adrenal cortex) which plays an electron transfer role in the hydroxylation of steroids other examples exist from plant sources - rubredoxin (from spinach). Here they play important...
active site of Laccase

active site of cytochrome-c-oxidase
Fe .... Cu 3.75Å

active site of superoxide dismutase

structure of azidomethaemerythrin

---

Fig. 48
electron transfer roles in photosynthetic processes of the chloroplast. Studies of models suggest an Fe ... Fe distance of 2.7Å and antiferromagnetic coupling ($J^v$ = 183 cm$^{-1}$).

**THERMOLYSIN:**

Thermolysin is a bacillus zinc endopeptidase of molecular weight 34,600. The protein contains four calcium ions two of which are in close proximity (3.8Å). The calcium plays a structural role imparting stability even at high temperature - apoenzyme stable up to 40° native enzyme up to ~80°.

**Mo - Mo in NITROGENASE:**

Nitrogenase is made up of two proteins one containing iron, the other iron and molybdenum. Strictly speaking, the Mo - Fe protein contains a metal cluster. Structural studies on models suggest each Mo is involved in a MoFe$_3$S$_4$ cluster with the two Mo atoms bridged by three sulphur atoms, Fig.48a.
The compounds described are only typical examples of binuclear chemistry in life processes. Numerous variations (depending on source) exist for each protein. Many known examples have had to be omitted, undoubtedly some yet remain to be found. The message for a coordination chemist that binucleating ligands, are valuable not just as synthetic models for the less manageable natural systems, but are probes for magnetic and electronic exchange mechanisms. They are also important as potential catalysts in the oxidation of organic substrates.
COPPER COMPLEXES AND CATALYTIC OXIDATIONS:

Attempts have been made to mimic the O$_2$ ability of natural systems and copper complexes have been found to activate molecular oxygen towards electron transfer on a variety of organic substrate oxidations. Some of them are now briefly considered.

CATECHOLS:

Catechol is a two-electron reducing agent whose oxidation to quinone, Fig. 49, is catalysed by Cu (II) and in particular by binuclear copper systems.

Studies by Lever on di-copper complexes of the phthalazine ligand have shown these systems to possess catecholase activity. He associates the catalytic properties with the binuclearity of the system. It is one of a growing number of synthetic, catalytic copper systems in which the binuclear framework retains its integrity upon reduction to Cu (I). Phenolase activity has been discovered. The system therefore resembles the activity of the type 3 copper protein tyrosinase.

Rogic found that induction periods (i.e. initial inactivity) for such reactions could be circumvented by using the oxidation product, Fig. 50, of CuCl in methylene chloride with four moles of pyridine as a catalyst. The inference being that ready-made, binuclear entity like $[\text{Cu}_2^0]$ is the active species.

Vigee and Bolus have studied a number of catechol oxidations for several macrocyclic and related acyclic binuclear copper (II) complexes, Fig. 51. O$_2$-uptake measurement were more complicated (>0.5 mol O$_2$ per catechol) than expected for the simple formation of quinone. The acyclic di-copper complexes, Fig. 52, proved more efficient catalysts than their macrocyclic counterparts but even they are $\sim 2 \times 10^3$ times less reactive than tyrosine itself.
Fig. 49

Fig. 50

Fig. 51
Again it is the binuclearity of the systems which is thought to be important for the catalytic function, the enhanced activity of the acyclic systems being a reflection of the accessibility to labile sites.

Fenton et al have observed similar catalytic behaviour for binuclear complexes, Fig.53, while Nelson et al have observed such properties in a macrocyclic (L$_{57a}$) di-copper system.

For CuCl/Pyridine/ROH systems the oxidation of phenols, catechols to o-benzoquinones to ring-closed muconic acid monoesters is known, Fig.53.

1. $\text{R} \text{OH} \rightarrow \text{R} \text{OH} -2\text{e}$
2. $\text{R} \text{OH} \rightarrow \text{R} \text{CO} -2\text{e}$
3. $\text{R} \text{CO} \rightarrow \text{R} \text{COOR} -2\text{e}$

$\text{R} \text{OH} + 15\text{O}_2 + \text{MeOH} \rightarrow \text{R} \text{COOR}$

Fig.53
The first step (1) will occur only in the presence of $O_2$ while the others can occur in the presence of the Cu (II) catalysts even without $O_2$.

**OTHER OXIDATIONS:**

Most copper-catalysed reactions with phenol produce coupled or polymeric products \(^{263,264}\) Fig.54. CuCl/pyridine slurries are known \(^{265,266}\) to catalyse production of a range of polyphenoxide materials.

Hay found that the Cu (I) halide/$O_2$/pyridine systems would initiate oxidations of aniline to azobenzene and polyazobenzene products \(^{266}\).

Oxidative coupling of secondary amines using the CuCl/$O_2$/pyridine system yields the dimeric product (2)-Fig.54 while o-phenylenediamine (3) undergoes ring cleavage giving cis, cis-mucononitrile.

Hydroquinone (4), acetylene (5) and thiols (6) have all been seen to undergo catalytic oxidations, Fig.54.

Recently Karlin and associates have discovered a synthetic dicopper system capable of simulating the monooxygenase activity of the copper proteins tyrosinase and dopamine $\beta$-hydroxylase which mediate the hydroxylation of organic substrates utilizing $O_2$ as an oxygen source \(^{272}\).

In his system the 3-coordinate dimeric Cu (I) compound (2)-Fig.55, when exposed to $O_2$ results in a di-Cu (II) complex of the hydroxylated ligand (3)-Fig.55. When performed in inert solvent double-bridging by one phenolate and one hydroxide is found \(^{273-276}\). Isotopic studies using $^{18}O_2$ have shown that both the phenolate and hydioxide oxygen atoms come from the one mol. of molecular oxygen atoms that is consumed per di-Cu (I) complex.

The di-bridged di-Cu (II) compounds are, in themselves models for the oxidized form of haemocyanin. Effort is presently being directed at the oxidation of organic substances other than the ligand \(^{275}\). Evidence exists, from the reaction of the di-Cu (I) derivatives containing the 'new' hydroxylated ligand, (4)-Fig.55, for the existence of di-Cu (II) peroxide-bridging intermediates in the reaction of $O_2$ with di-Cu (I) \(^{277}\).
1. \( \text{PhOH} \) \( \frac{n}{2} \text{O}_2 \rightarrow \text{PhO} \) \\
\( \text{Ph} \) \( \text{N} \) \( \text{NPh} \) + \( \text{H}_2\text{O} \)

2. \( 2 \text{Ph}_2\text{NH} \) \( \rightarrow \) \( \text{Ph}_2\text{N} = \text{NPh}_2 + \text{H}_2\text{O} \)

3. \( \text{NH}_2 \) \( \text{NH}_2 \) \( \rightarrow \) \( \text{CN} \) \( \text{CN} \)

4. \( \text{OH} \) \( \text{OH} \) \( \rightarrow \) \( \text{CO} \) \( \text{CO} \)

5. \( \text{RC}_2\text{CH} \) \( \rightarrow \) \( \text{RC} = \text{C} = \text{C} \equiv \text{CR} \)

6. \( \text{RSH} \) \( \rightarrow \) \( \text{RS} - \text{SR} \)

7. \( \text{Ph} \text{N} - \text{NPh} \) \( \rightarrow \) \( \text{Ph} \text{N} = \text{NPh} \)

8. \( \text{HO} \) \( \text{OH} \) \( \rightarrow \) \( \text{HO} \) \( \text{OH} \)

Fig. 54
(Binding of superoxide, $O_2^-$, is now known with a mononuclear Cu (II) complex $^{278}$).

These studies and others have shown that the best catalysts for copper-based oxidations are those which employ binuclear, square-based antiferromagnetically coupled, Cu (II) sites with at least some labile ligands.

$$\begin{align*}
(1) & \quad \text{[Diagram]} \\
(2) & \quad \text{[Diagram]} \\
(3) & \quad \text{[Diagram]} \\
(4) & \quad \text{[Diagram]} \\
(5) & \quad \text{[Diagram]} \\
(6) & \quad \text{[Diagram]} \\
\end{align*}$$

Fig. 55
CHAPTER 2 - EXPERIMENTAL
EXPERIMENTAL

ORGANIC SYNTHESIS

2,6-Diacetylpyridine (DAP)

This was obtained from the Aldrich Chemical Company Ltd., and used without further purification.

Infrared Spectrum

* Inter alia: 3070, 2970, 1705, 600 (cm⁻¹)

2,5-Diformylfuran (DFF)

This compound was prepared by the modification of existing preparations. Sucrose (100 g) was dissolved in water (300 ml), hydrated oxalic acid (0.7 g) was added and the solution heated to 145°C in an autoclave under 3 atm of air, maintained at that temperature for 15 minutes and then heated at 125°C for 2.25 h. After cooling to room temperature and neutralization with CaCO₃, basic lead acetate (5 g) was added and the solution stirred for 1 h. The precipitate was removed by filtration and the clear filtrate extracted with ethyl acetate (6 x 500 ml). The combined extracts were dried (MgSO₄), filtered and evaporated to dryness yielding the product, 5-hydroxymethyl-2-furancarbaldehyde, as an orange syrup (12 g). This was used for the next stage without further purification.

5-Hydroxymethyl-2-furancarbaldehyde (6 g) was dissolved in 300 ml toluene (dried over molecular sieves) and freshly activated manganese dioxide (below) (45 g) was added. The mixture was stirred and refluxed for 6 h, after which the solution had changed colour from deep orange/brown to yellow. The solution was cooled, manganese dioxide removed by filtration and washed with 1,4-dioxan until no further yellow colour appeared in the washings. The combined washings plus filtrate were rotary evaporated to dryness, giving 2,5-diformylfuran as a pale yellow solid, yield 80%
The compound was recrystallized from chloroform/carbon tetrachloride, and then sublimed at ca 60° C/0.45 mm Hg as a fine white powder. The product was characterized from C, H, N analysis, n.m.r, i.r. and mass spectra.

Analysis
Calc: C 58.0 H 3.2%
Found: C 57.6 H 3.4%

Infrared Spectrum
Inter alia 3140 (C - H), 2860 (C - H), 1680 (C = O), 1510, 1410, 1260, 800 (cm⁻¹)

1H n.m.r Spectrum

<table>
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<th>Protons</th>
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</thead>
<tbody>
<tr>
<td>H¹</td>
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</tr>
<tr>
<td>H²</td>
<td>7.5 (S)</td>
</tr>
</tbody>
</table>

Mass Spectrum
P⁺ m/e 124

Preparation of Manganese dioxide

The compound was prepared by literature methods.²⁸²,²⁸³ Concentrated aqueous potassium permanganate was added to a stirred aqueous solution of manganese (II) sulphate above 90° C until a slight excess of potassium permanganate was indicated by a pink colouration of the supernatant liquid. Stirring and heating was continued for 0.25 h. The oxide was then collected by filtration and washed well with hot water. The product was thoroughly dried in an oven at 120-130° C and, just before use, ground to a fine black powder in a well ventilated fume cupboard.
3,3'-Diaminodipropylamine \( H_2N(CH_2)_3N(H)(CH_2)_3NH_2 \)

The amine was used as obtained from the Aldrich Chemical Company Ltd.

3,3'-Diamino-N-methyldipropylamine \( H_2N(CH_2)_3N(CH_3)(CH_2)_3NH_2 \)

The compound was used, without further purification, as obtained from the Aldrich Chemical Company Ltd.

1,5-Diaminopentane \( H_2N(CH_2)_5NH_2 \)

The compound was used, without further purification, as obtained from the Aldrich Chemical Company Ltd.

1,6-Diaminohexane. \( H_2N(CH_2)_6NH_2 \)

The compound was obtained from the Aldrich Chemical Company Ltd and used without further purification.
3-Oxapentane-1,5-diamine (NON) \( \text{H}_2\text{N(CH}_2\text{O(CH}_2\text{)\text{2NH}}_2 \)

This ligand was prepared by a method based on that described for 2,6-dioxaoctane-1,8-diamine in ref. 42.

Phosphorus tribromide (0.53 mol.) was added dropwise to a cooled, stirred solution of diethylene glycol (0.68 mol.). A white precipitate developed, and the mixture was stirred overnight at room temperature. The precipitate was filtered off and the pale yellow liquid was carefully distilled under water vacuum, yielding 3-oxapentane-1,5-dibromide (140 g; 0.60 mol).

The dibromide (0.60 mol.), potassium phthalimide (1.35 mol.) and diethylamine (3 ml) were heated together at 140° C for 3 hours. On cooling, the solid mass was broken up and washed with hot water (3 l). The solid was then recrystallized from glacial acetic acid with some decolourizing charcoal yielding the cream solid 3-oxapentane-1,5-diphthalimide (128 g; 0.35 mol.).

The diphthalimide compound (0.35 mol.) was suspended in refluxing methanol (1 l) and hydrazine hydrate (99%) (62 ml) was slowly added producing a brown solution. A white solid was preccipitated and after 2 hours refluxing, hydrochloric acid 10M (144 ml) was added. The methanol was distilled off and the white solid filtered out leaving a brown solution. To this solution, sodium hydroxide pellets (200 g) were added slowly. The top brown layer was separated off and extracted with ether (1 l) on a continuous extraction column for 48 hours. The ether was removed and the remaining oil was vacuum distilled yielding the clear product (13 g; 0.16 mol. at 90° C (1mm Hg). The yield in this synthesis is greatly reduced by the formation of large amounts of the heterocycle, morpholine. The product was characterized by its infrared and n.m.r spectra.
Infrared Spectrum

Inter alia 3370 (N - H), 3300 (N - H), 2930 (C - H)
2860 (C - H), 1600 (N - H bend), 1460 (C - H)
1120 (C - H), 1050 (C - 0), 940, 890 (cm⁻¹)

n.m.r Spectrum

\[
\begin{array}{cccccc}
 & 1 & 2 & 3 & 2 & 1 \\
\text{H} & H & H & H & H & H \\
\text{N} & \text{C} - & \text{C} - & \text{O} - & \text{C} - & \text{C} - \text{N} \\
\text{H} & H & H & H & H & H \\
\end{array}
\]

<table>
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<th>Protons</th>
<th>ppm</th>
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<td>H¹</td>
<td>1.4 (s)</td>
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</tr>
<tr>
<td>H²</td>
<td>2.8 (t)</td>
<td>1</td>
</tr>
<tr>
<td>H³</td>
<td>3.4 (t)</td>
<td>1</td>
</tr>
</tbody>
</table>

3-Dimethylaminopropylamine (CH₃)₂N(CH₂)₃NH₂

This ligand was used as obtained from the Aldrich Chemical Company Ltd and required no further purification.

Diallylamine (CH₂ = CH)₂NH

This was used as obtained from the Aldrich Chemical Company Ltd.

Infrared Spectrum

Inter alia 3280 (w, br), 3070, 2910, 2800, 1640
1450, 1410, 990, 925 (cm⁻¹)

n.m.r Spectrum (in CDCl₃)

<table>
<thead>
<tr>
<th>Protons</th>
<th>ppm</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
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<td>H¹</td>
<td>1.27 (a)</td>
<td>1</td>
</tr>
<tr>
<td>H²</td>
<td>3.26 (d)</td>
<td>4</td>
</tr>
<tr>
<td>H³</td>
<td>5.83</td>
<td>4</td>
</tr>
<tr>
<td>H⁴</td>
<td>5.99 (m)</td>
<td>2</td>
</tr>
<tr>
<td>H⁵</td>
<td>5.07 (d)</td>
<td>4</td>
</tr>
</tbody>
</table>

Mass Spectrum

M/e 97 (P⁺)
3,3'-diallylamino [ethyl/propyl] amine H₂N(CH₂)nN(CH₂CH = CH₂)₂  n = 2,3

(a) Preparation of N-bromoalkylphthalimide

Two mole of 1,2-dibromoalkane (ethyl, propyl) were mixed with acetone (1 1) and brought to reflux. Then, over a period of 1 hour, was added, in small amounts potassium phthalimide (185·2 g; 1 mol.). The suspension was refluxed for 24 hours. It was then cooled to room temperature and filtered. The filtrate was then rotary evaporated to remove acetone, yielding a thick, heavy liquid. A small amount of ethanol was added and the mixture allowed to stand. After 1 hour a large crop of white crystals had appeared. These were filtered off and the liquor rotary evaporated to remove excess dibromo compound, and then warm ethanol added and the solution seeded. Another crop of white crystals appeared. The fractions (3) were added together and dried in vacuo, to yield 83% of N-bromo[ethyl/propyl] phthalimide M.P. 71° C (Lit. 71-72). One further crop was obtainable from the liquor. This product was used in part (b).

(b) The N-bromo[ethyl/propyl] phthalimide (0.19 mol.) was added to diallylamine (56.6 g; 0.58 mol.) and heated to 140° C with stirring for 2 hours. Then excess diallylamine was distilled off and recovered, ca 150 ml of ethanol added and brought to reflux. Then 18 ml hydrazine hydrate was added. After 5 minutes a heavy beige precipitate formed. After 0.30 h reflux, the ethanol was distilled off and the precipitate added in small amounts to 80 ml of concentrated hydrochloric acid, producing a white solid. After leaving overnight this was filtered and washed with water (200 ml). Addition of sodium hydroxide (with ice-cooling) yielded a brown upper layer. This was extracted with ether by distillation, the residual oil was vacuum distilled yielding (after some diallylamine at 40° C) product (0.1 mol.) at 24° C (2mm Hg). The product
was characterized by infrared and n.m.r spectroscopy and used for subsequent syntheses in this state (yield 53%).

**Infrared Spectrum**

*Inter alia* 3360, 3280, 3070, 2920 (s, br), 2800 (s, br)

1640, 1585 (m, br), 1425, 920

**1H n.m.r Spectrum** (in CDCl₃)

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<tr>
<td>H²</td>
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<td>2</td>
</tr>
<tr>
<td>H³</td>
<td>2.75 (t)</td>
<td>2</td>
</tr>
<tr>
<td>H⁴</td>
<td>3.11 (d)</td>
<td>4</td>
</tr>
<tr>
<td>H⁵</td>
<td>5.77-5.93 (m)</td>
<td>2</td>
</tr>
<tr>
<td>H⁶</td>
<td>5.10-5.22 (m)</td>
<td>4</td>
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</table>

Preparation of EDAAF (C₂₂H₃₂N₄O)

DFF (0.004 mol.) was refluxed in dry acetonitrile with diallylaminomethylamine (0.008 mol.). After 4 hours reflux the reaction (as judged by i.r. data) was complete. The orange solution was then rotary evaporated to remove all traces of acetonitrile. The resultant dark oil was characterized by n.m.r, i.r and mass spectrometry.

**Infrared Spectrum**

*Inter alia*

**1H n.m.r Spectrum** 3064(m), 2850(s,br), 1636(s), 1442(m), 820(m), 800(m).
$^1$H: (in CDCl$_3$)

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</tr>
<tr>
<td>$H^2$</td>
<td>8.15 (s)</td>
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</tr>
<tr>
<td>$H^3$</td>
<td>3.71 (t)</td>
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<tr>
<td>$H^4$</td>
<td>2.79 (t)</td>
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<td>$H^5$</td>
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<tr>
<td>$H^6$</td>
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</tr>
<tr>
<td>$H^7$</td>
<td>5.11-5.28 (m)</td>
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$^{13}$C: (in CDCl$_3$)

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<td>C$^2$</td>
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<td>C$^3$</td>
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<td>C$^4$</td>
<td>57.3</td>
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<td>C$^5$</td>
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<tr>
<td>C$^6$</td>
<td>60.0</td>
<td>t</td>
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<tr>
<td>C$^7$</td>
<td>113.8</td>
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<tr>
<td>C$^8$</td>
<td>117.3</td>
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Preparation of PDAAF (C$_{24}$H$_{36}$N$_4$O)

This ligand was prepared by methods analogous to those for EDAAF, using diallylaminopropylamine. The oil was characterized by n.m.r, i.r and mass spectrometry.
Infrared Spectrum

Inter alia 3064(m), 2950(s,br), 1635(s), 1440(m), 1115(m), 795(m)

n.m.r. Spectrum

$^1$H: (in CD Cl$_3$)

<table>
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<td>$^2$H</td>
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<td>$^3$H</td>
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<td>$^4$H</td>
<td>1.87 ( )</td>
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$^{13}$C: (in CD Cl$_3$)

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<td>m/e 396 (P$^+$)</td>
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<tr>
<td>$^9$C</td>
<td>117.2</td>
<td>t</td>
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</table>
Preparation of J

This ligand was prepared by the same method as EDAAF and PDAAF using DFF and 3,3'-dimethylaminopropylamine as reactants. The resultant red-brown oil was characterized by n.m.r, i.r and mass spectrometry.

Infrared Spectrum

Inter alia 3090(w), 2850(s,br), 1635(s), 1455(m), 800(m)

n.m.r Spectra

\[
\begin{array}{|c|c|c|}
\hline
\text{Proton} & \text{Ppm} & \text{Integral} \\
\hline
\text{H}^1 & 6.9 (S) & 2 \\
\text{H}^2 & 8.2 (S) & 2 \\
\text{H}^3 & 3.6 (t) & 4 \\
\text{H}^4 & 1.9 (p) & 4 \\
\text{H}^5 & 2.3 (t) & 4 \\
\text{Me} & 2.2 (S) & 12 \\
\hline
\end{array}
\]

\[
\begin{array}{|c|c|c|}
\hline
\text{Atom} & \text{ppm (Decoupling)} & \text{Pattern (Off-Resonance)} \\
\hline
\text{C}^1 & 135 & d \\
\text{C}^2 & 154 & s \\
\text{C}^3 & 151 & d \\
\text{C}^4 & 60 & t \\
\text{C}^5 & 29 & t \\
\text{C}^6 & 58 & t \\
\text{Me} & 46 & q \\
\hline
\end{array}
\]

Mass Spectrum

\[m/e \quad 292 \quad (P^+)]
R33N and R33NMe

The reduced ligands were prepared from the parent \([\text{Pb}_2\text{L} \cdot (\text{NCS})_4]\) \((L = 33\text{N}, 33\text{NMe})\) complexes described later.

\([\text{Pb}_2\text{L}(\text{NCS})_4]\) \((0.0025 \text{ mol.})\) was suspended in 200 ml of refluxing ethanol. Excess \((0.013 \text{ mol.})\) \(\text{NaBH}_4\) was added in small portions. The solution was filtered to remove the black precipitate and evaporated to dryness on a rotary evaporator. The resulting white product was dissolved in a small amount of sodium hydroxide solution \((0.4 \text{ g}, 0.01 \text{ mol.} \text{ in ca 5ml})\) and extracted with chloroform \((\text{ca 200 ml in 6-8 portions})\). The resulting chloroform solution was washed with water, dried over sodium sulphate and evaporated to dryness. The yellow oil was redissolved in methanol and filtered to remove any quantities of insoluble white material. Finally, the solvent was removed on a rotary evaporator and the product pumped on a vacuum line overnight. The product was a brown oil \((\text{yield ca 60%})\) pure enough for use in subsequent synthesis. The amine was characterized from its mass spectrum, i.r and n.m.r spectra.

Infrared Spectrum

Inter alia 3270(m,br), 3040(w), 2905(s), 1588(m), 1568(m), 1470(m)-1440(m), 1170(m), 750(m) cm\(^{-1}\)

\(^1\text{H} \text{n.m.r spectra in CDCl}_3\)

<table>
<thead>
<tr>
<th>Proton</th>
<th>ppm</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>7.3(m)</td>
<td>6</td>
</tr>
<tr>
<td>(^2\text{H})</td>
<td>3.8(q)</td>
<td>4</td>
</tr>
<tr>
<td>(^3\text{H})</td>
<td>2.5(t)</td>
<td>16</td>
</tr>
<tr>
<td>(^4\text{H})</td>
<td>1.6(m)</td>
<td>8</td>
</tr>
<tr>
<td>(^6\text{Me})</td>
<td>1.3(d)</td>
<td>12</td>
</tr>
<tr>
<td>*(^6\text{H})</td>
<td>2.1(s)</td>
<td>6</td>
</tr>
</tbody>
</table>

* Signal removed with \(\text{D}_2\text{O}\) shake.

MASS SPECTRUM
R33NMe

Infrared Spectrum

Inter alia 3240 (w, br), 3040 (w), 2900 (s, br), 1585 (m), 1570 (m),
1450 (m, br), 1100 (s, br), 750 (m) cm⁻¹

¹H n.m.r Spectrum in CDCl₃

Broad and not well resolved but outline similar to that of R33N.

Mass Spectrum

m/e 552 (P⁺)
2,2'-Bi-thiazoline (bt)

The ligand bt was prepared by a modification of the method of Tomalia and Paige. A mixture of ethanolamine (50 g; 0.82 mol.) and dithioxamide (40 g; 0.33 mol.) in ethanol (160 ml) was stirred at room temperature until evolution of ammonia had ceased (ca 24 h). The resulting dark brown liquid was filtered and concentrated to a semi-solid state. Addition of water gave a gold-coloured solid, N,N'-bis-(2-hydroxyethyl)-dithioxamide, which was filtered, dried and used in the next stage.

The compound prepared above was slurred in toluene (35 g; 0.17 mol. in 250 ml) and thionyl chloride (80 g; 0.67 mol) in two equal proportions over 90 minutes. The temperature of the mixture was maintained at 45-50°C for a further 2 hours. The resulting yellow solid, 2,2'-bi-2-thiazolinium dihydrochloride, was filtered, washed with hexane and dried. The cation was neutralized by adding it, in small portions, to a stirred solution of sodium bicarbonate in water. The grey precipitate which forms was filtered, washed with water and dried. Extraction into hexane and recrystallization from ethyl acetate gave a white crystalline compound. The product was characterized from analysis, infrared, n.m.r and mass spectra.

**Analysis**  \( \text{C}_6\text{H}_8\text{N}_2\text{S}_2 \)

<table>
<thead>
<tr>
<th></th>
<th>Calc:</th>
<th></th>
<th>Found:</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>41.8</td>
<td>H</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>N 16.3%</td>
<td></td>
<td>N 16.1%</td>
</tr>
</tbody>
</table>

**Infrared Spectrum**

*Inter alia* 1588 (s), 1440 (m), 1430 (m) (cm\(^{-1}\))
n.m.r Spectrum

2,2'-Bi-4,5-dihydrothiazine (btz)

Btz was prepared in the same way as bt. 3-Aminopropanol was used as the starting material for the preparation of btz and the product was recrystallized from carbon tetrachloride.

Analysis C₂H₁₂N₂S₂

Calc:  C 48.0   H 6.0   N 14.0%
Found:  C 47.8   H 6.0   N 13.7%

Infrared Spectrum

Inter alia  1620 (s), 1445 (m), 1430 (m) (cm⁻¹)

n.m.r Spectrum

CD Cl₃ solvent
2,2'-Bi-2-imidazoline (bi)

The ligand was prepared by the method of Forssel, as modified by Wang and Bauman. Dithioxamide (20 g; 0.166 mol.) suspended in ethanol (100 ml) was treated with ethyl bromide (30 g; 0.4 mol.) and stirred at 60° C for four hours. After cooling to room temperature, 1,2-diaminoethane (75 ml; 1.1 mol.) was slowly added over 1 hour, maintaining a steady evolution of ethanediol. The mixture was heated briefly to 80° C and then stirred for 1 hour at 0° C. The resulting crude product was filtered off and recrystallized from boiling ethanol. (Yield 75%).

Analysis

\[
\text{C}_6\text{H}_{10}\text{N}_4
\]

Calc: C 52.1 H 7.3 N 40.5%

Found: C 52.0 H 7.3 N 40.3%

Infrared Spectrum

Inter alia 3190 (s), 1620 (w), 1573 (s), 1495 (s), 1450 (s) (cm\(^{-1}\))

n.m.r Spectrum

\[^6\text{d} - \text{DMSO solvent}\]

<table>
<thead>
<tr>
<th>Proton</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H^1)</td>
<td>3.3 (s)</td>
</tr>
<tr>
<td>(H^2)</td>
<td>3.5 (s br)</td>
</tr>
</tbody>
</table>

\(^{13}\text{C}: \) Ligand was insufficiently soluble in all tried solvents.

The equivalence of \(H^1\) and \(H^2\) indicates that in solution the exchange between the tautomers shown below is rapid (i.e. faster than the n.m.r time scale).
2,2'-Bi-4,5-dihydroimidazine (biz)

Ligand biz was prepared in the same way as bi but using 1,3-diaminopropane instead of 1,2-diaminoethane. The crude product was recrystallized from carbon tetrachloride (yield 70%). The resulting white crystals were characterized from their analysis, infrared, n.m.r and mass spectra.

Analysis $C_8H_{14}N_4$

Calc: C 57.8 H 8.5 N 33.7%
Found: C 57.9 H 8.5 N 33.7%

Infrared Spectrum

Inter alia 3250 (s, br), 1665 (w), 1500 (s), 1469 (m), 1439 (m) (cm$^{-1}$)

n.m.r Spectrum

in CDCl$_3$ solvent

$^1$H:

<table>
<thead>
<tr>
<th>Proton</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^1$</td>
<td>7.9 (s, br)</td>
</tr>
<tr>
<td>$H^2$</td>
<td>3.2 (d)</td>
</tr>
<tr>
<td>$H^3$</td>
<td>1.6 (p)</td>
</tr>
</tbody>
</table>

$^{13}$C:

<table>
<thead>
<tr>
<th>Atom</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C^1$</td>
<td>20.67</td>
</tr>
<tr>
<td>$C^2$</td>
<td>41.53</td>
</tr>
<tr>
<td>$C^3$</td>
<td>149.54</td>
</tr>
</tbody>
</table>

The equivalence of $C^1$ and $C^2$ and of $H^2$ and $H^3$ again indicates that all atoms are equivalent in the free state. (This evidence is, of course, removed in coordination to a metal.)

2,2'-Bi-2-oxazoline (bo)

Oxamide (15 g; 0.17 mol.) was suspended in excess ethanolamine (75 ml, 1 mol.) and refluxed for 2 hours. The resulting $N,N'$-bis-(2-hydroxyethyl)-oxamide was recrystallized from ethanol and the synthesis was continued by WenkIr's method, with slight alterations.
N,N-bis-(2-hydroxyethyl) oxamide was suspended in toluene (100 ml) and heated to 60°C. Excess thionyl chloride (40 g; 0.33 mol.) was added in two portions. Vigorous reaction occurred after addition of the second portion. The mixture was maintained at 60°C for 30 minutes, and then heated for 90 minutes on a boiling water bath. The mixture was cooled and the resulting crystals of 1,2-(dichloroethyl)-o amide were filtered off. This product refluxed for 1 hour in a methanol solution of potassium hydroxide, the solution was filtered and allowed to cool. 2,2'-Bi-2-oxazoline crystallized out of white needles which did not require further purification (yield 65%). The product was characterized, from its analysis, mass spectrum, infrared and n.m.r spectra.

Analysis \( \text{C}_6\text{H}_2\text{N}_2\text{O}_2 \)

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc:</td>
<td>C 51.4</td>
<td>H 5.7</td>
</tr>
<tr>
<td>Found:</td>
<td>C 49.9</td>
<td>H 5.6</td>
</tr>
</tbody>
</table>

Infrared Spectrum

Inter alia 1675 (w), 1625 (s), 1475 (m), 1455 (m) (cm\(^{-1}\))

n.m.r Spectrum

![Diagram of 2,2'-Bi-2-oxazoline]

\[ ^1\text{H}: \]

<table>
<thead>
<tr>
<th>Proton</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^1 )</td>
<td>4.08 (m)</td>
</tr>
<tr>
<td>( \text{H}^2 )</td>
<td>4.46 (m)</td>
</tr>
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</table>

\[ ^{13}\text{C}: \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}^1 )</td>
<td>55.24</td>
</tr>
<tr>
<td>( \text{C}^2 )</td>
<td>68.43</td>
</tr>
<tr>
<td>( \text{C}^3 )</td>
<td>155.78</td>
</tr>
</tbody>
</table>

\[
\left[\text{Cu(CH}_3\text{CN)}_4\right] \text{ClO}_4
\]

This complex was prepared by the method of Hemmerich and Sigwart. 7.0 g (0.05 mol.) of Cu\(_2\)O and 16 ml (0.4 mol.) of acetonitrile were refluxed in 60 ml of deoxygenated 2N HClO\(_4\) until all the Cu\(_2\)O had dissolved (2 hours). The white crystalline product formed on cooling under nitrogen,
it was filtered, washed with cold, deoxygenated acetonitrile and dried under a stream of nitrogen. \([\text{Cu} (\text{CH}_3\text{CN})_4]\text{ClO}_4\) was stored in a sealed flask under nitrogen.

Preparation of \((\text{CH}_3\text{CN})_2\text{Pd Cl}_2\)

\(\text{Na}_2\text{Pd Cl}_4\) (2.5 g) was dissolved in dry acetonitrile (100 ml) at 20° C, with vigorous stirring. After filtering off the precipitated NaCl the light-red filtrate was rotary evaporated (without heating) to dryness, yielding the yellow-orange microcrystalline product.

Infrared Spectrum

\(^{\text{Inter alia}}\) 2975, 2920, 2305, 2290, 1400, 1390, 1010, 400, 347, 285 (cm\(^{-1}\))
The macrocycles 33N and 33NMe

![Diagram of macrocycles 33N and 33NMe]

33N : R = H
33NMe : R = Me

Template syntheses

\[ \text{Sr}(33N) \text{ (BPh}_4 \text{)}_2 \text{ and } \text{Ca}(33N) \text{ (BPh}_4 \text{)}_2 \]

0.01 mol. \( M(ClO_4)_2 \text{H}_2 \text{O} \) (\( M = \text{Ca, Sr} \)) was dissolved in ca 100 ml of Mg-dried methanol. 6 ml (0.04 mol.) of 3,3\(^1\)-diamino-dipropylamine was added to the warm solution and also 0.02 mol. (3.26 g) DAP. The solution turned bright yellow. 0.02 mol. NaBPh\(_4\) dissolved in the minimum quantity of dry methanol was filtered into the warm yellow solution. A precipitate of \([M(33N)](BPh_4)_2\) started to form within ca 1 hour and was filtered by suction.

Analysis \([\text{Sr}(33N)](BPh_4)_2\)

- Calc: C 75.40 H 7.14 N 9.01%
- Found: C 75.32 H 7.01 N 9.06%

\([\text{Ca}(33N)](BPh_4)_2\)

- Calc: C 78.40 H 7.08 N 9.38%
- Found: C 78.40 H 7.14 N 9.08%

No perchlorate derivatives were isolated, or was the template effective when using 3,3\(^1\)-diamino-N-methyl diproplamine.
The macrocyclic ligand was prepared by the Schiff-base condensation of equimolar quantities of DAP and 3,3'-diaminodipropylamine, in the presence of AgClO₄ in refluxing methanol. After ca 12 hours refluxing the solution was filtered hot and the solvent removed by slow evaporation on standing. On cooling and concentration the required complex crystallized out and was recrystallized from acetonitrile - dull yellow crystals. (Yield 75%).

**Analysis**  \( \text{Ag}_2(33N)(\text{ClO}_4)_2 \)

Calc:  C 38.7  H 4.8  N 12.0%
Found: C 38.6  H 4.7  N 12.2%

To an acetonitrile solution of \( \text{Ag}_2(33N)(\text{ClO}_4)_2 \) an equimolar quantity of NaBPh₄ was added with stirring. Slow evaporation was unsuccessful but residue could be recrystallized from a 1:4 acetonitrile-methanol mixture. Yellow crystals. (Yield 63%).

**Analysis**  \( \text{Ag}_2(33N)(\text{BPh}_4)_2 \)

Calc:  C 68.3  H 6.2  N 8.2%
Found: C 67.7  H 6.1  N 7.9%

\[ \text{Ag}_2(33\text{NMe})[\text{BPh}_4]_2 \]

AgNO₃ (0.006 mol.) was refluxed in 600 ml methanol; amine (0.005 mol.) was added and DAP (0.005 mol.). The yellow solution was refluxed overnight (a silver-mirror develops on the inside surface of the flask). The mixture is then filtered, cooled and NaBPh₄ (0.006 mol.) added. The resultant beige precipitate was filtered off and recrystallized from acetonitrile.
No perchlorate derivative could be obtained by this template procedure.

**Analysis**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc C (%)</th>
<th>Calc H (%)</th>
<th>Calc N (%)</th>
<th>Found C (%)</th>
<th>Found H (%)</th>
<th>Found N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pb}_2(33N)(\text{NCS})_4 )</td>
<td>35.1</td>
<td>3.81</td>
<td>14.4</td>
<td>35.4</td>
<td>3.8</td>
<td>14.3</td>
</tr>
<tr>
<td>( \text{Pb}_2(33\text{NMe})(\text{NCS})_4 )</td>
<td>36.3</td>
<td>4.1</td>
<td>14.1</td>
<td>36.2</td>
<td>4.2</td>
<td>14.0</td>
</tr>
</tbody>
</table>

0.01 mol. of finely ground Pb(NCS) was suspended in 400-500 ml of methanol, DAP (0.012 mol.) and the appropriate amine (i.e. \(3,3^1\)-diaminodipropylamine or \(3,3^1\)-diamino-N-methylidipropylamine) (0.012 mol.) were added and the suspension stirred at 60°C for 3-4 hours until all Pb(NCS)\(_2\) (heavy pale solid) disappeared. The solution was filtered and on evaporation yielded a small quantity of yellow crystals of good analytical quality. The yellow solid that is filtered out contains some unreacted Pb(NCS)\(_2\) contaminant. This however did not prevent it being used for subsequent transmetallations.

**Analysis**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc C (%)</th>
<th>Calc H (%)</th>
<th>Calc N (%)</th>
<th>Found C (%)</th>
<th>Found H (%)</th>
<th>Found N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pb}_2(33N)(\text{NCS})_4 )</td>
<td>35.1</td>
<td>3.81</td>
<td>14.4</td>
<td>35.4</td>
<td>3.8</td>
<td>14.3</td>
</tr>
<tr>
<td>( \text{Pb}_2(33\text{NMe})(\text{NCS})_4 )</td>
<td>36.3</td>
<td>4.1</td>
<td>14.1</td>
<td>36.2</td>
<td>4.2</td>
<td>14.0</td>
</tr>
</tbody>
</table>

**Transmetallation**

(a) **Mononuclear complexes:**

\[ \text{Fe}(33N)[\text{BPh}_4]_2 \]

To \(\text{Sr}(33N)(\text{BPh}_4)_2\) (0.0005 mol.) in 10-15 ml of dry acetonitrile under \(\text{N}_2\) was added \(\text{Fe}(_{\text{C10}})_2\) (0.0005 mol.) and NaBPh (0.001 mol). ca 15 ml dry deoxygenated ethanol was added gradually and dark-purple crystals appeared on slight evaporation.
Analysis
Calc: C 77.4 H 7.0 N 9.3%
Found: C 77.6 H 7.1 N 9.4%

\[
\left[ \text{M(33NMe)} \right]\left[ \text{BPh}_4 \right]_2 \cdot 2\text{MeCN} \quad M = \text{Fe, Co, Ni}
\]

\[
\left[ \text{Ag}_2(33N)\right]\left[ \text{BPh}_4 \right]_2 \ (0.001 \text{ mol.}) \text{ was dissolved in } 200 \text{ ml acetonitrile at ca } 50-60^\circ \text{ C, and } 0.001 \text{ mol. } \text{M(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \text{ and } 0.002 \text{ mol. NaBPh}_4 \text{ added. The precipitate of AgBPh}_4 \text{ was filtered out and the solution evaporated down to 10-20 ml. The product was recrystallized from acetonitrile/ ethanol.}
\]

Analysis
Calc: C 75.3 H 7.4 N 10.5%
Found: C 75.2 H 7.1 N 10.8%

\[
\left[ \text{Co(33NMe)} \right]\left[ \text{BPh}_4 \right]_2 \cdot 2\text{MeCN}
\]
Calc: C 76.2 H 7.2 N 10.6%
Found: C 76.2 H 7.3 N 10.8%

\[
\left[ \text{Ni(33NMe)} \right]\left[ \text{BPh}_4 \right]_2 \cdot 2\text{MeCN}
\]
Calc: C 76.2 H 7.2 N 10.6%
Found: C 76.5 H 7.2 N 10.7%

(b) Binuclear Complexes

\[
\left[ \text{M}_2(33\text{N})(\text{NCS})_4 \right] \cdot \text{H}_2\text{O} \quad M = \text{Mn, Co, Ni, Zn}
\]

To 0.001 mol. M(NCS)_2 in dry ethanol was added 0.005 mol. \[
\left[ \text{Sr}(33\text{N})\right]\left[ \text{BPh}_4 \right]_2 \text{ in 20-30 ml dry acetonitrile. The solution was left overnight to crystallize.}
\]

Analysis
Calc: C 46.1 H 5.5 N 19.0%
Found: C 45.8 H 5.3 N 19.2%
[\text{Co}_2(33\text{N})(\text{NCS})_4\text{]}\cdot 4\text{H}_2\text{O}

\text{Calc: C 43.5 H 5.6 N 17.9}
\text{Found: C 43.5 H 4.9 N 17.3%}

[\text{Ni}_2(33\text{N})(\text{NCS})_4\text{]}\cdot 2\text{H}_2\text{O}

\text{Calc: C 45.5 H 5.4 N 18.7%}
\text{Found: C 46.1 H 5.3 N 18.5%}

[\text{Zn}_2(33\text{N})(\text{NCS})_4\text{]}\cdot 2\text{H}_2\text{O}

\text{Calc: C 44.6 H 5.3 N 18.4%}
\text{Found: C 44.9 H 4.9 N 18.5%}

[\text{Fe}_2(33\text{N})(\text{H}_2\text{O})_4\text{]}\text{[ClO}_4\text{]}_4

\text{Solid Fe(ClO}_4\text{)}_2\cdot 6\text{H}_2\text{O (0.0015 mol.) was added to 0.0005 mol.}

[\text{Sr}(33\text{N})][\text{BPh}_4\text{]}_2 \text{in 15 ml dry deoxygenated acetonitrile. 20 ml ethanol was added and N}_2\text{ bubbled ca 2 hours, after which time dark crystals were filtered off, which contained BPh}_4\text{ impurity. Recrystallization from acetonitrile under N}_2\text{ yielded pure [Fe}_2(33\text{N})(\text{H}_2\text{O})_4\text{][ClO}_4\text{]}_4.}

\text{N.B. This solid explodes readily under slight friction.}

\text{Analysis}

\text{Calc: C 32.8 H 4.8 N 10.2%}
\text{Found: C 33.2 H 4.7 N 10.3%}

[\text{M}_2(33\text{N})(\text{MeCN})_2\text{][ClO}_4\text{]}_4\cdot \text{H}_2\text{O} \quad \text{M = Co, Ni}

[\text{Sr}(33\text{N})][\text{BPh}_4\text{]}_2 (0.001 mol.) was dissolved in the minimum quantity of dry acetonitrile, and to this was added M(ClO}_4\text{)}_2\cdot 6\text{H}_2\text{O (0.002 mol.) and 0.5 g NaClO}_4\text{. ca 15 ml ethanol was added, and the solution left in a fridge to crystallize.}
Analyses

\[ \text{[Co}_2\text{(33N)(MeCN)}_2\text{][ClO}_4\text{]}_4\cdot\text{H}_2\text{O} \]

Calc: C 36.1 H 4.6 N 12.4%
Found: C 36.0 H 4.6 N 12.2%

\[ \text{[Ni}_2\text{(33N)(MeCN)}_2\text{][ClO}_4\text{]}_4\cdot\text{H}_2\text{O} \]

Calc: C 35.9 H 4.4 N 13.2
Found: C 35.6 H 4.4 N 13.0

\[ \text{[Co}_2\text{(33NMe)(NCS)}]\text{][BPh}_4\text{]}_3\cdot\text{3H}_2\text{O}\cdot\text{MeCN} \]

To a suspension of 0.0004 mol. \([\text{Pb}_2\text{(33NMe)(NCS)}]\text{]}_4\] in 100 ml acetonitrile, \(\text{Co(ClO}_4\text{)}_2\cdot\text{6H}_2\text{O} \) (0.0008 mol.) was added, and refluxed ca 20 minutes until a red-brown solution forms. \(\text{Pb(NCS)}_2\) was filtered off. 0.003 mol. \(\text{NaBPh}_4\) was added to the filtrate, which was evaporated to low volume, and red-brown crystals filtered off.

Analysis
Calc: C 72.4 H 6.3 N 7.5%
Found: C 72.6 H 6.6 N 7.9%

\[ \text{[Co}_2\text{(33N)(NCS)}]\text{][BPh}_4\text{]}_3\cdot\text{H}_2\text{O}\cdot\text{5MeCN} \]

Prepared in an analogous fashion to that described for \([\text{Co}_2\text{(33NMe)(NCS)}]\text{][BPh}_4\text{]}_2\cdot\text{3H}_2\text{O}\cdot\text{MeCN} \) except substituting \([\text{Pb}_2\text{(33N)(NCS)}]\text{]}_4\] for \([\text{Pb}_2\text{(33NMe)(NCS)}]\text{]}_4\]. Again red-brown crystals were obtained on evaporation.

Analysis
Calc: C 72.4 H 6.5 N 10.5%
Found: C 72.1 H 6.7 N 10.7%
To 0.001 mol. $[\text{Ag}_2(33\text{NMe})][\text{ClO}_4]_2$ in 100 ml dry methanol was added 0.005 mol. of the appropriate metal halide, and the mixture was refluxed for 1 hour. The precipitate of AgCl was filtered off, and volume reduced to ca 20 ml when crystals of the desired product were obtained.

N.B. $[\text{Fe}_2(33\text{NMe})\text{Cl}_2][\text{ClO}_4]_2$ explodes readily under slight friction.

**Analyses**

$[\text{Ni}_2(33\text{NMe})\text{Cl}_2][\text{ClO}_4]_2 \cdot 4\text{H}_2\text{O}$

- Calc: C 38.3 H 5.6 N 11.2%
- Found: C 38.9 H 5.3 N 11.1%

$[\text{Fe}_2(33\text{NMe})\text{Cl}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2$

- Calc: C 39.9 H 5.2 N 11.6%
- Found: C 40.4 H 5.3 N 12.0%

**The Copper Complexes**

$[\text{Cu}_2(33\text{N})][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O}$

Prepared on m.molar scale by refluxing 1 m.mol. Cu(CIO$_4$)$_2$ 6H$_2$O with 0.5 m.mol. $[\text{Ag}_2(33\text{N})][\text{ClO}_4]_2$ in 100 ml of an acetonitrile/methanol (2 : 1) mixture for ca $\frac{1}{2}$ hour. Bright blue crystals were obtained on cooling. (Yield 50%).

**Analysis**

- Calc: C 32.4 H 4.7 N 10.1%
- Found: C 32.0 H 4.4 N 10.0%

$[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3 \cdot 2\text{MeCN}$

To a solution of 1 m.mol. $[\text{Sr}(33\text{N})][\text{BPh}_4]_3$ in 50 ml acetonitrile was added excess (ca 1 g) NaBPh$_4$ and 2.1 m.mol. Cu(O Ac)$_2$ · H$_2$O in 50 ml dry acetonitrile. The Sr(OAc)$_2$ precipitate was filtered off and the resulting blue-green solution concentrated to ca 30 ml on rotary evaporator. The concentrated solution crystallized out, on cooling, the product which could be recrystallized either from acetonitrile or DMF.
Analysis of $[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3\cdot\text{2MeCN}$

Calc: C 74.8 H 0.5 N 8.2%

Found: C 74.5 H 6.4 N 8.4%

$[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3\cdot\text{2DMF} \cdot \text{3H}_2\text{O}$

Calc: C 72.0 H 6.9 N 7.7%

Found: C 71.7 H 6.9 N 7.8%

$[\text{Cu}_2(33\text{N})(\text{NCX})_4]$ X = S, Se

To 0.1 m.m-1. $[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3\cdot\text{2MeCN}$ or $[\text{Cu}_3(33\text{N})][\text{ClO}_4]_4\cdot\text{4H}_2\text{O}$ in ca 40 ml of acetonitrile, were added, in slight excess, a methanol solution of LiNCS or KNCSe respectively. The pseudohalide complex crystallized out rapidly as very small crystals. (Yield 60-70%).

Analyses of $[\text{Cu}_2(33\text{N})(\text{NCS})_4]$ and $[\text{Cu}_2(33\text{N})(\text{NCSe})_4]$

Calc: C 46.6 H 5.1 N 19.3%

Found: C 46.5 H 5.1 N 19.2%

Calc: C 38.4 H 4.4 N 15.9%

Found: C 38.2 H 4.2 N 15.7%

$[\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{BPh}_4]_2\cdot\text{MeCN}$ and $[\text{Cu}_2(33\text{N})(\text{N}_3)_2][\text{BPh}_4]_2\cdot\text{H}_2\text{O}$

To 0.05 m.mol of $[\text{Cu}_2(33\text{N})(\text{BPh}_4)_3]$ 2MeCN in ca 30 ml acetonitrile was added a slight deficit of an alcoholic solution of LiNCS or NaN3 (0.9 m.mol.) respectively, and the complex allowed to crystallize. The green needles of $[\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{BPh}_4]_2\cdot\text{MeCN}$ were stable in the solid state, while the fine blue-green needles of the azido complex turned brownish on standing, particularly in light. As this azido complex appeared to be potentially explosive (e.g. on grinding or heating) few measurements were carried out on it. (Yield 55, 70% respectively).
Analyses

$[\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{BPh}_4]_2 \cdot \text{MeCN}$

Calc: C 68.4  H 6.1  N 10.7%
Found: C 68.5  H 6.1  N 10.7%

$[\text{Cu}_2(33\text{N})(\text{N}_3)_2][\text{BPh}_4]_2 \cdot \text{H}_2\text{O}$

Calc: C 67.7  H 6.3  N 14.2%
Found: C 67.6  H 6.2  N 14.4%

$[\text{Cu}_2(\text{R33N})][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O}$

1 m.mol. Cu(ClO$_4$)$_2$·6H$_2$O was added to $\frac{1}{4}$ m.mol. of R33N in ca 150 ml methanol. A deep-blue solution was produced which crystallized out on concentration.

Analysis

Calc: C 32.1  H 5.4  N 10.0%
Found: C 32.7  H 4.9  N 10.0%

$[\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$

Addition of 1 m.mol. of Cu(ClO$_4$)$_2$·6H$_2$O to a suspension of $[\text{Pb}_2(33\text{N})(\text{NCS})_4](0.5$ m.mol.) in ca 200 ml warm acetonitrile produced a green solution and a brown solid. The solid was filtered off and the filtrate rotary evaporated to ca 25 ml. Addition of 10 ml methanol induces crystallization of a blue-green product.

Analysis

Calc: C 38.6  H 4.8  N 14.1%
Found: C 38.0  H 4.4  N 14.2%
[Cu$_2$(33NMe)](CIO$_4$)$_4$ 4H$_2$O

[Ag$_2$(33NMe) (CIO$_4$)$_2$] * (0.05 g) was dissolved in 200 ml methanol, close to reflux. Any insoluble impurities were filtered out at this stage. 0.15 m.mol. of Cu(CIO$_4$)$_2$ 6H$_2$O in methanol was added to the solution which was then refluxed for ca 10 minutes. Rotary evaporation to low volume results in an amorphous blue solid. (Yield 65%).

Analysis

Calc:  C 38.6  H 4.9  N 14.1%
Found: C 38.0  H 4.4  N 14.2%

* Although, for convenience, this compound has been assigned the formula as stated it is in fact of indefinite composition, - analytical data being inconsistent from preparation to preparation. It may be that it contains both di-Pb (II) and di-Ag (I) complexes. In any case i.r confirms the absence of thiocyanate and is consistent with the presence of the macrocycle. It was found that, although not pure, it was capable of being used as a precursor to other complexes. It was prepared as follows:-

2.5 g (2.0 m.mol.) [Pb$_2$(33NMe) (NCS)$_4$] was suspended in 250 ml of methanol and brought to reflux. 5.0 g (20 m.mol.; ca 10X excess) of AgCIO$_4$ was then added as a solution in ca 75 ml of methanol while vigorously stirring. The suspension becomes white immediately on addition. Thereafter it gradually darkens to brown, after ca 1½ hours refluxing. The solution was then filtered and the yellow filtrate evaporated to the last 100 ml. At this stage a resultant creamy solid is filtered off and dried. (Yield 1.9 g) The solid is photosensitive and should be used within several days of synthesis.

Infrared Spectrum

Inter alia 3500 (m, br) 3080 (m)  2920 (m)  2860 (m)  1633 (m)
1580 (m) 1445 (m)  1090 (s, br)  813 (m)  623 (s).
The Macrocycles $P + H$

$P: R = (CH_2)_5$

$P: R = (CH_2)_6$

$[\text{P}b_2\text{P}(\text{NCS})_4]$ (Template Synthesis)

$\text{Pb}(\text{NCS})_2$ (0.01 mol.), DAP (0.01 mol.) and 1,5-diaminopentane (0.01 mol.) were stirred vigorously at $60^\circ$ C in a 400 ml methanol/500 ml acetonitrile solvent mixture for 3 hours, after which a grey powder was filtered off. The orange filtrate, on cooling and slow evaporation, gave yellow crystals.

**Analysis**

Calc:  C 34.8  H 3.5  N 12.7%

Found: C 34.7  H 3.7  N 12.4%

$[\text{P}b_2\text{P}[\text{ClO}_4]_4$

$[\text{P}b_2\text{P}(\text{NCS})_4]$ (0.0005 mol.) and AgClO$_4$ (0.003 mol.) on mixing, in 80 ml acetonitrile, produced an immediate white precipitate. After stirring and warming for ½ hour, the solution was filtered and rotary evaporated, giving a pinkish solid. This solid was recrystallized from acetonitrile as small white crystals.

**Analysis**

Calc:  C 26.5  H 3.0  N 6.6%

Found: C 26.0  H 3.1  N 6.0%
\[
\text{[Pb}_2\text{P}(\text{NCS})_2][\text{ClO}_4]_2
\]

\(\text{Pb}_2\text{P(ClO}_4)_4\) (0.0002 mol.) was dissolved, on warming in 100 ml dry acetonitrile. \(\text{Li(NCS)}_2\) (0.0002 mol.) in 5 ml dry acetonitrile was added with stirring. The solution became turbid before the addition was complete. After filtration the pale yellow filtrate was left to cool slowly. Primrose yellow crystals were obtained.

**Analysis**

Calc: C 30.3 H 3.2 N 9.4%

Found: C 30.1 H 3.2 N 9.4%

\[
\text{[Pb}_2\text{P}(\text{NCS})][\text{ClO}_4]_3
\]

\(\left[\text{Pb}_2\text{P(NCS)}_4\right]_3\) (0.001 mol.) and \(\text{AgClO}_4\) (0.003 mol.) were stirred together in 300 ml dry acetonitrile. The resulting precipitate of AgNCS was removed by filtration and the filtrate evaporated to ca 120 ml. Cooling on ice then produced pale cream crystals. Further crops were obtainable on subsequent evaporations.

**Analysis**

Calc: C 28.3 H 3.1 N 8.0%

Found: C 28.7 H 3.1 N 7.7%

**Transmetallations**

(a) **Heterobinuclear**

\(\text{[Pb Mn P(NCS)}_4]\)

\(\text{[Pb}_2\text{P}[\text{ClO}_4]_4\) (0.00025 mol.) and \(\text{Mn(ClO}_4)_2\) \(\_6\text{H}_2\text{O}\) (0.0005 mol.) dissolved in 100 ml dry acetonitrile. Excess LiNCS (0.001 mol.) was added. The precipitate produced on adding LiNCS was filtered leaving a yellow filtrate. This was set aside in a draft to evaporate slowly. Orange crystals were separated from an accompanying white precipitate.
Analysis

Calc: C 40.3 H 4.0 N 14.7%
Found: C 39.4 H 3.9 N 14.4%

\([\text{Pb Fe P(NCS)}_2][\text{ClO}_4]_2 \cdot 2\text{MeCN}\]

\([\text{Pb}_2\text{P(NCS)}_4] (0.001 \text{ mol.})\) were stirred together in 120 ml dry de-oxygenated acetonitrile under a nitrogen stream. The resultant deep wine coloured solution was reduced in volume by bubbling nitrogen. Addition of 80 ml ethanol and evaporation to 30 ml produced a dark solid.

Analysis

Calc: C 36.5 H 4.0 N 11.5%
Found: C 36.3 H 4.1 N 12.0%

\([\text{Pb Ni P(NCS)}_2][\text{ClO}_4]_2 \cdot 2\text{MeCN}\]

\(\text{Pb}_2\text{P(NCS)}_4 (0.0005 \text{ mol.})\) and \(\text{Ni(ClO)}_4 \cdot 6\text{H}_2\text{O} (0.001 \text{ mol.})\) were mixed in 80 ml acetonitrile. A resultant white precipitate was filtered off and the green filtrate reduced in volume to yield khaki-green crystals.

Analysis

Calc: C 35.4 H 4.2 N 12.1%
Found: C 35.9 H 3.8 N 12.1%

(b) Homobinuclear

\([\text{Cu}_2\text{P}][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O}\]

\(\text{Pb}_2\text{P}[\text{ClO}_4]_4 (0.0005 \text{ mol.})\) and \(\text{Cu(ClO)}_4 \cdot 6\text{H}_2\text{O} (0.001 \text{ mol.})\) were stirred in 100 ml dry acetonitrile with 10 ml dry ethanol. The volume was reduced to 50 ml and the solution set aside. By next day crystallization had begun. Dry ethanol (ca 30 ml) and cooling encouraged further production of the blue product.
Analysis
Calc:  C 31.9  H 4.4  N 8.0%
Found: C 32.1  H 4.3  N 8.2%

\[ \text{[Cu}_2\text{P(NCS)}_2]\text{[ClO}_4\text{]}_2\cdot\text{H}_2\text{O} \]

\[ \text{[Pb}_2\text{P(NCS)}_4\text{]}(0.001 \text{ mol.}) \text{ and Cu(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O (0.002 mol.) in 150 ml acetonitrile. The solution was filtered, 50 ml ethanol added and volume reduced to 100 ml. On standing the filtrate produced blue/green crystals.} \]

Analysis
Calc:  C 39.2  H 4.4  N 12.2%
Found: C 39.3  H 4.3  N 12.3%

\[ \text{[Cu}_2\text{P(NCS)}_2]\text{[BPh}_4\text{]}_2\cdot\text{H}_2\text{O} \]

This complex was prepared by a simple metathesis reaction between excess NaBPh₄ and \([\text{Cu}_2\text{P(NCS)}_2]\text{[ClO}_4\text{]}_2\cdot\text{H}_2\text{O}\) (molar ratios 3:1 respectively). Followed by recrystallization from acetonitrile to give green crystals in 70% yield.

Analysis
Calc:  C 69.0  H 5.8  N 8.3%
Found: C 68.8  H 5.8  N 8.4%

\[ \text{[Co}_2\text{P(NCS)}_2]\text{[ClO}_4\text{]}_2\cdot\text{MeCN} \]

\[ \text{[Pb}_2\text{P(NCS)}_4\text{]}(0.001 \text{ mol.}) \text{ and Co(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O (0.002 mol.) in 300 ml acetonitrile. After 3/4 hour stirring and warming the solution was filtered, the filtrate rotary evaporated to 150 ml and cooled to produce dark-brown crystals.} \]

Analysis
Calc:  C 41.2  H 4.4  N 13.5%
Found: C 40.8  H 4.4  N 13.7%
To a stirring solution of \([\text{Pb}_2\text{P(NCS)}_4]\) (0.0005 mol) in 70 ml dry deoxygenated acetonitrile, under nitrogen, was added \(\text{Fe(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O}\) (0.002 mol) as solid. The resultant precipitate of \(\text{Pb(NCS)}_2\) was filtered off under a nitrogen atmosphere and the filtrate reduced by bubbling nitrogen. Dark crystals of product were obtained at low volume.

**Analysis**

Calc: C 40.7  H 4.3  N 12.7%

Found: C 40.5  H 4.5  N 12.4%

\([\text{Pb}_2\text{H(NCS)}_4]\) 2,6-DAP (0.025 mol.) was dissolved in methanol (500 ml). 1,6-diaminohexane (0.025 mol.) was added. With vigorous stirring finely divided \(\text{Pb(NCS)}_2\) (0.025 mol.). The mixture was brought to reflux to ca 45 minutes, and then left stirring overnight with the heat off. A crude yellow product (probably containing unreacted \(\text{Pb(NCS)}_2\) contaminant) was isolated. (Yield 72%). This product was used to form subsequent complexes.

**Analysis**

Calc: C 36.0  H 3.7  N 12.4%

Found: C 34.4  H 3.7  N 11.1%

\([\text{Pb}_2\text{H}]\text{[ClO}_4\text{]}_2\cdot\text{H}_2\text{O}\)

To a suspension of \([\text{Pb}_2\text{H(NCS)}_4]\) (0.002 mol.) in methanol (200 ml) was added, with stirring, \(\text{AgClO}_4\) (0.007 mol.) dissolved in methanol. The mixture was maintained at 50°C for 1 hour, during which time the colour gradually changed from yellow to off-white. A fine precipitate of \(\text{AgNCS}\) was then filtered out and the filtrate reduced in volume to yield (15%) of product.

**Analysis**

Calc: C 27.4  H 3.4  N 6.4%

Found: C 27.5  H 3.4  N 6.3%
The Macrocycle Q

Template Synthesis

\[\text{[MQ][ClO}_4\text{]}_2\cdot\text{EtOH} \cdot \text{H}_2\text{O} \quad (M = \text{Ca (II), Ba (II)})\]

\(\text{N(ClO}_4\text{)}_2\cdot\text{XH}_2\text{O} \quad (X = 3, 4) \quad (0.01 \text{ mol.}) \text{ and DFF (0.01 mol.) were dissolved in 500 ml of dry ethanol containing 10% dry acetonitrile.}\)

3-oxapentane-1,5-diamine (0.01 mol.) dissolved in 5 ml ethanol was then slowly added, dropwise, with vigorous stirring. The mixture was then refluxed. A darkening of the solution is noticeable during the first 15 minutes of refluxing. Reflux was maintained for a total 3/4 hour. The solution was then filtered, rotary evaporated to half-volume and set aside. Crystals appear on standing (beige for Ca (II); pink for Ba (II)). Further crops were obtainable on subsequent evaporations. Use of ethanol as solvent results in the corresponding methanol solvate. (Yield 75%).

Analyses

\[\text{[CaQ][ClO}_4\text{]}_2\cdot\text{EtOH} \cdot \text{H}_2\text{O}\]

Calc: C 38.4 H 4.7 N 8.1%
Found: C 38.1 H 4.1 N 7.5%

\[\text{[BaQ][ClO}_4\text{]}_2\cdot\text{EtOH} \cdot \text{H}_2\text{O}\]

Calc: C 33.7 H 4.1 N 7.1%
Found: C 33.2 H 4.1 N 7.0%

\[\text{[BaQ][ClO}_4\text{]}_2\cdot\text{MeOH} \cdot \text{H}_2\text{O}\]

Calc: C 32.7 H 3.9 N 7.3%
Found: C 32.7 H 3.9 N 7.1%

N.B. (a) Attempts to use Sr (II) as a template proved unsuccessful.
(b) \[\text{[CaQ][ClO}_4\text{]}_2\cdot\text{EtOH} \cdot \text{H}_2\text{O}\] has a shelf life of ca 2 months, during which it gradually turns brown and sticky. \[\text{[BaQ][ClO}_4\text{]}_2\cdot\text{EtOH} \cdot \text{H}_2\text{O},\] on the other hand, appears to be stable.
Non-macrocyclic templates (3/4Q)

\[ \text{[M}(3/4Q)\text{][C}_{10}^4\text{]}_2 \cdot \text{H}_2\text{O} \quad (\text{M} = \text{Ca (II), Sr (II)}) \]

M(C\text{10}_4\text{)}_2 \cdot \text{H}_2\text{O} (0.002 \text{ mol.}) and DFF (0.002 \text{ mol.}) were dissolved in 100 ml dry ethanol. 3-oxapentane-1,5-diamine (0.002 \text{ mol.}) dissolved in 5 ml ethanol was slowly added dropwise, with vigorous stirring at room temperature. Stirring was maintained for 1 hour, during which time a white crystalline product had developed. The product was isolated by filtration and dried.

Analyses

\[ \text{[Ca}(3/4Q)\text{][C}_{10}^4\text{]}_2 \cdot \text{H}_2\text{O} \]
Calc: C 30.4 H 4.7 N 10.1%
Found: C 30.5 H 4.3 N 10.1%

\[ \text{[Sr}(3/4Q)\text{][C}_{10}^4\text{]}_2 \cdot \text{H}_2\text{O} \]
Calc: C 28.0 H 4.4 N 9.3%
Found: C 28.1 H 4.0 N 9.2%

N.B.

(a) The Ca (II) product was unstable over long time periods, unlike Sr (II) product.

(b) Attempts to prepare a Ba (II) analogue proved unsuccessful.
[QH][BPH₄] 

[Ag₂Q][ClO₄]₂·2H₂O (0.0005 mol.) in 30 ml of 3:1 ethanol:acetonitrile solvent. A solution containing NaBPH₄ (0.002 mol.) dissolved in the minimum of acetonitrile was then added at room temperature. The white precipitate of AgBPH₄ was filtered off and the filtrate evaporated to give white needles in low yield.

Analysis

Calc:  C 75.0  H 6.4  N 8.0%

Found: C 74.9  H 6.7  N 7.8%
[Ag₂Q][ClO₄]₂·2H₂O

[BaQ][ClO₄]₂·EtOH·H₂O (0.0005 mol.) was dissolved in 300 ml methanol and 50 ml acetonitrile. Excess AgClO₄ (0.002 mol.) dissolved in 10 ml acetonitrile was added dropwise at room temperature. Further additions of acetonitrile may be used to prevent turbidity developing. The solution was then rotary evaporated to low volume to obtain a white solid.

Analysis
Calc: C 28.8 H 3.4 N 6.7%
Found: C 28.6 H 3.1 N 6.5%

[Cu₂Q][ClO₄]₂·3H₂O

[BaQ][ClO₄]₂·EtOH (0.0008 mol.) in cold dry deoxygenated methanol. [Cu(MeCN)₄][ClO₄] (0.0016 mol.) in cold dry deoxygenated methanol. Mix under a nitrogen stream (total volume ca 80 ml). The resultant orange solution was stirred under nitrogen until crystalization occurred. The yellow crystals were filtered off under nitrogen, washed with ice-cold deoxygenated methanol and dried. Yield ca 65%. The solid is slightly air sensitive and as a precaution should be stored in vacuo.

Analysis
Calc: C 32.8 H 4.1 N 7.6%
Found: C 32.5 H 4.0 N 7.2%

[Cu₂Q(pdz)₂][BPh₄]₂ (pdz = pyridazine)

[MO][ClO₄]₂·EtOH·H₂O (M = Ca (II) or Ba (II) (0.0003 mol.) dissolved in 50 ml of deoxygenated acetonitrile/methanol (1:1) solvent mixture. Cu(MeCN)₄ClO₄ (0.0006 mol.) was added as solid to the above solution at room temperature, under a nitrogen stream. Pyridazine (0.0006 mol.) was then added dropwise to the yellow solution without any observed colour change. NaBPh₄ (0.0012 mol.) was then added as a solid and dissolved on stirring. After 15-20 seconds red crystals began to develop. The solution
was evaporated under nitrogen until the supernatant was devoid of most colour. The red fluorescent crystals were isolated under nitrogen and recrystallized from acetonitrile. (Yield 83%).

**Analysis**

Calc:  C 69.7   H 5.4   N 8.6%
       Found: C 69.4   H 5.5   N 8.6%

\[[\text{Cu}_2\text{Q}][\text{BPh}_4]\text{2} \cdot 2\text{MeCN}\]

(a) This complex was obtained as a by-product in attempted preparations of Cu (II) derivatives: \[[\text{BaQ}][\text{ClO}_4]_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O} (0.0012 \text{ mol.}), \text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O} (0.0006 \text{ mol.})\] and \(\text{NaBPh}_4 (0.0003 \text{ mol.})\) were reacted at room temperature in 30 ml acetonitrile. The first crop of crystals were blue (see \[[\text{CuQ}][\text{BPh}_4]\text{2}\]). The filtrate of the above was red. Addition of methanol helped produce orange crystals of the title complex.

**Analysis**

Calc:  C 69.6   H 5.8   N 7.0%
       Found C 69.9   H 5.9   N 6.9%

(b) Alternatively it may be prepared by recrystallization of the complex \[[\text{Cu}_2\text{Q}][\text{ClO}_4]\text{2} \cdot \text{H}_2\text{O}\] from acetonitrile, in the presence of equivalent of \(\text{NaBPh}_4\).

\[[\text{CuQ}][\text{BPh}_4]\text{2} \quad (Q = \text{C}_{24}\text{H}_{36}\text{N}_6\text{O}_5)\]

The various routes in this isolation of \[[\text{CuQ}^1][\text{BPh}_4]\text{2}\] are summarized in Fig 82.

**Method (a):** \[[\text{MQ}][\text{ClO}_4]\text{2} \cdot \text{EtOH} \cdot \text{H}_2\text{O} (\text{M = Ca (II) or Ba (II); 0.0003 mol.})\] dissolved in 50 ml acetonitrile. Addition of \(\text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O} (0.0006 \text{ mol.})\) produced a green solution at room temperature. This solution was then cooled on ice and stirred while \(\text{NaBPh}_4 (0.0012 \text{ mol.})\), dissolved in
Acetonitrile was added. After ca 1 minute a pale blue solid appeared. This solid was recrystallized from cold acetonitrile using a rotary evaporator with a room temperature water bath. The resultant aquamarine coloured crystals were obtained in 50% yield.

**Method (b):** $[\text{M(ClO}_4\text{)}][\text{ClO}_4\text{]}_2\cdot\text{H}_2\text{O}$ (M = Ca (II) or Sr (II); 0.0003 mol.) and Cu(ClO$_4$)$_2\cdot$6H$_2$O (0.0006 mol.) were heated in 50 ml acetonitrile at room temperature. Addition of NaBPh$_4$ (0.0012 mol.) precipitates a pale blue solid which was recrystallized as described above. (Yield 36%).

**Method (c):** $[\text{AgClO}_4][\text{ClO}_4\text{]}_2\cdot2\text{H}_2\text{O}$ (0.0003 mol.), Cu(ClO$_4$)$_2\cdot$6H$_2$O (0.0006 mol.) and NaBPh$_4$ (0.0024 mol) were reacted together in 100 ml acetonitrile. The precipitate of AgPBPh$_4$ was filtered off before evaporating to yield 45% aquamarine crystals.

**Method (d):** DFF (0.001 mol.), 3-oxapentane-1,5-diamine (0.001 mol.) and Cu(ClO$_4$)$_2\cdot$6H$_2$O (0.001 mol.) were reacted at room temperature in acetonitrile. NaBPh$_4$ (0.003 mol.) produces product.

**Analysis**

<table>
<thead>
<tr>
<th>Calc:</th>
<th>C 72.6</th>
<th>H 6.4</th>
<th>N 7.1</th>
<th>Cu 5.4%</th>
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<tbody>
<tr>
<td>Found:</td>
<td>C 72.5</td>
<td>H 6.5</td>
<td>N 7.1</td>
<td>Cu 5.4%</td>
</tr>
</tbody>
</table>

$[\text{Cu}_2\text{Q(O Me)}_2(\text{py})_2][\text{ClO}_4\text{]}_2\cdot2\text{H}_2\text{O}$

$[\text{BaQ}][\text{ClO}_4\text{]}_2\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ (0.0008 mol.) in cold dry deoxygenated methanol. Mixed in, under nitrogen a solution of $[\text{Cu(MeCN)}_4][\text{ClO}_4\text{]}$ (0.0016 mol.) in cold, dry deoxygenated methanol. Excess pyridine (ca 3 ml) is then added and the whole solution exposed to atmosphere oxygen. The orange solution becomes green, then bright green crystals of product separate out. (Yield ca 80%).

**Analysis**

<table>
<thead>
<tr>
<th>Calc:</th>
<th>C 39.8</th>
<th>H 4.6</th>
<th>N 8.7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 39.9</td>
<td>H 4.6</td>
<td>N 8.4%</td>
<td></td>
</tr>
</tbody>
</table>
Complexes of the Acyclic Ligands J and EDAAF

\[
\text{[CuI} _4 J\text{]}
\]

DFF (0.0005 mol.) and 3,3'-dimethylamino-propylamine (0.001 mol) in 30 ml. dry deoxygenated acetonitrile under a stream of nitrogen. Addition of CuI solid (0.001 mol.) produced a red solution. Dry deoxygenated ethanol (8 ml.) was added and the solution evaporated and cooled by bubbling nitrogen. The resultant orange lustrous compound was filtered and dried under N\textsubscript{2}.

Analysis

Calc: C 18.2  H 2.7  N 5.3  I 48.1%  
Found: C 18.9  H 2.7  N 5.0  I 48.0%

\[
\text{[Cu}_2 J\text{(NCS)} _2\text{]}
\]

The free ligand J (0.003 mol.) in dry deoxygenated acetonitrile (30 ml.) under nitrogen, at room temperature. Cu(MeCN)\textsubscript{4}ClO\textsubscript{4} (0.006 mol.) was added as solid followed by NaNCS (0.006 mol.). The red solution produced was stirred under nitrogen. After ca 15 s precipitation of product began (Yield 80%
Analysis

Calc:  C 40.4  H 5.3  N 15.7%
Found: C 40.3  H 5.3  N 15.7%

\[\text{[Cu}_2\text{J(OH)}_2]\text{[ClO}_4\text{]_2}\cdot\text{EtOH}\]

DFF (0.001 mol.), 3,3'-dimethylamino-propylamine (0.002 mol.) and Sr(ClO_4)_2•4H_2O (0.001 mol.) in ethanol (30 ml.). The mixture was then treated with solid Cu(MeCN)_4ClO_4 (0.002 mol.) and the solution stirred open to the atmosphere, at room temperature. After ca 2 minutes the green solution began to produce a blue solid. Yield 70%

Analysis

Calc:  C 30.1  H 5.2  N 8.0%
Found: C 30.2  H 4.9  N 7.8%

\[\text{[Cu}_2\text{J(OAc)}_2]\text{[BPh}_4\text{]_2}\cdot2\text{H}_2\text{O}\]

DFF (0.0005 mol.), 3,3'-dimethylamino-propylamine (0.001 mol.) and Sr(ClO_4)_2•3H_2O (0.0005 mol.) and NaBPh_4 (0.005 mol.) were stirred together in methanol solvent (10 ml.). Cu(OAc)_2•H_2O (in 50 ml. MeOH) was added slowly at room temperature. A green solid separated as the Cu(OAc) H_2O is added.

Analysis

Calc:  67.4  H 6.5  N 4.6%
Found: 67.8  H 6.3  N 4.7%

\[\text{[Cu}_2\text{J(OMe)}_2]\text{[BPh}_4\text{]_2}\cdot\text{MeCN}•\text{H}_2\text{O}\]

The free ligand J (0.0004 mol.) was dissolved in methanol (30 ml.) at room temperature. Any soluble impurities were filtered out at this stage. Cu(ClO_4)_2•6H_2O (0.0001 mol.) was added and followed by addition of NaBPh_4 (dissolved in min. of acetonitrile). On standing emerald green crystals separated.
Analysis

Calc:  C 69.2  H 6.8  N 5.9%
Found: C 69.4  H 6.6  N 5.8%

\[\text{[Cu}_2\text{J(N}_3\text{)}_3][\text{ClO}_4]\]

The free ligand J (0.0003 mol.) and Cu(ClO\(_4\))\(_2\) 6H\(_2\)O (0.0006 mol.) were mixed together in 40 ml. methanol. NaN\(_3\) (0.0006 mol.) dissolved in methanol was added dropwise with stirring at room temperature. The whole solution was left stirring for ca 15 minutes during which time a brown crystalline solid developed.

Analysis

Calc:  C 29.8  H 4.4  N 28.2%
Found: C 29.6  H 4.3  N 28.0%

* despite several attempts using deficient quantities of azide no monoazide product was obtained, only that described above.

\[\text{[(PdCl}_2\text{)}_2\text{EDAAF]}\]

The ligand EDAAF (0.0003 mol.) was dissolved in dry MeCN (20 ml.). To this stirring solution was added Pd(MeCN)_2Cl\(_2\) (0.0006 mol.) as a solution also acetonitrile (10 ml.). The solution was filtered and rotary evaporated to 8 ml. A yellow solid was subsequently isolated.

Analysis

Calc:  C 36.5  H 4.5  N 7.7%
Found: C 35.7  H 4.5  N 7.7%

* despite attempts with other metals e.g. Cu (I), Cu (II), Ag (I), Fe (II), Fe (III), Co (II), Mn (II), Cu (II), Sr (II), Ba (II) and Cd (II) no good quality products were obtained with either EDAAF and PDAAF.
Complexes of the \( \kappa^2 \)-dimine ligands

\[ [\text{Cu}(\text{btz})_2]\text{BPh}_4 \]

The ligand (6 m.mol.) was dissolved in warm deoxygenated acetonitrile under nitrogen. 2 m.mol. \( \text{Cu}(%28\text{MeCN}\%)_2\text{ClO}_4 \) was added to the stirred solution, producing a dark orange solution. Excess (8 mol.) \( \text{NaBPh}_4 \) was then added to this solution which was sealed under nitrogen and left overnight in fridge. Large brown crystals came which were filtered under nitrogen and dried.

Analysis

Calc:  C 61.3  H 7.2  N 5.7%

Found: C 61.3  H 7.2  N 5.7%

No perchlorate derivative could be isolated.

\[ [\text{Cu}(\text{btz})_I]_2 \]

Btz ligand (2.8 m.mol.; excess) in deoxygenated acetonitrile under nitrogen. Gradually add with stirring powdered CuI (2.5 m.mol.). Very dark purple-brown crystals (red on crushing) form as the insoluble CuI reacts. Additional quantities of btz may be added to remove any traces of unreacted CuI (buff colour) until only crystals of product remain.

(Yield 73%).

Analysis

Calc:  C 24.6  H 3.1  N 7.2%

Found: C 24.5  H 3.1  N 7.0%
The complex was prepared by addition of \([\text{Cu(MeCN)}_4] \text{ClO}_4\) to a solution of warm deoxygenated acetonitrile under nitrogen containing excess bt ligand. The resultant orange solution was filtered under nitrogen (if necessary), concentrated, and dry deoxygenated methanol added to assist crystallization.

**Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Calc:</th>
<th>Found:</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>28.4</td>
<td>28.3</td>
</tr>
<tr>
<td>H</td>
<td>3.2</td>
<td>3.1</td>
</tr>
<tr>
<td>N</td>
<td>11.0%</td>
<td>11.1%</td>
</tr>
</tbody>
</table>

This complex was prepared by methods analogous to those already described for the complex \([\text{Cu(btz)}_2] \text{ClO}_4\) - substituting btz for the ligand bt. An orange solid.

**Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Calc:</th>
<th>Found:</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>13.0</td>
<td>13.1</td>
</tr>
<tr>
<td>H</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>N</td>
<td>5.1%</td>
<td>4.9%</td>
</tr>
</tbody>
</table>

Prepare in dry deoxygenated acetonitrile by the procedure used in the preparation of \([\text{Cu}_2(\text{bt})_4] \text{ClO}_4\)_2 using bo as ligand.

**Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Calc:</th>
<th>Found:</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>32.5</td>
<td>32.7</td>
</tr>
<tr>
<td>H</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>N</td>
<td>12.6%</td>
<td>12.5%</td>
</tr>
</tbody>
</table>
[(CuI)₂bo]

The complex was prepared using the ligand bo by the methods already described in the preparation of [Cu(btz)I]₂ and [(CuI)₂bt]. A yellow solid was separated.

Analysis

<table>
<thead>
<tr>
<th></th>
<th>Calc:</th>
<th>Found:</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>13.8</td>
<td>14.3</td>
</tr>
<tr>
<td>H</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>N</td>
<td>5.4%</td>
<td>5.3%</td>
</tr>
</tbody>
</table>

[Cu(biz)₂][CIO₄]₂

Cu(CIO₄)₂ 6H₂O and btz are reacted in 1:2 metal:ligand molar ratios in methanol at room temperature. Blue crystals of [Cu(biz)₂][CIO₄]₂ appeared on evaporation.

Analysis

<table>
<thead>
<tr>
<th></th>
<th>Calc:</th>
<th>Found:</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>32.3</td>
<td>32.5</td>
</tr>
<tr>
<td>H</td>
<td>4.7</td>
<td>4.8</td>
</tr>
<tr>
<td>N</td>
<td>18.8%</td>
<td>18.7%</td>
</tr>
</tbody>
</table>

[Cu(biz)₂][BPh₄]₂

[Cu(biz)₂][CIO₄]₂ was dissolved in methanol and 2 equivalents of NaBPh₄ added as a solution (again in methanol). Addition was performed slowly and dropwise stirring. After completion blue crystals slowly appear. (Yield 98%).

Recrystallization from acetonitrile gives same product.

Analysis

<table>
<thead>
<tr>
<th></th>
<th>Calc:</th>
<th>Found:</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>74.3</td>
<td>73.9</td>
</tr>
<tr>
<td>H</td>
<td>6.6</td>
<td>6.8</td>
</tr>
<tr>
<td>N</td>
<td>10.8%</td>
<td>10.7%</td>
</tr>
</tbody>
</table>
Blue $[\text{Cu(bi)}_2][\text{ClO}_4]_2$

(a) Bi and Cu( ClO$_4$)$_2$ 6H$_2$O (2:1 molar quantities respectively) were reacted in ethanol giving a blue-green solution. The solution was refluxed for 1 hour, then filtered and rotary evaporated. On cooling, blue crystals of product separated. These were filtered out and dried. (Yield 70%)

Analysis

Calc: C 26.8  H 3.7  N 20.8%

Found: C 26.7  H 3.7  N 20.5%

(b) from purple $[\text{Cu(bi)}_2][\text{ClO}_4]_2$

0.1 g of purple $[\text{Cu(bi)}_2][\text{ClO}_4]_2$ was dissolved in ca of ethanol. The blue-green solution was refluxed for 1 hour, then evaporated producing blue crystals in high yield.

Analysis

Calc: C 26.8  H 3.7  N 20.8%

Found: C 26.6  H 3.6  N 20.9%

Purple $[\text{Cu(bi)}_2][\text{ClO}_4]_2$

(a) 2:1 molar ratio of bi: Cu( ClO$_4$)$_2$ 6H$_2$O in minimum of methanol to produce a blue-green solution. Diethylether was slowly infused to precipitate purple crystals in high yield.

Analysis

Calc: C 26.8  H 3.7  N 20.8%

Found: C 26.8  H 3.8  N 20.5%

(b) from blue $[\text{Cu(bi)}_2][\text{ClO}_4]_2$

0.15 g of blue $[\text{Cu(bi)}_2][\text{ClO}_4]_2$ was dissolved in ca 20 ml methanol. The blue solution was slowly infused with diethylether. After 5-10 ml ether has been added, purple crystals began to appear. Standing and occasionally 'topping-up' with ether gave a high yield of the purple product.
[Cu(bi)₂][BPh₄]₂

Excess of NaBPh₄, dissolved in methanol, was added to a solution containing purple [Cu(bi)₂][ClO₄]₂ dissolved in the minimum quantity of methanol. Blue-green crystals precipitated.

Analysis

<table>
<thead>
<tr>
<th>Calc:</th>
<th>C 73.7</th>
<th>H 6.2</th>
<th>N 11.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found:</td>
<td>C 73.3</td>
<td>H 6.3</td>
<td>N 11.6%</td>
</tr>
</tbody>
</table>

[Cu(bi)₂(MeCN)₂][BPh₄]₂

2 molar and molar equivalents of bi ligand and Cu(ClO₄)₂·6H₂O were dissolved in acetonitrile, giving a green solution. NaBPh₄ (excess; in acetonitrile) was mixed in and the solution slowly evaporated to low volume when green crystals appeared. These were filtered and washed with ice-cold acetonitrile. (Yield 80%).

Analysis

<table>
<thead>
<tr>
<th>Calc:</th>
<th>C 72.5</th>
<th>H 6.3</th>
<th>N 13.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found:</td>
<td>C 72.6</td>
<td>H 6.6</td>
<td>N 13.3%</td>
</tr>
</tbody>
</table>
CHAPTER 3 - RESULTS AND DISCUSSION
RESULTS AND DISCUSSION

Complexes of the Macro cyclic Ligands 33N and 33NMe

As described in Chapter 1 the condensation of 3,3'-diaminodipropylamine
and DAP in the presence of Ag (I), produces the di-Ag (I) complex of the
28-membered N₈ macrocycle L or '33N' \(^\text{139}\). When an analogous condensation
was attempted using Ag (I) and 3,3'-diamino-N-methyl dipropylamine it was
found that a (2 + 2) condensation had occurred. The macrocyclic nature of
the product was confirmed by mass spectra, observation of the molecular ion
peak at macrocycle 544, Table VII. Use of Pb(NCS)₂ as template gave the
28-membered N₈ macrocycles with both the >NH and >NMe amines. This was
shown by borohydride reduction of the condensation product to give the
hydrogenated ligands R33N and R33NMe whose molecular ion peaks were ob­
served at \( M/e \) 524 and 552 respectively, Table VII. N.m.r spectra of
these free ligands are described in the experimental section, the Pb
complexes were too insoluble.

Condensation of 3,3'-diaminodipropylamine with DAP on Ca (II) or
Sr (II) takes place rapidly in dry alcohol at 60°C, where addition of
NaBPh₄ precipitates out complexes of stoichiometry \([M(33N)][BPh₄]_2\). Significantly when the N-methylated amine is used the Group (II) ions are
ineffective as templates. This suggests that, on Group (II) ions, 33N may
adopt a ring contracted form analogous to that already observed in the
Ba (II)-assisted template condensation of diethylenetriamine with DAP \(^\text{196}\).

Such contraction may be achieved by intramolecular attack on the C = N
group by the secondary NH function, which in the present system is accom­
panied by extrusion from the macrocycle of a tetrahydropyrimidine ring.
This attack may involve one or both secondary amine functions, reducing
the size of the macrocycle from 28- to 24- or 20-member atoms. This
smaller size presumably allows more efficient coordination of the remaining
N-donors by the single Sr (II) or Ca (II) ion.
Evidence for the presence of macrocyclic product in the above complexes comes from analytical data, mass spectra (already discussed), i.r and n.m.r spectra, Table VII. All the complexes exhibited a moderate-to-strong band at $1620-1640 \text{ cm}^{-1}$, diagnostic in these systems, of the azomethine group. None showed any absorption at ca $1700 \text{ cm}^{-1}$ attributable to $\nu_{C=O}$ of unreacted carbonyl. Absorptions in the region $3200-3400 \text{ cm}^{-1}$, indicative of unchanged primary amine, were, also absent. These observations indicate that the Schiff-base condensation has taken place, but do not, on their own, distinguish between cyclic and polymeric condensations. However, the crystalline nature of the complex suggests low-molecular weight i.e cyclic constitution while the direct mass spectral observations in the Ag (I) and Pb (II) cases confirms the $[2 + 2]$ nature of both macrocycles in these complexes. In the cases of the Ca (II) and Sr (II) complexes, molecular model studies show $[1 + 1]$ cyclic products to have too small a cavity and $[3 + 3]$ and larger products to have too large a cavity to accommodate these ions. The $[2 + 2]$ macrocycle is suggested also by analogy to a closely related system $L^{53a}$ based on DAP and diethylenetriamine for which an X-ray crystal structure of the Ba (II) complex exists $^{196}$.

An n.m.r study was undertaken in order to compare ligand geometry in products of template condensation on the different metal ions. Both di-Ag (I) complexes exhibit an easily interpretable $^1H$ n.m.r spectrum, Table VIII, as expected for a normal, fully extended, 28-membered macrocycle.

The $^1H$ n.m.r spectra of $[\text{Ca(33N)}][\text{BPh}_4]_2$ and $[\text{Sr(33N)}][\text{BPh}_4]_2$, Fig.56, however, are far from simple and quite different from those of Ag (I) complexes. The prominent feature is a multiplet lying between 2.65 and 2.45 ppm which appears to contain three singlets underlain by other less intense complex absorption. There is a fourth singlet to the high field side of these three at 1.93 ppm and numerous complex multiplets of low intensity covering the range 3.8-1.6 ppm. Using the aromatic signals
### TABLE VII

**PHYSICAL DATA FOR THE TEMPLATED COMPLEXES**

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>$P^+$(m/e)</th>
<th>$\Lambda$/Scm$^2$ mol$^{-1}$</th>
<th>$\nu_{\text{NH}}$ OR $\nu_{\text{NMe}}$</th>
<th>$\nu_{\text{C} = \text{N}}$</th>
<th>$\nu_{\text{py}}$</th>
<th>$\nu_{\text{NCS}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sr(33N)][BPh$_4$]$_2$</td>
<td>white</td>
<td>-</td>
<td>253</td>
<td>3268m</td>
<td>1625m</td>
<td>1574</td>
<td>-</td>
</tr>
<tr>
<td>[Ca(33N)][BPh$_4$]$_2$</td>
<td>white</td>
<td>-</td>
<td>259</td>
<td>3260w</td>
<td>1627m</td>
<td>1574</td>
<td>-</td>
</tr>
<tr>
<td>[Ag$_2$(33NMe)][BPh$_4$]$_2$</td>
<td>dull yellow</td>
<td>544</td>
<td>259</td>
<td>2790m</td>
<td>1630ms</td>
<td>1575</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2840m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pb$_2$(33N)(NCS)$_4$]</td>
<td>bright yellow</td>
<td>524$^b$</td>
<td>Insol.</td>
<td>3240ms</td>
<td>1643ms</td>
<td>1585</td>
<td>2080</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2058</td>
</tr>
<tr>
<td>[Pb$_2$(33NMe)(NCS)$_4$]</td>
<td>bright yellow</td>
<td>552$^b$</td>
<td>Insol.</td>
<td>2790m</td>
<td>1635ms</td>
<td>1588</td>
<td>2090sh</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2058</td>
</tr>
</tbody>
</table>

$^a$ $10^{-3}$ mol. l. $^{-1}$ in acetonitrile solution at 20° C.

$^b$ $P^+$ observed for the reduced free ligands R33N(M.w 524) and R33NMe(M.w 552).
as reference, the total integral over the 2.75-1.8 ppm range includes these four singlets (which are of approximate equal intensity) is ca 14H. We believe that the four singlets correspond to four non-equivalent methyl groups, with the rest of the integral being accounted for by the underlying broad, low-intensity absorption. The three singlets grouped around 2.66 ppm presumably arise from \((\text{C})\text{Me} -\) group in a similar chemical environment to that in \([\text{Ag}_2(33\text{N})][\text{BPh}_4]_2\) or \([\text{Ag}_2(33\text{NMe})][\text{BPh}_4]_2\), but in a situation of lower symmetry. The remaining high-field singlet at 1.93 ppm must therefore lie in a magnetic or chemical environment significantly different from the other three and from the \((\text{C})\text{Me} -\) groups in the di-Ag (I) compounds. By comparison to the analogous L system, this high-field signal is tentatively assigned to the methyl group on the tetrahydro-pyrimidine ring.

The simplest interpretation of \(\text{H}\) n.m.r evidence would be to suggest formation of a 24-membered ring, contracted by expulsion of one tetrahydro-pyrimidine ring, containing three methyl groups on imine carbons and one fully substituted carbon of the tetrahydropyrimidine ring. The low symmetry of such an arrangement would result in none of the \(\text{CH}_3\) or \(\text{CH}_2\) groups being equivalent, explaining the complexity of the n.m.r spectra.

\(^1\text{A C n.m.r investigation of the more soluble [Fe(33\text{N})][BPh}_4]_2\) and \([\text{Fe}(33\text{NMe})][\text{BPh}_4]_2\) complexes (described later) supports this idea. These mononuclear, low-spin, complexes gave simple \(^{13}\text{C}\) spectra, Table IX, with just one peak for each of the chemically different carbon atoms in the molecule. \([\text{Sr}(33\text{N})][\text{BPh}_4]_2\), on the other hand, gave complex \(^{13}\text{C}\) spectra with four times as many macrocyclic signals as were observed for the Fe (II) compounds. The inference is that each carbon atom in the macrocycle is giving rise to its own signal. The \(^{13}\text{C}\) evidence suggesting low symmetry and four magnetically individual methyl carbons favours the \(\text{N}_7\) 24-membered
Fig. 56

$^1$H n.m.r of [M(33N)](BPh$_4$)$_2$

M = Ca(11), Sr(11)
ring macrocycle. Independent evidence for this structure comes from the i.r intensity of the $\nu_{C=N}$ absorption. The intensity of this absorption in $[\text{Sr}(33\text{N})][\text{BPh}_4]_2$ is only about three-quarters that in $[\text{Ag}_2(33\text{N})][\text{BPh}_4]_2$ (using the $\nu_{\text{py}}$ absorption as intensity reference). This suggests that only one of the four imine groups has been lost in the ring contracted form.

**TABLE VIII**

$^1$H n.m.r SPECTRA OF D$_2$-Ag (1) COMPLEXES OF 33N and 33NMe$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>ppm</th>
<th>Rel. Int.</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ag}_2(33\text{N})][\text{ClO}_4]_2$</td>
<td>8.26 (m)</td>
<td>3</td>
<td>pyridine protons</td>
</tr>
<tr>
<td></td>
<td>3.86 (t)</td>
<td>4</td>
<td>$^3$H</td>
</tr>
<tr>
<td></td>
<td>3.06 (t)</td>
<td>4</td>
<td>$^1$H</td>
</tr>
<tr>
<td></td>
<td>2.56 (s)</td>
<td>6</td>
<td>(c)Me</td>
</tr>
<tr>
<td></td>
<td>2.29 (p)</td>
<td>4</td>
<td>$^3$H</td>
</tr>
<tr>
<td></td>
<td>2.45$^b$ (s)</td>
<td></td>
<td>(NH + H$_2$O)</td>
</tr>
<tr>
<td>$[\text{Ag}_2(33\text{NMe})][\text{BPh}_4]_2$</td>
<td>8.30-8.54 (m)</td>
<td>3</td>
<td>pyridine protons</td>
</tr>
<tr>
<td></td>
<td>3.97 (t)</td>
<td>4</td>
<td>$^3$H</td>
</tr>
<tr>
<td></td>
<td>2.88 (t)</td>
<td>4</td>
<td>$^1$H</td>
</tr>
<tr>
<td></td>
<td>2.74 (s)</td>
<td>3</td>
<td>(N)Me</td>
</tr>
<tr>
<td></td>
<td>2.69 (s)</td>
<td>6</td>
<td>(C)Me</td>
</tr>
<tr>
<td></td>
<td>2.40 (p)</td>
<td>4</td>
<td>$^3$H</td>
</tr>
</tbody>
</table>

a. CD$_3$CN solvent, TMS reference.

b. D$_2$O shake removes 2.45 signal, sharpens $^3$H.
TABLE IX

$^{13}$C n.m.r SPECTRA FOR DIAMAGNETIC COMPLEXES OF 33N and 33NMe$^a$

<table>
<thead>
<tr>
<th></th>
<th>[Fe(33N)][BPh$_4$]$_2$</th>
<th>[Fe(33NMe)][BPh$_4$]$_2$</th>
<th>[Sr(33N)][BPh$_4$]$_2$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.3</td>
<td>17.9</td>
<td>11.3$^b$, 16.8$^b$, 16.2$^b$, 23.5$^b$.</td>
<td>CH$_3$</td>
<td></td>
</tr>
<tr>
<td>26.1</td>
<td>25.6</td>
<td>28.9, 29.4, 29.7, 29.9</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>43.1</td>
<td>44.5</td>
<td>39.6, 44.3, 50.2, 50.4$^c$</td>
<td>C</td>
<td></td>
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<tr>
<td>50.0</td>
<td>50.8</td>
<td>50.6, 51.8, 52.0</td>
<td>C$_1$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(N)Me</td>
<td></td>
</tr>
<tr>
<td>121.7</td>
<td>122.4</td>
<td>122.6</td>
<td>[BPh$_4$]$^-$</td>
<td></td>
</tr>
<tr>
<td>125.5</td>
<td>126.5</td>
<td>126.2</td>
<td>[BPh$_4$]$^-$</td>
<td></td>
</tr>
<tr>
<td>135.7</td>
<td>136.5</td>
<td>136.8</td>
<td>[BPh$_4$]$^-$</td>
<td></td>
</tr>
</tbody>
</table>

a. CD$_3$CN solvent, TMS reference.

b. Off-resonance quartet.

c. Closely spaced doublet.

Transmetallated Complexes

Although template condensation on Sr (II) yields a ring-contracted form of the macrocycle 33N, treatment with transition metal ions easily converts this to the extended 28-membered ring form. A similar facile ring expansion was noticed with the analogous L$^{53a}$ ring system.

Binuclear derivatives Ni (II) and Co (II) were obtained by refluxing di-Ag (I) and di-Pb (II) complexes of 33N with methanolic solutions of the appropriate transition metal salt. An identical product could be
obtained by starting with an acetonitrile solution of [Sr(33N)][BPh$_4$],
so in general, [Sr(33N)][BPh$_4$]$_2$ was the preferred starting material for
the synthesis of transition metal derivatives of 33N. Mononuclear deriv-
avatives were similarly obtained by refluxing [Ag$_2$(33NMe)][BPh$_4$]$_2$
in
acetonitrile with the appropriate (Fe (II), Co (II), Ni (II)) salt. A
similar series of mononuclear derivatives of 33N does not exist, only
[Fe(33N)][BPh$_4$]$_2$ could be obtained for this macrocycle.

Mononuclear Complexes

These complexes are listed in Table X, along with their physical
properties. In each case the properties of the complexes show them to have
approximately octahedral coordination geometry. Conductivities in aceto-
nitrile fall at the lower end of the range appropriate to 1:2 electro-
lytes, as is typical for the bulky tetraphenylborate salt. The i.r
spectrum of the ligand moiety, outside the 1700–1500 cm$^{-1}$ region, remained
largely unaltered on transmetallation; however, there were significant
changes in the 1600 cm$^{-1}$ region. The precursors [Pb$_2$(33N)(NCS)$_4$],
[Pb$_2$(33NMe)(NCS)$_4$] etc., all show at least two strong bands ca 1630 and
ca 1590 cm$^{-1}$, assigned to the $\nu_C=N$ and pyridine ring vibrations
respectively. Of the mononuclear derivatives only [Ni(33NMe)][BPh$_4$]$_2$·2MeCN
displays this pattern. [Co(33NMe)][BPh$_4$]$_2$·2MeCN has a pair of weak
absorptions at 1620 and 1590 cm$^{-1}$, while no absorption is observed for the
Fe (II) complexes at these frequencies. This indicates, as magnetic
results confirm, that Co (II) and Fe (II) are in low-spin octahedral
coordination in these mononuclear complexes. A strong octahedral field
can be achieved with these macrocycles if the ring is sufficiently flexible
to allow both trimethine entities to lie at right angles to each other.
The -NH or -NMe groups are then 'squeezed out' and not coordinated to the
metal ion.
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>(\mu_{\text{ef}}/\mu_{\text{B}})^a</th>
<th>V(\text{NH}) OR V(\text{NMe})</th>
<th>COLOUR</th>
<th>INFRARED</th>
<th>MOSSBAUER</th>
<th>ELECTRONIC SPECTRUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}(33\text{Me})][\text{BPh}_4]_2)</td>
<td>0.60</td>
<td>-</td>
<td>dark purple</td>
<td>1.61</td>
<td>28235 m s</td>
<td>0.14</td>
</tr>
<tr>
<td>([\text{Fe}(33\text{Me})][\text{BPh}_4]_2\cdot 2\text{MeCN}\cdot \text{H}_2\text{O})</td>
<td>1.21</td>
<td>-</td>
<td>dark purple</td>
<td>2.32</td>
<td>2830 m s</td>
<td>0.13</td>
</tr>
<tr>
<td>([\text{Co}(33\text{Me})][\text{BPh}_4]_2\cdot 2\text{MeCN})</td>
<td>3.25</td>
<td>-</td>
<td>dark brown</td>
<td>3.12</td>
<td>2830 m s</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni}(33\text{Me})][\text{BPh}_4]_2\cdot 2\text{MeCN})</td>
<td>3.12</td>
<td>-</td>
<td>pale brown</td>
<td>3.12</td>
<td>2830 m s</td>
<td>1618 (\nu)</td>
</tr>
</tbody>
</table>

a: Moment per metal ion; b: Isomer Shifts in mm \(5\) vs Fe foil; c: Quadrupole Splitting in mm \(5\); d: Observed by broad H-bonded absorption.
Magnetic susceptibility data for both Fe (II) compounds confirms
the existence of spin-pairing. Mossbauer spectra isomer shifts are in
the range expected for low-spin octahedral Fe (II). The quadrupole splittings
are large, comparable to the values obtained in the [Fe L \(^{55}\) \(^{2+}\)] cation
where the macrocycle has folded to allow 6-Coordination of the Fe (II)
by both trimethine groups. These large quadrupole splittings presumably
reflect splitting of the t\(_{2g}\) orbitals as a result of distortion from O\(_h\)
symmetry. This distortion appears to be somewhat larger in 33N and 33NMe com-
plexes than in the L series, as judged by the magnitude of \(\Delta E\). This
may arise because of steric constraints in the smaller 33N and 33NMe
macrocycles.

A thermally controlled high-spin \(\rightarrow\) low-spin equilibrium exists in
the case of [Co(33NMe)][BPh\(_4\)]\(_2\cdot2\)MeCN, as shown by variable temperature
magnetic susceptibility measurements. Such an equilibrium is fairly com-
mon in \(\alpha\)-diimine complexes of Co (II), and also has been observed
in mononuclear Co (II) complexes of L. In the present case, equilibrium
lies well, but not completely, to the low-spin side at 93K. The e.s.r
spectrum, Fig.57, obtained at this temperature shows only peaks due to the
low-spin form. The e.s.r parameters of a polycrystalline sample at 93K
\((g_1 2.02; g_{11} 2.30; \Lambda_{11} 93\) ) demonstrate that the octahedral arrangement
around Co (II) is distorted by axial compression.

Examination of the electronic spectra of the complexes likewise pro-
vides evidence of the distortion from regular O\(_h\) symmetry both [Fe(33N)]\(^{2+}\)
and [Fe(33NMe)]\(^{2+}\) cations display a pair of equally intense charge-transfer
absorptions close to 20,000 and 17,000 cm\(^{-1}\). Such a splitting has been
attributed to separation of the t\(_{2g}\) level into e and b\(_2\) levels as the
symmetry diminishes from octahedral. No absorption attributable to d-d
transitions were observed. The two strong bands in the [Co(33NMe)][BPh\(_4\)]\(_2\cdot2\)MeCN
electronic spectrum at 20,800, 18,250 cm\(^{-1}\) are thought to be d-d rather
than charge-transfer in origin.
Fig. 57

E.s.r spectrum of [Co(33NMe)][BPh₄]₂·2MeCN

Fig. 58

Disposition of donors in octahedral coordination mode of 33N and 33NMe.
The electronic spectrum is the only physical measurement to offer information about coordination geometry in $[\text{Ni}(33\text{NMe})]^{2+}$. Of the three bands expected for octahedral Ni (II), two are observed at 19,000 cm$^{-1}$ and 12,000 cm$^{-1}$, ascribed, respectively, to the $A_2g \rightarrow T_2g$ and $A_2g \rightarrow T_1g$ (F) transitions.

It seems clear from the above results that, in mononuclear complexes, the ligands 33N and 33NMe have twisted as in Fig. 58, to adopt an $N_6$ octahedral conformation using only the trimethine entities as donors, and leaving the amine nitrogen uncoordinated. The local symmetry about metal ion is less than octahedral.

**BINUCLEAR COMPLEXES**

(a) **The non-copper derivatives**

X-ray studies on $^{139}$ on di-Ag (I) complex of 33N suggest that the ligands 33N and 33NMe afford an intermetallic distance of ca 7 Å. A shorter intermetallic distance would be attainable were the ligands able to fold into a U-shape with co-facial trimethine entities; however models suggest that this arrangement would be highly strained.

Tables XI and XII summarize the physical data for the non-copper derivatives of the macrocycles. Where solubility permitted conductivity data in acetonitrile typical of 1:4 electrolytes were observed for di-Fe (II), di-Co (II) and di-Ni (II) complexes of 33N and 33NMe; 1:3 electrolytes for $[\text{Co}_2(33\text{N})(\text{NCS})]^{3+}$ and $[\text{Co}_2(33\text{NMe})(\text{NCS})]^{3+}$; the tetrathiocyanate complexes proved too insoluble for conductivity measurements, but their infrared spectra suggest N-coordination.

Variable temperature magnetic susceptibility measurements in the temperature range 293-93K do not indicate significant interaction between the metal centres; an observation in accord with data on the Cu (II)
complexes (discussed in section (b)), where the existence of weak dipolar interaction between the metal centres can be inferred only from e.s.r spectra.

In Zn (II) and Mn (II) complexes the ions are assumed to be 6-coordinate because i.r spectra show -NCS to be coordinated in both cases.

The absence of $v_{\text{C} = \text{N}}$ absorptions in the 1600 cm$^{-1}$ region suggests that both 33N and 33NMe complexes of Fe (II) are low-spin, and this inference is confirmed by the Mossbauer parameters. Magnetic susceptibility measurements on these complexes were restricted by their unpredictability explosive nature. Nonetheless, the room temperature moment (measured on a 100 mg sample) of $[\text{Fe}_2(33\text{NMe})(\text{Cl})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2$ was low enough to rule out any residual paramagnetism, so no low temperature moments were measured. Both room temperature and 110K moments were determined for $[\text{Fe}_2(33\text{N})(\text{H}_2\text{O})_4][\text{ClO}_4]_4$. The values obtained clearly rule out a high-spin ground state; the small paramagnetism observed at 293K could be attributable either to paramagnetic impurity or to the presence of small quantities of high-spin form at this temperature. As the axial ligands (Cl$^-$ or H$_2$O) in these complexes are weak, spin-pairing must rise from an unusually strong field in the N$_4$ plane. This arises presumably, from particularly good fit of the Fe (II) ion in the macrocycle cavity.

The i.r spectrum of $[\text{Co}_2(33\text{N})(\text{NCS})_4] \cdot 4\text{H}_2\text{O}$ shows the NCS to be N-coordinated and the magnetic moment has the normal value associated with high-spin octahedral Co (II). The electronic spectrum of the mull shows the three absorptions at 24,000, 18,000 and 10,000 cm$^{-1}$ corresponding to $T_{1g}(F) \rightarrow T_{1g}(P)$; $T_{1g}(F) \rightarrow A_{2g}$; $T_{1g}(F) \rightarrow T_{2g}$ transitions expected in octahedral symmetry.
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$\mu_{\text{eff}}/\mu_{\text{BM}}^a$</th>
<th>MOSSBAUER</th>
<th>INFRARED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313K</td>
<td>93K</td>
<td>$\delta^b$</td>
</tr>
<tr>
<td>$[\text{Mn}_2(\text{3N})(\text{NCS})_4] \cdot 4\text{H}_2\text{O}$</td>
<td>5.78</td>
<td>5.80</td>
<td>3225</td>
</tr>
<tr>
<td>$[\text{Co}_2(\text{3N})(\text{NCS})_4] \cdot 4\text{H}_2\text{O}$</td>
<td>4.80</td>
<td>-</td>
<td>3215</td>
</tr>
<tr>
<td>$[\text{Ni}_2(\text{3N})(\text{NCS})_4] \cdot 2\text{H}_2\text{O}$</td>
<td>3.18</td>
<td>3.02</td>
<td>3230</td>
</tr>
<tr>
<td>$[\text{Zn}_2(\text{3N})(\text{NCS})_4] \cdot 2\text{H}_2\text{O}$</td>
<td>-</td>
<td>-</td>
<td>3220</td>
</tr>
<tr>
<td>$[\text{Fe}_2(\text{3N})(\text{H}_2\text{O})_4][\text{CO}_2]_4$</td>
<td>1.3</td>
<td>0.98$^d$</td>
<td>0.17</td>
</tr>
<tr>
<td>$[\text{Co}_2(\text{3N})(\text{MeCN})_2][\text{CO}_2]_4 \cdot \text{H}_2\text{O}$</td>
<td>4.15</td>
<td>4.02</td>
<td>3240</td>
</tr>
<tr>
<td>$[\text{Ni}_2(\text{3N})(\text{MeCN})_2][\text{CO}_2]_4 \cdot \text{H}_2\text{O}$</td>
<td>3.13</td>
<td>3.15</td>
<td>3250</td>
</tr>
<tr>
<td>$[\text{Co}_2(\text{3N})(\text{NCS})_2][\text{BPh}_4]_3 \cdot 5\text{MeCN} \cdot \text{H}_2\text{O}$</td>
<td>4.09</td>
<td>3.88</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Co}_2(\text{3NMe})(\text{NCS})_2][\text{BPh}_4]_3 \cdot \text{MeCN} \cdot 3\text{H}_2\text{O}$</td>
<td>4.10</td>
<td>3.92</td>
<td>-</td>
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Cont..
TABLE XI continued

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<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
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<tr>
<td>([\text{Ni}_2(33\text{NMe})(\text{Cl})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2)</td>
<td>3.06</td>
<td>-</td>
<td>-</td>
<td>-e</td>
<td></td>
<td>1620(m,s)</td>
<td>1090(vs,b)</td>
</tr>
<tr>
<td>([\text{Fe}_2(33\text{NMe})(\text{Cl})_2][\text{ClO}_4]_2\cdot 4\text{H}_2\text{O})</td>
<td>0.20</td>
<td>0.15</td>
<td>1.11</td>
<td>e</td>
<td></td>
<td>-</td>
<td>1090(vs,b)</td>
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</tbody>
</table>

- **a** Moment per metal ion.
- **b** Isomer Shifts/mm s\(^{-1}\) vs Fe foil.
- **c** Quadrupole Splitting/mm s\(^{-1}\).
- **d** Measured at 110K.
- **e** Obscured by broad H-bond absorption.
<table>
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<tr>
<th>COMPLEX</th>
<th>$\Lambda_m^a$</th>
<th>COLOUR</th>
<th>ELECTRONIC SPECTRA $^b$</th>
</tr>
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<tbody>
<tr>
<td>[Mn$_2$(33N)(NCS)$_4$]·4H$_2$O</td>
<td>-</td>
<td>apricot</td>
<td>26,200$^c$</td>
</tr>
<tr>
<td>[Co$_2$(33N)(NCS)$_4$]·4H$_2$O</td>
<td>-</td>
<td>brown</td>
<td>24,600$^b$; 21,200$^c$ sh; 18,000$^c$ sh; 10,300$^c$</td>
</tr>
<tr>
<td>[Ni$_2$(33N)(NCS)$_4$]·2H$_2$O</td>
<td>-</td>
<td>light brown</td>
<td>19,800$^c$; 11,800$^c$</td>
</tr>
<tr>
<td>[Zn$_2$(33N)(NCS)$_4$]·2H$_2$O</td>
<td>-</td>
<td>white</td>
<td>21,000$^c$</td>
</tr>
<tr>
<td>[Fe$_2$(33N)(H$_2$O)$_4$][ClO$_4$]$_4$</td>
<td>495</td>
<td>dark blue</td>
<td>21,100 (7000); 16,900 (9400)</td>
</tr>
<tr>
<td>[Co$_2$(33N)(MeCN)$_2$][ClO$_4$]$_4$·H$_2$O</td>
<td>440</td>
<td>mid brown</td>
<td>23,700sh; 18,600 (250; 15,000 (85); 9,600 (40)</td>
</tr>
<tr>
<td>[Ni$_2$(33N)(MeCN)$_2$][ClO$_4$]$_4$·2H$_2$O</td>
<td>421</td>
<td>beige</td>
<td>22,800 (180); 19,000 (45); 11,600 (160)</td>
</tr>
<tr>
<td>[Co$_2$(33N)(NCS)][BPh$_4$]$_3$·5MeCN·H$_2$O</td>
<td>280</td>
<td>brown</td>
<td>23,400sh; 19,200 (200)</td>
</tr>
<tr>
<td>[Co$_2$(33NMe)(NCS)][BPh$_4$]$_3$·MeCN·3H$_2$O</td>
<td>306</td>
<td>brown</td>
<td>23,530 (700); 19,000 (173); 15,000 (22); 9800</td>
</tr>
<tr>
<td>[Ni$_2$(33NMe)(Cl)$_2$(H$_2$O)$_2$][ClO$_4$]$_2$</td>
<td>380</td>
<td>beige</td>
<td>19,230sh; 11,900 (42)</td>
</tr>
<tr>
<td>[Fe$_2$(33NMe)(Cl)$_2$][ClO$_4$]$_2$·4H$_2$O</td>
<td>406</td>
<td>dark purple</td>
<td>20,830 (6800); 18010sh; 17,390sh; 16,950 (9600)</td>
</tr>
</tbody>
</table>

$^a$ For 10$^{-3}$ mol·l$^{-1}$ in MeCN at 20$^\circ$ C; $^b$ Frequency in cm$^{-1}$, $\epsilon$/dm mol$^{-1}$ cm$^{-1}$ in parentheses; $^c$ Nujol mull
The low virtually temperature-independent value of $\mu_{\text{eff}}$ for $[\text{Co}_2(33\text{N})(\text{MeCN})_2][\text{ClO}_4]_4\cdot4\text{H}_2\text{O}$ suggests a 5-coordinate geometry for the Co (II) ion, made up of four ligand donors in a square plane with an acetonitrile molecule coordinated in the apical position. The observed moment of 4.15 BM is presumably explained by the decreased orbital contribution expected for Co (II) in square pyramidal (or trigonal bipyramidal) fields. $[\text{Co}_2(33\text{N})(\text{NCS})][\text{BPh}_4]_3\cdot5\text{MeCN}\cdot\text{H}_2\text{O}$ and $[\text{Co}_2(33\text{MeN})][\text{BPh}_4]_3\cdot\text{MeCN}\cdot3\text{H}_2\text{O}^{301}$ may also be assumed to be 5-coordinate. The high $v_{\text{NCS}}$ i.r frequency indicates bridging thiocyanate so we suggest a dimeric $[\text{Co}_4(\text{Mac})_2(\text{NCS})_2]^{6+}$ assembly where the two binuclear entities are held together by two $-\text{NCS}-$ bridges linking one metal atom in the first macrocycle with another in the second, Fig.59. An analogous dimeric assembly has recently been characterized.

The $[\text{Ni}_2(33\text{N})(\text{NCS})_4]\cdot2\text{H}_2\text{O}$ complex clearly contains 6-coodinate Ni (II), as the i.r spectrum show that $-\text{NCS}$ is coordinated. The electronic spectrum is as expected for octahedral Ni (II), absorption occurring at similar frequencies to that observed for the octahedral mononuclear complex $[\text{Ni}(33\text{NMe})][\text{BPh}_4]_2\cdot2\text{MeCN}$, showing that substitution of two $-\text{NCS}$ and one amine NH ligand for the second trimethine unit has had little effect on the ligand field. In $[\text{Ni}_2(33\text{NMe})(\text{Cl})_2(\text{H}_2\text{O})_2]^{6+}$ the electronic absorptions are shifted to slightly lower energies as a consequence for NCS of weaker axial ligands. The Ni (II) complexes have moments in the range expected for octahedral Ni (II).
Electrochemical Measurements

Table XIII lists the results of cyclic voltammetry studies on the mononuclear transition metal complexes and selected binuclear derivatives. These studies were performed by M. Fernanda Cabral, Laboratorio Ferreira da Silva, Faculdade de Ciencias 4000 Porto, Portugal. Fig. 60, displays the voltammograms.

The mononuclear iron complexes show three reversible or quasi-reversible processes. The most anodic waves at $E^\text{a} = +1.23 \, \text{V}$ for $[\text{Fe(33NMe)}]^2^+\text{ and } +1.16 \, \text{V}$ for $[\text{Fe(33N)}]^2^+$, correspond to an $\text{Fe}^{2+}/\text{Fe}^{4+}$ redox interconversion. This would indicate a slight stabilization of the $+2$ state over that in $[\text{FeL}]^2^+$ where $E^\text{a} (\text{Fe}^{2+}/\text{Fe}^{4+})$ is found at ca 100-150 mV less positive.

The enhanced difficulty of oxidation in the case of 33N and 33NMe complexes may arise from a hole-size effect in these more strained arrangements, producing a larger effective cavity than in the relatively strain-free $L$ complex. A large hole size is expected to favour the larger Fe (II) ion.

Two reversible waves are seen at cathodic potentials corresponding to successive one-electron reductions of $[\text{Fe(Mac)}]^2^+$. Without e.s.r. investigation of the reduction products it is difficult to decide the extent to which these reductions are metal-centred. However, the intense charge-transfer absorption described above suggests at least one of these processes involves the ligand. We believe that the least cathodic of the two reversible waves in 33NMe and 33N complexes should be assigned to the formation of an Fe (II) complex of the radical anion of the ligand. The second wave probably corresponds to further ligand reduction.

If the process (2)-Table XIII is an Fe (II) complex of the ligand anion then it may be expected that the energy of the charge-transfer absorption would be comparable to the difference between the energies of the two most anodic processes, i.e. $F[\text{E}^{0}(1) - \text{E}^{0}(2)]$. This difference
corresponds to an energy ($\Delta G \approx 238\text{kJ}$) within 10% of the average energy ($ca \ 220\text{kJ}$) of the charge-transfer band in the electronic spectrum. While it is a good correspondence, it must be remembered that the two energies refer to slightly different processes. They are the same in that both cases an electron is transferred from a molecular orbital localized mainly on the metal of the ground-state complex. They differ in that in the electro-chemical process the reduced species is a ground-state anion complex of Fe (II) whereas, in the spectral process, the reduced species is an excited state of a complex having appreciable Fe (III) character.

The complex $[\text{Co(33NMe)}][\text{BPh}_4]_2 \cdot 2\text{MeCN}$ also shows three reversible or quasi-reversible processes; the most anodic quasi-reversible at 0.15 V, the second reversible, at -0.82 V, and a third quasi-reversible at -1.78 V in acetonitrile. The first two processes are attributed to redox activity occurring at the metal; the $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Co}^{2+}/\text{Co}^{+}$ transformations, which are found at very similar potentials in the $[\text{Co L}^5]^{2+}$ system. The process is thought to be mainly metal-centred in this case because it occurs at much more positive potential than for Fe. The reduced species in process (3) (the most cathodic) may be either a Co(0) complex of neutral ligand or, more probably, a Co(I) complex of the radical anion.

Cyclovoltammograms of $[\text{Ni(33NMe)}][\text{BPh}_4]_2 \cdot 2\text{MeCN}$ show a reversible process at -1.39 V (in MeCN)) which may correspond either to a metal-centred $\text{Ni}^{2+}/\text{Ni}^{+}$ or ligand-centred $\text{Ni}^{2+}/\text{Ni}^{2+}$ redox process where the added electron goes into a $\pi^*$ ligand orbital. E.s.r experiments would be required to clarify whether this and other reductions effect a change in metal oxidation state.

Some preliminary measurements on the binuclear complexes show that redox processes are more complex than for the mononuclear species. A comparison of the cyclovoltammograms for the mono- and binuclear Fe (II) complexes can be seen in, Fig.60. Because of differences in the coordination
<table>
<thead>
<tr>
<th>COMPLEX (Acetonitrile Solvent)</th>
<th>SCAN RATE mV s⁻¹</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(33NMe)][BPh₄]₂ 2MeCN H₂O</td>
<td>50</td>
<td>1.23</td>
<td>100</td>
<td>-1.26</td>
</tr>
<tr>
<td>[Fe(33N)][BPh₄]₂</td>
<td>50</td>
<td>1.16</td>
<td>70</td>
<td>-1.31</td>
</tr>
<tr>
<td>[Co(33NMe)][BPh₄]₂ 2MeCN</td>
<td>50</td>
<td>0.15</td>
<td>80</td>
<td>-0.82</td>
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<tr>
<td>[Ni(33NMe)][BPh₄]₂ 2MeCN</td>
<td>50</td>
<td>c</td>
<td>-</td>
<td>-1.39</td>
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<tr>
<td>[Fe₂(33N)(H₂O)₄][ClO₄]₄</td>
<td>100</td>
<td>1.22(br)</td>
<td>180</td>
<td>-1.23</td>
</tr>
<tr>
<td>[Co₂(33N)(MeCN)₂][ClO₄]₄ H₂O</td>
<td>100</td>
<td>0.17</td>
<td>irr</td>
<td>-0.74</td>
</tr>
</tbody>
</table>

a All potentials vs S.C.E.; for irreversible waves, Eₚ is quoted; b BPh₄⁻ salts shows an irreversible anodic peak at 0.8 V due to BPh₄⁻ oxidation; c No cathodic wave assignable to Ni²⁺/Ni⁺ was observed; d Broad irreversible cathodic peak at -1.01 V; e Wave independent of scan rate (50-200 mV s⁻¹)
Fig. 60
Cyclic Voltammograms for the complexes.
A 2-electron process in

\[[\text{Fe}_2(33N)(\text{H}_2\text{O})]_2(\text{ClO}_4)_4\]?

**PROCESS** (TABLE XIII) | **POSSIBLE MECHANISMS** | \(E_{\nu_{\text{A}}}(\text{mV})\) | \(A\) | \(B\)
--- | --- | --- | --- | ---

\[\text{LFe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}\] | \[\text{LFe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}\] | \[\text{LFe}^{\text{II}}\text{Fe}^{\text{II}}\text{L}^-\] | \[\text{LFe}^{\text{II}}\text{Fe}^{\text{III}}\text{L}^-\]

(2) \(-1.23\) | e⁻ | e⁻ | LFe²⁺Fe³⁻L⁻ | LFe²⁺Fe³⁻L⁻

(2') \(-1.37\) | 2e⁻ | e⁻ | LFe²⁺Fe¹⁺L⁻ | LFe²⁺Fe³⁻L⁻

(3) \(-1.50\) | e⁻ | e⁻ | LFe¹⁺Fe¹⁺L⁻ | LFe¹⁺Fe¹⁺L⁻

\[\text{not observed}\]


\[\text{Scheme 1.}\]
environment on exact correspondence of $E_{1/2}$ values cannot be expected. However, there is considerable similarity between two, the major difference being the appearance in the case of the binuclear complex of an irreversible reduction peak at $-1.01\,V$, and a pair of reversible peaks in the place of the $-1.31\,V$ wave seen in the mononuclear complex. One of these has a peak to peak separation of only 30 mV, which might mean that a two electron process is taking place. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ interconversion takes place at virtually the same potential in mono- and binuclear complexes, although the wave is much broader in the di-$\text{Fe}$ (II) case. The occurrence of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple at the relatively positive potential in the di-$\text{Fe}$ (II) complex shows that $\text{Fe}$ (II) is stabilized to the same extent in the binuclear as in the mononuclear complex, owing presumably, to the unusually good fit of the ion in the $\text{N}_4$ macrocyclic plane. Given that $E_{1/2}(\text{Fe}^{3+}/\text{Fe}^{2+})$ has a very similar value in mono- and binuclear complexes, formation of the ligand radical anion complex might also be expected to require similar potential in the two cases. The correspondence of $E_{1/2}(2)$ and $E_{1/2}(3)$ values in mono- and binuclear cases supports the idea that the reversible waves which appear at cathodic potential are ligand centered (in so far as the term can apply to delocalized systems such as these) in both cases. Possible mechanisms are summarized in Scheme 1.

(b) The Binuclear Cu (II) derivatives

A range of di-$\text{Cu}$ (II) complexes, listed in, Table XIV, were obtained by simple transmetallation reactions using an excess of Cu (II) salt. These complexes were usually isolated as perchlorate or tetraphenyl borate derivatives. Other derivatives were also possible by replacing these counter ions by more strongly coordinating ions e.g. $\text{NCS}^-$ and $\text{NCSe}^-$. The stoichiometry of the complex $[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3\cdot2\text{MeCN}$ and its DMF derivative $[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3\cdot2\text{DMF}\cdot3\text{H}_2\text{O}$ obtained on recrystallization
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<th>COMPLEX</th>
<th>$\mu_{\text{eff}}^b$</th>
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<td>293K</td>
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<td>$[\text{Cu}_2(33N)][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O}$</td>
<td>1.87</td>
<td>1.81</td>
<td>$-10^\circ$</td>
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<tr>
<td>$[\text{Cu}_2(33N)(\text{NCS})]_4$</td>
<td>1.82</td>
<td>1.77</td>
<td>$-10^\circ$</td>
<td>Insol.</td>
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<td>2035</td>
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<td>1.71</td>
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<td>$[\text{Cu}_2(33N)(\text{NCS})_2][\text{BPh}_4]_2 \cdot 2\text{MeCN}^c$</td>
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<td>1.76</td>
<td>$-15^\circ$</td>
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<td>$[\text{Cu}_2(33N)(\text{NCS})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$</td>
<td>1.82</td>
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<td>$-10^\circ$</td>
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<td>$[\text{Cu}_2(33N)][\text{BPh}_4]_3 \cdot 2\text{DMF} \cdot 3\text{H}_2\text{O}^c$</td>
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<td>3170(w)</td>
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### TABLE XIV continued

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</table>

- For $10^{-3}$ mol. l$^{-1}$ in acetonitrile at 20° C.
- in B.M. per metal ion.
- Formulation used for this complex is not strictly correct. See later for special discussion.
from dimethylformamide may at first sight, seem unusual. No infrared absorption corresponding to coordinated hydroxide ion was found and since their physical properties were not consistent with a mixed valence Cu^{2+}/Cu^{+} system, the cation [Cu₂(33N)]^{3+} was assumed to be di-Cu (II) complex of the monodeprotonated ligand [33N-H].

The reduced ligand R33N was obtained from 33N by borohydride reduction of the [Pb₂(33N)(NCS)₄] complex. The free ligand isolated was then treated with excess of Cu(ClO₄)₂·6H₂O to give the di-Cu (II) complexes listed in Table XIV.

The infrared spectra for the complexes show that the macrocycles have remained intact during the transmetallation process. All the spectra exhibit medium intensity ν_C-N absorption in the 1610-1625 cm⁻¹ region. In the case of 33N the ν_NH absorption appears as a medium-weak band around 3200 cm⁻¹; R33N shows a similar band although much enhanced in intensity - which is consistent with the existence of six >N-H groups in this macrocycle. The frequency of the ν_NH absorption varies significantly from one complex to another indicating hydrogen bonding interactions. For the two perchlorate derivatives, [Cu₂(33N)][ClO₄]₄·4H₂O and [Cu₂(R33N)][ClO₄]₄·4H₂O, the symmetric stretching ν₃ and bending ν₄ vibration of ClO₄⁻ show up strongly as unsplit bands at the normal ionic frequencies, so there is no indication of ClO₄⁻ coordination in these complexes. Those infrared bands corresponding to the pseudohalide vibrations demonstrate coordination in all cases. As these frequencies appear at the low end of the ν_CN range the inference is that coordination is terminal and through nitrogen. The uniquely low ν_NCS frequency for [Cu₂(33N)(NCS)₂][BPh₄]₂·2MeCN will be discussed in detail later.

Where solubility permitted the conductivity measurements (Table XII) were consistent with, ionic ClO₄⁻, coordinated NCS⁻ in solution.
TABLE XV
ELECTRONIC SPECTRA OF THE Cu (II) COMPLEXES
OF 33N, 33NMe and R33N

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>ELECTRONIC SPECTRUM&lt;sup&gt;a&lt;/sup&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33N)][ClO&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;4&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>15,900 (333)</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33N)(NCS)&lt;sub&gt;4&lt;/sub&gt;]</td>
<td>15,900 (MULL)</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33N)(NCSe)&lt;sub&gt;4&lt;/sub&gt;]</td>
<td>16,300 (MULL)</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33N)(NCS)&lt;sub&gt;2&lt;/sub&gt;][BPh&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;·2MeCN</td>
<td>15,100 (280); 16,300 (MULL)</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33N)(NCS)&lt;sub&gt;2&lt;/sub&gt;][ClO&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>14,900(190) 15,500 (MULL)</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33N)(N&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;][BPh&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;·H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Unstable; not studied</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33N)][BPh&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;3&lt;/sub&gt;·2MeCN</td>
<td>16,200(190)</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(33NMe)][ClO&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;4&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>14,900(350) 15,100 (MULL)</td>
</tr>
<tr>
<td>[Cu&lt;sub&gt;2&lt;/sub&gt;(R33N)][ClO&lt;sub&gt;4&lt;/sub&gt;]&lt;sub&gt;4&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>16,950 (347)</td>
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<sup>a</sup> In acetonitrile solution; extinction coefficients, ε, in parenthesis (1 mol<sup>-1</sup> cm<sup>-1</sup>).
The electronic spectra were recorded between 30,000 and 5,000 cm\(^{-1}\), as acetonitrile solutions and for Nujol mulls. These are summarized in Table XV. All the complexes show one, broad, medium intensity absorption close to 16,000 cm\(^{-1}\). This is consistent with octahedral or square-based 5-coordinate geometry around the metal. The high values obtained for the extinction coefficients is probably a consequence of distortion from these ideal geometries.

The magnetic data (Table XIV) suggest the existence of a very weak interaction (\(J = -15-20\) cm\(^{-1}\)) between the copper centres; the Curie -Weiss plots lie close to linear with \(\theta\) values ranging from -10 to -20°.

X-band e.s.r spectra were studied to further investigate the extent of interaction between the copper ions. Table XVI shows that the Cu (II) ions are in a \(d_{xy}\) ground state in all cases; the \(g_\perp\) and \(g_{11}\) values lying in the range expected for tetragonally extended octahedral or square-pyramidal geometry (see appendix on e.s.r). Powder spectra of the Cu\(_2\)(Mac)\(X_4\) complexes show only broad signals at \(g_\perp\) and \(g_{11}\) with no resolved hyperfine structure. When studied as frozen solutions, these signals sharpen and the hyperfine splitting on \(g_{11}\) becomes apparent. When BPh\(_4\) is used as the counterion, the polycrystalline sample is already sufficiently magnetically dilute to show hyperfine coupling in the neat solid; frozen solution spectra merely sharpen the pattern. Fig.61 shows the \(g = 2\) signal obtained from [Cu\(_2\)(33N)][ClO\(_4\)]\(_4\) 4H\(_2\)O frozen solutions in DMF . The spectrum is axial, showing in the parallel signal five lines of relative intensity 1:2:3:4:3; the remainder of the parallel signal being overlapped by the more intense \(g_\perp\) component. Because of the intensity pattern and the non-appearance of any parallel component lines to high-field of the perpendicular signal, these five lines are interpreted as originating from a 7-line, 1:2:3:4:3:2:1 \(g_{11}\) pattern. The hyperfine splitting constant, \(A_{11}\), is around half the value expected for mononuclear compounds of this type, and is close to the value typically observed for Cu (II) dimers .
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>( g_1 ) SOLID</th>
<th>( g_1 ) FROZEN SOLUTION</th>
<th>( g_{11} ) SOLID</th>
<th>( g_{11} ) FROZEN SOLUTION</th>
<th>( A_{11}/G )</th>
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<tr>
<td>([\text{Cu}_2(33\text{N})][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O})</td>
<td>2.05</td>
<td>2.07</td>
<td>2.14</td>
<td>2.21</td>
<td>81</td>
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<td>([\text{Cu}_2(33\text{N})(\text{NCS})_4]_4)</td>
<td>2.07</td>
<td>2.07</td>
<td>2.16</td>
<td>2.21</td>
<td>77</td>
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<td>([\text{Cu}_2(33\text{N})(\text{NCSe})_4]_4)</td>
<td>2.05</td>
<td>2.08</td>
<td>2.17</td>
<td>2.20</td>
<td>82</td>
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<td>([\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{BPh}_4]_2 \cdot 2\text{MeCN})</td>
<td>2.06</td>
<td>2.07</td>
<td>2.20</td>
<td>2.19</td>
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<td>([\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O})</td>
<td>2.07</td>
<td>2.07</td>
<td>2.21</td>
<td>2.21</td>
<td>80</td>
</tr>
<tr>
<td>([\text{Cu}_2(33\text{N})][\text{BPh}_4]_3 \cdot 2\text{MeCN})</td>
<td>2.07</td>
<td>2.08</td>
<td>2.20</td>
<td>2.21</td>
<td>78</td>
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<tr>
<td>([\text{Cu}_2(33\text{N})][\text{BPh}_4]_3 \cdot 2\text{DMF} \cdot 3\text{H}_2\text{O})</td>
<td>2.08</td>
<td>2.08</td>
<td>2.21</td>
<td>2.21</td>
<td>78</td>
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<tr>
<td>([\text{Cu}_2(33\text{NMe})][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O})</td>
<td>2.09</td>
<td>2.08</td>
<td>2.20</td>
<td>2.23</td>
<td>80</td>
</tr>
</tbody>
</table>

a In DMSO/MeOH solvent;  b DMF solvent;  c Spectrum broadened making parallel signal unresolved.
All the complexes of Table XVI have the same hyperfine splitting pattern in frozen solution; although some spectra are better resolved than others, in all cases five lines can be discerned on the side of the $g_\perp$ signal with similar intensity ratio to those in the [Cu$_2$(33N)][ClO$_4$]$_4$·4H$_2$O spectrum. The ca 80 G hyperfine coupling is clear indication of interaction between the metal centres in these di-Cu (II) complexes. Examination of the 1500-1600 G region of the [Cu$_2$(33N)][ClO$_4$]$_6$·4H$_2$O spectrum at high sensitivity provides further corroboration; the forbidden 'half-band' $\Delta M=2$, signal appears weakly. The signal, which appears approximately $10^{-3}$X the intensity of the $g=2$ signal, is split by hyperfine coupling to the two equivalent copper nuclei into the expected 7-line pattern. Similar 7-line half-bands were observed for the other species listed in table XVI, though not for the relatively insoluble tetrathiocyanato and tetraseselenocyanato...
SOLID-STATE MAIN-BAND AND HALF-BAND SIGNALS OF $\text{[Cu}_2(33N)\text{]}^{3+}$

$T = -160^\circ \text{C}$

Fig. 62
ZERO FIELD SPLITTING IN $[\text{Cu}_2(33\text{N})]^{3+}$

$T = 160^\circ \text{C}$

$D \text{ ca 30 G}$

Fig. 63
complexes where even the main band signals are weak. The appearance of the 
$\Delta M=2$ signal in both solid state and frozen solution spectra of 
$[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3$ solvates is proof that these are dimers and not mixed 
valence Cu (II)/Cu (I) compounds, Fig. 62. The weak interaction in both 
these complexes is reflected also by the observed, small zero-field splitting, $D$, ($D<|A_{11}|$) of ca 30 G, Fig. 63.

$[\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{BPh}_4]_2\cdot2\text{MeCN}$

This thiocyanate derivative merits individual discussion by virtue of the unusual $v_{\text{as}}(\text{NCS})$ observed for the complex in its Mull and KBr disc infrared spectra. In these media absorption was found at 1992 cm$^{-1}$; infrared studies performed in acetonitrile solution demonstrated only the more usual $v^\text{vs}(\text{NCS})$ frequency around 2080 cm$^{-1}$.

Chapter 1 has already reviewed the usefulness of infrared data in determining the bonding mode adopted by coordinating thiocyanate. Of all the studies the most distinctive correlation, albeit based on a handful of known examples, appears to be the association of nitrogen-atom-only bridges with the occurrence of the thiocyanate asymmetric stretch below 2000 cm$^{-1}$. If this was the case in $[\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{BPh}_4]_2\cdot2\text{MeCN}$ then (a) it would represent a further example of what is still rarely observed bonding mode and; (b) we could expect to see substantial interaction between the copper centres - an expectation which is in conflict with the observed e.s.r and magnetic behaviour, indicating only weak interaction. Accordingly an X-ray crystallographic investigation was undertaken to establish the structure of $[\text{Cu}_2(33\text{N})(\text{NCS})_2][\text{BPh}_4]_2\cdot2\text{MeCN}$. As described below the complex does not contain bridging NCS$^-$ but, rather terminally N-coordinated HNCS$^-$.

This result requires the reformulation of the title compound as $[\text{Cu}_2(33\text{N})-2\text{H})(\text{HNCS})_2][\text{BPh}_4]_2\cdot2\text{MeCN}$. It would therefore appear that proton
\[ \text{Fig. 64} \]
transfer from the secondary amine nitrogen to the thiocyanate has occurred to produce anionic \((\text{33N-2H})^2-\) macrocycle and coordinated isothiocyanic acid, Fig. 64.

**X-ray Crystal Structure**

The structure, Fig. 65 of large green needles of \([\text{Cu}_2(\text{33N-2H})(\text{HNCS})_2][\text{BPh}_4]_2\cdot 2\text{MeCN}\) was performed by Dr MGB Drew of the University, Reading. A difference Fourier map was used to indicate possible positions for the hydrogen atoms on the thiocyanate nitrogens. Refinement was obtained to an R value of 0.087.

The unit cell contains two independent centrosymmetric \([\text{Cu}_2(\text{33N-2H})(\text{HNCS})_2]^2+\) cations, four tetraphenylborate anions and four acetonitrile solvent molecules. In each complex cation, each 5-coordinate copper ion is bonded to three nitrogens of a tri-methylene unit and to one deprotonated secondary amine group, these forming a distorted square-planar arrangement around the metal ions with the four Cu-N distances falling in the range 1.91-2.10 Å. The nitrogen atom of the isothiocyanic acid molecule occupies the apical position. The Cu-N distances for the axial isothiocyanic acid are considerably larger than those in the square-plane, although it is short enough to constitute a definite bonding interaction. An unusual feature of the structure is the very small Cu-NC(S) angle \((109.1(22)^\circ \text{ and } 99.6(19)^\circ)\). This appears to be the smallest yet observed. Where angles in the range 150-180° are usually observed for M-N-C(S). Of the two thiocyanic acid molecules one is disordered; angles for the ordered molecules are 104(2)° for Cu-N-H and 152(10)° for H-N-C(S). There are no close contacts between the HNCS molecule and the BPh₄⁻ anions and no obvious reason for the small Cu-N-C(S) angle other than protonation at the NCS⁻ nitrogen atom. The MeCN solvent molecules do not interact with the complex cation.
X-RAY CRYSTAL STRUCTURE OF $[\text{Cu}_2(33\text{H})\text{(HNCS)}_2][\text{BPh}_4]_2\cdot2\text{MeCN}$

Fig. 65
## TABLE XVII

**SELECTED CRYSTALLOGRAPHIC PARAMETERS**

FOR \([\text{Cu}_2(33\text{N}-2\text{H})(\text{HNCS})_2][\text{BPh}_4]_2\cdot2\text{MeCN}\)

<table>
<thead>
<tr>
<th>DISTANCES (Å)</th>
<th>ANGLES (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-Cu(2)</td>
<td>Cu(1)-N(5)C(S) 109.1(22)</td>
</tr>
<tr>
<td>Cu(1)-N(1)</td>
<td>Cu(2)-N(10)C(S) 99.6(19)</td>
</tr>
<tr>
<td>Cu(1)-N(2)</td>
<td>Cu-N(5)-H 104(2)</td>
</tr>
<tr>
<td>Cu(1)-N(3)</td>
<td>H-N(5)C(S) 152(10)</td>
</tr>
<tr>
<td>Cu(1)-N(4)</td>
<td>Cu(2)-N(6) 2.022(012)</td>
</tr>
<tr>
<td>Cu(2)-N(6)</td>
<td>Cu(2)-N(7) 2.098(015)</td>
</tr>
<tr>
<td>Cu(2)-N(7)</td>
<td>Cu(2)-N(8) 1.909(016)</td>
</tr>
<tr>
<td>Cu(2)-N(8)</td>
<td>Cu(2)-N(9) 2.066(013)</td>
</tr>
<tr>
<td>Cu(1)-N(5)</td>
<td>Cu(1)-N(5) 2.314(20)</td>
</tr>
<tr>
<td>Cu(2)-N(10)</td>
<td>Cu(2)-N(10) 2.329(18)</td>
</tr>
<tr>
<td>N(5)-C</td>
<td>N(5)-C 1.06(3)</td>
</tr>
<tr>
<td>N(5)C-S</td>
<td>N(5)C-S 1.78(3)</td>
</tr>
</tbody>
</table>
[\text{Cu}_2(33N-2H)(HNCS)_2][\text{BPh}_4]_2·2\text{MeCN} is the first authentic example of a compound containing coordinated thiocyanic acid, although protonation (presumed to be at sulfur) of N-coordinated \text{NCS}^- in some Co (III) complexes in conc. \text{H}_2\text{SO}_4 has been proposed. The title compound is also unique in the context of other thiocyanato complexes of this related macrocyclic ligands. Thus, in [\text{Cu}_2(33N)(\text{NCS})_2][\text{ClO}_4]_2·2\text{H}_2\text{O} and [\text{Cu}_2(33N)(\text{NCS})_4] \nu_\text{as} (\text{NCS}) occurs at ca 2035-2075 cm\(^{-1}\) i.e. in the normal range for terminal \text{N}-bonded \text{NCS}^-\). The effect is also restricted to the solid state since acetonitrile solutions show only normal \nu_\text{as} at 2070 cm\(^{-1}\).

An important factor in the stabilization of coordinated HNCS in [\text{Cu}_2(33N-2H)(HNCS)_2][\text{BPh}_4]_2·2\text{MeCN} appears to be the acidity of the secondary amino groups of the macrocyclic ligand which are strongly coordinated in the equatorial plane of the copper (II) polyhedron, leading to NH to \text{NCS}^- proton transfer. This view is supported by the isolation of the tritetraphenylborate salt [\text{Cu}_2(33N)][\text{BPh}_4]_3·2\text{MeCN} which on the basis of its stoichiometry, magnetic properties (\mu_{\text{eff}} \approx 2.93 \text{ per Cu atom} = 1.86 \text{ BM}), e.s.r spectra (half-band at \text{g ca} 4) and the absence of other anions such as \text{OH}^-, must be formulated as a di-Cu (II) complex of the mono-deprotonated ligand (33N-H)^-, i.e. [\text{Cu}_2(33N-H)][\text{BPh}_4]_3·2\text{MeCN}. Some preliminary X-ray studies on this compound were conducted; however, disordering of the tetraphenylborate anions complicated the refinement. Cu ... Cu distance was estimated to be ca 7.0 Å. No tetraphenylborate salt could be isolated, although a tetrapерchlorate, diperchlorate-ditetraphenylborate were readily prepared. This could be due to difference in anion size and more efficient crystal packing for the perchlorate. Indeed [\text{BPh}_4]^- may be further implicated in that the occurrence of coordinated HNCS in [\text{Cu}_2(33N-2H)(HNCS)_2][\text{BPh}_4]_2·2\text{MeCN} and not in [\text{Cu}_2(33N)(\text{NCS})_2][\text{ClO}_4]_2·2\text{H}_2\text{O} may be related to the provision in the former of a non-polar environment wherein the usual (i.e. aqueous) Bronsted acidities of coordinated amine and thiocyanic acid are reversed.
Complexes of the macrocyclic ligands P and H

\[
P : R = (\text{CH}_2)_5 \\
H : R = (\text{CH}_2)_6
\]

The macrocycles P and H

Fig.66

It has already been demonstrated that the macrocycles 33N and 33NMe are capable of binding two metals at relatively remote positions. We attempted the synthesis of the smaller macrocycles, P(24-members) and H(26-members) which contain only three equatorial donors to a binuclear site to see whether bridging configurations, making use of vacant sites, could be obtained using NCS\(^-\), N\(_3\)\(^-\) etc. Attempts to condense 1,4-diaminobutane and DAF or DFP on Pb(NCS)\(_2\) were unsuccessful.

The ligands were prepared by template methods in the presence of Pb(NCS)\(_2\), as described in the experimental section. Transmetallation was employed in the preparation of the transition metal complexes.
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>$\nu_{C=N}$</th>
<th>$\nu_{py}$</th>
<th>$\nu_{NCS}$</th>
<th>$\nu_{ClO_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Pb}_2\text{P(NCS)}_4]^a$</td>
<td>yellow</td>
<td>1636 (m)</td>
<td>1582 (m)</td>
<td>2084 (s)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2041 (s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2019 (s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1970 (vs, br)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pb}_2\text{P(NCS)}_2][\text{ClO}_4]_2$</td>
<td>primrose yellow</td>
<td>1640 (m)</td>
<td>1583 (m)</td>
<td>2090 (s)</td>
<td>1090 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1965 (s)</td>
<td>625 (m)</td>
</tr>
<tr>
<td>$[\text{Pb}_2\text{P(NCS)}][\text{ClO}_4]_3$</td>
<td>pale cream</td>
<td>1645 (m)</td>
<td>1585 (m)</td>
<td>1947 (s)</td>
<td>1090 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>918 (m)</td>
<td>625 (m)</td>
</tr>
<tr>
<td>$[\text{Pb}_2\text{P}][\text{ClO}_4]_4$</td>
<td>white</td>
<td>1643 (m)</td>
<td>1585 (m)</td>
<td>-</td>
<td>1090 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>625 (m)</td>
</tr>
<tr>
<td>$[\text{Pb}_2\text{H(NCS)}_4]^a$</td>
<td>yellow</td>
<td>1635 (m)</td>
<td>1580 (m)</td>
<td>2085 (s)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2068 (s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2010 (s)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Pb}_2\text{H(NCS)}][\text{ClO}_4]_3\cdot2\text{H}_2\text{O}$</td>
<td>beige</td>
<td>1635 (m)</td>
<td>1582 (m)</td>
<td>2085 (s)</td>
<td>1090 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>625 (m)</td>
</tr>
<tr>
<td>$[\text{Pb}_2\text{H}][\text{ClO}_4]_4\cdot\text{H}_2\text{O}$</td>
<td>white</td>
<td>1634 (m)</td>
<td>1580 (m)</td>
<td>-</td>
<td>1090 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>625 (m)</td>
</tr>
</tbody>
</table>

*a* Complexes produced directly from template synthesis. *c* prepared as in Ref. 304.
The various Pb (II) complexes isolated are listed in Table XVIII together with selected i.r data. The spectra, in all cases, show the presence of $\nu(C=N)$ at ca 1635 cm$^{-1}$, implying that the Schiff-base formation has occurred in the synthesis and has been retained throughout the various derivatives. The crystalline nature of the complexes and the similarities, in all respects, that they display to the analogous $[\text{Pb}_2\text{L(NCS)}_4]$ systems where $\text{L} = 33\text{N}, 33\text{NMe}$ and $\text{L}$, lead us to believe that $[2 + 2]$ macrocyclic condensation has taken place. The complexes $[\text{Pb}_2\text{L(NCS)}_4]$, when $\text{L} = \text{P}$ and $\text{H}$ were interesting because of their unusual thiocyanate infrared spectra.

The presence of abnormal $\nu_{(\text{NCS})}$ frequencies less than 2000 cm$^{-1}$ in the complexes suggested the presence of single-atom N-only NCS bridges. In chapter one the presence of i.r absorptions below 2000 cm$^{-1}$ was considered diagnostic of the single-atom bridging mode NCS$^-$. Earlier in this chapter I introduced a new bonding mode of thiocyanate, in its acid form, which also exhibits $\nu_{(\text{NCS})}$ below 2000 cm$^{-1}$. The absence, in $\text{P}$ and $\text{H}$, of acidic protons leads us to believe that in this case N-only bridging thiocyanate was present. Subsequent X-ray crystallographic confirmation was supplied by Dr MGB.Drew and P. Yates of the University of Reading.

The Structure of $[\text{Pb}_2\text{P(NCS)}_4]$

The structure is still in a preliminary stage of refinement. Each lead atom is bonded to three nitrogens from the macrocycle and one terminal S-bonded thiocyanate; this Pb$_2$P(NCS)$_2$ fragment fits $C_2$ symmetry. In addition, the two metals are bridged by two thiocyanates which are disordered. There is one NCS group bridged through nitrogen to both lead ions. This nitrogen atom sits on the two-fold axis but the C and S atoms are disordered either side of the two-fold axis. The other bridge is more
TABLE XIX
SELECTED CRYSTALLOGRAPHIC DATA
FOR [Pb_2P(NCS)_4]

<table>
<thead>
<tr>
<th>BOND DISTANCES Å</th>
<th>BOND ANGLES (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-N(CS)</td>
<td>2.73</td>
</tr>
<tr>
<td>Pb-N(1)</td>
<td>2.48</td>
</tr>
<tr>
<td>Pb-N(2)</td>
<td>2.43</td>
</tr>
<tr>
<td>Pb-N(3)</td>
<td>2.55</td>
</tr>
<tr>
<td>Pb-S(CN)</td>
<td>2.89</td>
</tr>
<tr>
<td>Pb-S*(CN)</td>
<td>3.06</td>
</tr>
<tr>
<td>Pb-N* (CS)</td>
<td>3.49</td>
</tr>
<tr>
<td>Pb ... Pb</td>
<td>4.34</td>
</tr>
<tr>
<td>S-Pb-N</td>
<td>163.0 (21)</td>
</tr>
<tr>
<td>S*-Pb-N</td>
<td>121.3 (15)</td>
</tr>
<tr>
<td>S-Pb-S*</td>
<td>72.0 (10)</td>
</tr>
<tr>
<td>S-Pb-N(1)</td>
<td>91.2 (8)</td>
</tr>
<tr>
<td>S-Pb-N(2)</td>
<td>95.2 (11)</td>
</tr>
<tr>
<td>S-Pb-N(3)</td>
<td>77.1 (10)</td>
</tr>
<tr>
<td>N(1) - Pb - N</td>
<td>81.0 (15)</td>
</tr>
<tr>
<td>N(2) - Pb - N</td>
<td>38.4 (27)</td>
</tr>
<tr>
<td>N(1) - Pb - N</td>
<td>91.5 (22)</td>
</tr>
<tr>
<td>Pb - N(1) - N(2)</td>
<td>118.0 (16)</td>
</tr>
<tr>
<td>Pb - S* - N(2)</td>
<td>157.2 (15)</td>
</tr>
<tr>
<td>Pb - S* - N(3)</td>
<td>105.8 (13)</td>
</tr>
<tr>
<td>N(1) - Pb - N(2)</td>
<td>63.9 (13)</td>
</tr>
<tr>
<td>N(1) - Pb - N(3)</td>
<td>130.5 (62)</td>
</tr>
</tbody>
</table>
complicated. The two Pb (II) ions are bridged by a thiocyanate \((\text{NCS}^-)\) ligand in the 3-atom Pb-SCN-Pb manner. However, this bridge is only weakly bonded to the Pb ions and there are two different orientations in the approximate ratio 2:1. In addition these two orientations are disordered over the two fold-axis so that the electron density in this area represents four super-imposed thiocyanates. Only one orientation is shown in the figure. The Pb ... Pb separation is ca 4.34Å.

The N-only bridging configuration, as expected from i.r., was thus confirmed. The complex represents a further example of what is now a growing number of structurally defined compounds containing \text{NCS}^- in what hitherto was an extremely rare type of bonding. The results strengthen the correlation between structure and i.r spectra for this bonding mode.

In Fig. 68, the pseudo-asymmetric \(\nu_{\text{NCS}}\) region of all the di-Pb (II) thiocyanates of Pb are displayed. \([\text{Pb}_2\text{P(NCS)}_4]\) shows four bands in this region. The strong absorptions at 1970 and 2084 cm\(^{-1}\) are assigned, respectively, to the single-atom and the quasi-3-atom bridging thiocyanates. The closely spaced absorptions at 2041 and 2019 cm\(^{-1}\) are attributed to the S-terminal thiocyanates of both Pb (II) ions. On proceeding to the di- and mono-thiocyanates a progressive removal of the various types of thiocyanates is seen. In \([\text{Pb}_2\text{P(NCS)}_2]\)[\(\text{ClO}_4\)]\(_2\) only the frequencies due to the single and 3-atom bridging thiocyanates remain. The S-terminal \text{NCS}^- of \([\text{Pb}_2\text{P(NCS)}_4]\) have therefore been removed and the residual 2+ charge balanced by perchlorate ions. In \([\text{Pb}_2\text{P(NCS)}][\text{ClO}_4]_3\) only the single bridge remains. The removal of the 3-atom bridging \text{NCS}^- will create vacant coordination sites. Splitting of \(\nu_3\) and \(\nu_4\) \(\text{ClO}_4^-\) i.r absorptions into three components in this complex would be consistent with the di-coordination of perchlorate in (local) \(C_{2V}\) symmetry in order to satisfy the coordination requirements of the Pb (II) ions. The observations
I.r. spectra (1800-2200 cm\(^{-1}\) region) of Pb (II) thiocyanate complexes of Ph

Fig. 68
of the normally forbidden $\nu_1$ perchlorate absorption at 920 cm$^{-1}$ is tenta-
atively assigned to reduction of symmetry from $C_{2v}$ on bridging. The
persistence of the single atom bridge in all these complexes suggests that
it is a very stable configuration.

The macrocycle H, which contains six -(CH$_2$)$_2$- groups in each flank
behaves similarly. Thus in the examples [Pb$_2$H(NCS)$_4$] the various $\nu_{\text{NCS}}$
frequencies given are assigned as follows: N-only bridging, NCS, at
2010 cm$^{-1}$, S-terminal, -SCN, at 2068 cm$^{-1}$ and a long 3-atom bridging,
-NCS-, at 2085 cm$^{-1}$.

Both S-terminal thiocyanates in [Pb$_2$H(NCS)$_4$] appear as one absorp-
tion indicating that they exist in equivalent environments In [Pb$_2$P(NCS)$_4$]
S-terminal thiocyanate is split. This may be explained as arising from a non-
equivalence brought about by twisting of this smaller macrocycle which
is apparent from the structure given in, Fig.67.

The Heterobinuclear Complexes of P

Transmetalation under the conditions described, resulted in, rather
surprisingly, the isolation of a series analysing to [PbMP X$_2$Y$_2$] which
seemed to contain one Pb (II) and one M (II) ion (M = Mn, Fe, Ni) in the
macrocyclic cavity. X-ray structural confirmation has been obtained for
one of these complexes, namely [PbMnP(NCS)$_4$].

The physical data obtained for the complexes are summarized in
tables XX and XXI. The magnetic moments of the Mn and Ni complexes are
in the ranges expected for these ions in their high-spin forms.

$[\text{PbFeP(NCS)}_2]^{2+}$ appears to be in a high-spin/low-spin equilibrium. The
low solubility of the complexes in acetonitrile made conductivity and
solution electronic spectra measurements difficult. The mull spectra
of $[\text{PbNiP(NCS)}_2][\text{ClO}_4]_2\cdot2\text{MeCN}$ shows a well resolved band, maximizing at
# PHYSICAL DATA FOR THE HETEROBINUCLEAR COMPLEXES OF P

## TABLE XX

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>$\mu_{\text{eff (BM)}}^a$</th>
<th>$\gamma^c$</th>
<th>ELECTRONIC SPECTRA (MULL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{PbMnP} (\text{NCS})_4]$</td>
<td>orange</td>
<td>5.7</td>
<td>-</td>
<td>INSOL 26,000 (sh)</td>
</tr>
<tr>
<td>$[\text{PbFeP} (\text{NCS})_2] [\text{ClO}_4]_2 \cdot \text{2MeCN}$</td>
<td>deep purple</td>
<td>3.03, 1.22</td>
<td>230</td>
<td>24,000, 16,000</td>
</tr>
<tr>
<td>$[\text{PbNiP} (\text{NCS})_2] [\text{ClO}_4]_2 \cdot \text{2MeCN}$</td>
<td>khaki-green</td>
<td>3.38</td>
<td>-</td>
<td>18,600, 11,700</td>
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</tbody>
</table>

## TABLE XXI

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$\nu_{\text{C = N}}$</th>
<th>$\nu_{\text{Py}}$</th>
<th>$\nu_{\text{NCS}}$</th>
<th>$\nu_{\text{ClO}_4}$</th>
<th>$\nu_{\text{MeCN}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{PbMnP} (\text{NCS})_4]$</td>
<td>1635 (m)</td>
<td>1582 (m)</td>
<td>2088 (s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2070 (s)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2025 (s)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$[\text{PbFeP} (\text{NCS})_2] [\text{ClO}_4]_2 \cdot \text{2MeCN}$</td>
<td>1630 (m, br)</td>
<td>1582 (m)</td>
<td>2122 (s)</td>
<td>1090 (s, br)</td>
<td>2298 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2092 (s)</td>
<td>625 (m)</td>
<td>2265 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2070 (s)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$[\text{PbNiP} (\text{NCS})_2] [\text{ClO}_4]_2 \cdot \text{2MeCN}$</td>
<td>1630 (m)</td>
<td>1583 (m)</td>
<td>2130 (s)</td>
<td>1090 (s, br)</td>
<td>2300 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2118 (s)</td>
<td>625 (m)</td>
<td>2270 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2095 (s)</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

*a* Moment per transition metal ion, *b* Frequency in cm$^{-1}$; ε/dm$^3$ mol.$^{-1}$ cm$^{-1}$ in parenthesis

c* In 10$^{-3}$ M MeCN
11,700 cm\(^{-1}\) which is assigned to \(A + T\) (in \(O_h\) symmetry) while a weak band at 18,600 cm\(^{-1}\) is assigned to the \(A + T\) (F) transition. Intense ligand absorption around 25,600 cm\(^{-1}\) obscure the \(A + T\) (P) transition.

The physical and analytical data suggest one mol. of transition metal to be present per mol. of macrocycle. This gives rise to two possibilities; either (a) these compounds consist of an equimolar mixture of di-Pb (II) and di-M (II) complexes of the macrocycle P or, (b) the compounds consist of heterobinuclear cations, where one Pb (II) and one M (II) ion are encircled within a common macrocyclic cavity. We favour suggestion (b) since the probability that two different binuclear complexes would crystallize out in exact 1:1 ratio, in all three cases Mn, Fe and Ni, seems remote. The structural confirmation mentioned earlier was obtained for the case of PbMnP(NCS)\(_4\) by Dr MGB Drew and P Yates of the University of Reading.

The Structure of \([\text{PbMnP(NCS)}_4]\)

Refinement is still in a preliminary stage and is illustrated in Fig. 69. The structure consists of two metal atoms (separation 4.85\(\AA\)) enclosed in the macrocycle, each bonded to the nitrogens of one trimethine moiety. In addition each metal is coordinated to a terminal NCS via nitrogen. The result of disordering this PbMnP(NCS)\(_2\) unit within the macrocycle is to make the corresponding Pb-N and Mn-N bond lengths appear equivalent. The Pb ion is sulphur-bonded while the Mn ion is nitrogen-bonded.

The pseudo-antisymmetric \(\nu_{\text{NCS}}\) absorption occurs in the region characteristic of 3-atom bridging, NCS. This suggests that both metal ions have octahedral coordination spheres made up of three macrocyclic N-donors,
SELECTED CRYSTALLOGRAPHIC DATA FOR

\([\text{PbMnP(NCS)}_4]\]

<table>
<thead>
<tr>
<th>BOND DISTANCES (Å)</th>
<th>BOND ANGLES (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn–N(4) 2.391(2)</td>
<td>N(5)–Pb/Mn–N(6) 67.8(9)</td>
</tr>
<tr>
<td>Mn–N(5) 2.276(3)</td>
<td>N(6)–Pb/Mn–N(4) 70.2(10)</td>
</tr>
<tr>
<td>Mn–N(6) 2.43(1)</td>
<td>N(6)–Pb/Mn–N(4) 137.7(9)</td>
</tr>
<tr>
<td>Mn–N(3)CN 2.45(1)</td>
<td>N(5)–Pb/Mn–N(3) 81.0(10)</td>
</tr>
<tr>
<td>Mn–N(2)CN 2.31(1)</td>
<td>N(6)–Pb/Mn–N(5) 84.0(10)</td>
</tr>
<tr>
<td>Mn–N(1)CN 2.11(1)</td>
<td>N(4)–Pb/Mn–N(3) 84.7(10)</td>
</tr>
<tr>
<td>Pb–S(1)CN 3.36(1)</td>
<td></td>
</tr>
<tr>
<td>Pb–S(1')CN 3.278(1)</td>
<td></td>
</tr>
<tr>
<td>Pb ... Mn 4.85</td>
<td></td>
</tr>
</tbody>
</table>
two bridging NCS\(^-\) and one MeCN or terminal NCS. The suggested \(\text{Pb N}_3\text{S}_2\) and \(\text{M N}_5\) coordination confirmed for Mn (II) and suggested for Ni (II) and Fe (II) reflect the relative hard or soft nature, in the Pearson sense, of the Pb (II) versus M (II) ions. In the dithiocyanato complexes, \([\text{PbMP(NCS)}_2]\text{[ClO}_4\text{]}_2\cdot 2\text{MeCN (M = Ni, Fe)},\) acetonitrile is envisaged as replacing the terminal thiocyanates of \([\text{PbMnP(NCS)}_4]\).

The Homobinuclear Transition Metal Complexes of P and H

Tables XXIII and XXIV comprise the physical data for the five heterobinuclear complexes of P and the single complex of H. The i.r spectra of the thiocyanate complexes show the NCS\(^-\) acts, as a 'long' (3-atom) bridge. Bearing in mind that the conductivity measurements indicate 2:1 electrolytes and that the structure of \([\text{PbMnP(NCS)}_4]\) has demonstrated the feasibility of the double intramolecular bridge, it seems likely that coordination of the metal ion is octahedral with one axial and one equatorial NCS as depicted in Fig.70.

![Fig.70](image-url)
### TABLE XXIII

MAGNETIC CONDUCTIVITY AND ELECTRONIC DATA FOR THE HOMOBINUCLEAR COMPLEXES

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>$\mu_{\text{eff}}(\text{BN})^a$</th>
<th>ELECTRONIC SPECTRA$^b$</th>
<th>$\Lambda_M^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>293K</td>
<td>93K</td>
<td>(MULL)</td>
</tr>
<tr>
<td>$[\text{Cu}_2\text{P}][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O}$</td>
<td>blue</td>
<td>2.11</td>
<td>1.90</td>
<td>15,000</td>
</tr>
<tr>
<td>$[\text{Cu}_2\text{P} (\text{NCS})_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$</td>
<td>blue/green</td>
<td>1.92</td>
<td>1.77</td>
<td>22,200 (sh)</td>
</tr>
<tr>
<td>$[\text{Cu}_2\text{P} (\text{NCS})_2][\text{BPh}_4]_2 \cdot \text{H}_2\text{O}$</td>
<td>green</td>
<td>1.94</td>
<td>1.81</td>
<td>15,000</td>
</tr>
<tr>
<td>$[\text{Fe}_2\text{P} (\text{NCS})_2][\text{ClO}_4]_2 \cdot \text{MeCN}$</td>
<td>deep purple</td>
<td>3.82</td>
<td>1.91</td>
<td>20,500</td>
</tr>
<tr>
<td>$[\text{Co}_2\text{P} (\text{NCS})_2][\text{ClO}_4]_2 \cdot \text{MeCN}$</td>
<td>dark brown</td>
<td>3.20</td>
<td>2.17</td>
<td>22,800</td>
</tr>
<tr>
<td>$[\text{Co}_2\text{H} (\text{NCS})_2][\text{ClO}_4]_2$</td>
<td>dark brown</td>
<td>4.70</td>
<td>4.13</td>
<td>d</td>
</tr>
</tbody>
</table>

---

**a** Moments per metal ion.

**b** In acetonitrile solution; $e/\text{dm}^3 \text{mol}^{-1}$ in parenthesis.

**c** $10^{-3}$ M in acetonitrile at 20° C.

**d** Ref 304
### Table XIV

**SELECTED I.R. DATA FOR THE HOMOBINUCLEAR COMPLEXES**

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$\nu_{C=N}$</th>
<th>$\nu_{py}$</th>
<th>$\nu_{NCS}$</th>
<th>$\nu_{ClO_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cu}_2\text{P}][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O}$</td>
<td>1620 (m)</td>
<td>1587 (m)</td>
<td>-</td>
<td>1100 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>638 (m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>629 (m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>625 (sh, m)</td>
</tr>
<tr>
<td>$[\text{Cu}_2\text{P(NCS)}_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$</td>
<td>1625 (m)</td>
<td>1585 (m)</td>
<td>2118 (s)</td>
<td>1090 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>625 (m)</td>
</tr>
<tr>
<td>$[\text{Cu}_2\text{P(NCS)}_2][\text{BPh}_4]_2 \cdot 2\text{H}_2\text{O}$</td>
<td>1618 (m)</td>
<td>1584 (m)</td>
<td>2120 (s)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Fe}_2\text{P(NCS)}_2][\text{ClO}_4]_2 \cdot \text{MeCN}$</td>
<td>1623 (br)</td>
<td>1583 (m)</td>
<td>2100 (s)</td>
<td>1100 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>628 (sh)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>625 (m)</td>
</tr>
<tr>
<td>$[\text{Co}_2\text{P(NCS)}_2][\text{ClO}_4]_2 \cdot \text{MeCN}$</td>
<td>1628 (m)</td>
<td>1583 (m)</td>
<td>2110 (s)</td>
<td>1100 (m, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>640 (m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>628 (m)</td>
</tr>
<tr>
<td>$[\text{Co}_2\text{H(NCS)}_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$</td>
<td>1625 (m)</td>
<td>1582 (m)</td>
<td>2100 (s)</td>
<td>1100 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>630 (m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>625 (m)</td>
</tr>
</tbody>
</table>
The macrocyclic ligands P and H supply the N-donors for the remaining 3 equatorial sites. In this way five positions on a square pyramid are utilized. This geometry is to the liking of Cu (II) and probably exists in the [Cu₂P(NCS)₂]²⁺ cations. In the cases of Co (II) and Fe (II) where strict 6-coordinate octahedra are required the remaining 6th axial site is occupied by perchlorate. This is evident from the splitting of the \( \nu_3 \) and \( \nu_4 \) i.r vibration modes of ClO₄⁻ into two components as expected for \( C_{3v} \) local symmetry. Conductivity data implies that these weakly bound perchlorate ligands dissociate in solution, probably to be replaced by solvent acetonitrile.

Magnetic measurements in the range 293 to 93K demonstrate the evidence of high-spin ↔ low-spin equilibria in the compounds [Co₂L(NCS)₂][ClO₄]₂ \( L = P, H \). Equilibrium appears to lie much closer to low-spin at room temperature in the case of ligand P, than ligand H, though magnetic behaviour may be complicated by interactions stronger with P because of the shorter internuclear distance.

The three electronic transitions of each complex, listed in Table XX I, correspond, in order of decreasing energy, to the \( ^4 T_{18} (F) \rightarrow ^4 T_{18} (P) \), \( ^4 T_{18} (F) \rightarrow ^4 A_{28} \); and \( ^4 T_{18} (P) \rightarrow ^4 T_{28} \) transitions expected for octahedral symmetries. The di-Fe (II) complex, too, exhibits high-spin ↔ equilibria. This is responsible for the weakness of the \( \nu_{C=N} \) absorption at 1625 cm⁻¹, which is normally absent in low-spin Fe (II)-trimethine complexes (see [Fe(33NMe)]²⁺). The \( d_{II} \) orbitals are the non-bonding \( t_{2g} \) set which, in the low-spin Fe (II) became fully occupied, thus enhancing the degree of charge-transfer to the\( \Pi \)-antibonding orbitals of \( C=N \). The mull electronic spectrum of this complex displays a pair of intense charge-transfer absorptions at 21,500 and 17,200. Such a splitting has already been discussed for the low-spin mononuclear complexes of 33NMe mentioned earlier. It has
been attributed to a splitting of the $t_{2g}$ set into $e$ and $b_2$ levels due to distortions from octahedral symmetry. These signals dominate the spectrum to the extent that d-d transitions are obscured.

The electronic spectra of the Cu (II) complexes are not particularly helpful in assigning a structure to the cations. They are however consistent with the suggested square-based symmetry.

Magnetic moments, Table XXIII, would suggest weak antiferromagnetic interactions. The solid state e.s.r spectrum of $[\text{Cu}_2\text{P(NCS)}_2][\text{BPh}_4]_2 \cdot \text{H}_2\text{O}$ shows a poorly resolved pattern, which comes up clearly on the 2nd derivative function as 5 lines of the correct intensity ratio for a seven-line pattern, Fig.71. Observation of the 'forbidden' $M = 2$ signal at $10^3 \times$ the sensitivity of the main-band signal, provides further corroboration that the binuclear Cu (II) centres in this system are antiferromagnetically coupled. The magnetically non-dilute compounds $[\text{Cu}_2\text{P}][\text{ClO}_4]_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Cu}_2\text{P(NCS)}_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$ exhibit analogous spectra as DMF glasses, Figs.72,73. For $[\text{Cu}_2\text{P}][\text{ClO}_4]_4 \cdot 4\text{H}_2\text{O}$ two strong perpendicular signals are evident and correspond to zero-field splitting ($D = 70 \text{ G}$). By the same token the parallel signal around $g = 2.31$ is complicated by overlapping of two parallel patterns each split into seven lines by hyperfine coupling. The zero-field splitting parameter $D = 70 \text{ G}$ is greater than the value of ca $30 \text{ G}$ obtained for $[\text{Cu}_2(33\text{N})][\text{BPh}_4]_3 \cdot 2\text{MeCN}$ and is to be expected so because of the smaller ring-size of P allowing closer approach of the Cu (II) centres. However in the present case $D$ has almost the same value as the hyperfine coupling constant $A_{11} = 76 \text{ G}$ and it is this coincidence which complicates the parallel pattern. The pattern for the complex $[\text{Cu}_2\text{P(NCS)}_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ is also complicated - the parallel lines do not occur at regular intervals nor do the intensity ratios match the expected $1:2:3:4:3:2:1$ expected in a coupled binuclear Cu (II) system. The result may again be due to overlapping of more than one pattern as mentioned above.
Powder E.S.R. Spectra of 
\([\text{Cu}_2\text{P(NCS)}_2][\text{BF}_4]_2\), \(\text{H}_2\text{O}\)

Fig. 71
E.S.R SPECTRUM OF $[\text{Cu}_2\text{P}[\text{ClO}_4]_2 \cdot 4\text{H}_2\text{O}]$

$g_{||} = 2.30$
$g_{\perp} = 2.09$
$A_{||} = 76 \text{ G}$
$D = 70 \text{ G}$

Fig. 72
E.S.R. spectrum: \([\text{Cu}_2\text{P(NCS)}_2\text{][ClO}_4]_2\cdot\text{H}_2\text{O}\)
COMPLEXES OF THE MACROCYCLIC LIGAND Q

The ligand Q was prepared, as described in the experimental section, by the template synthesis and isolated as complexes of the template metal ion. The other complexes, in most cases, were obtained via transmetalation. Q differs from the earlier DAP-based macrocycles in:

(a) The nature of its 'N₄O₄' donor set, compared to the 'N₆' of P and H or 'N₈' of 33N and 33NMe and:

(b) The larger bite presented by the potentially tridentate moiety (A), Fig.74, compared to that of the trimethine group in the DAP-based macrocycle, which might be expected to reduce its complexing power. This effect will be compounded by the fact that nitrogen in pyridine is much more basic than oxygen in furan. The results of a study of di-Cu (I), di-Cu (II) and di-Co (II) complexes of closely related DFF-based macrocycles L⁷ᵃ and L⁷ᵇ show that these furan-based macrocycles function quite differently from those of the trimethine type. Thus, in P, H, 33N and 33NMe each metal is associated with one trimethine moiety in a 'North-South' manner, while in L⁷ᵃ and L⁷ᵇ and as will be demonstrated in Q, the metals are incorporated into the 'East-West' poles of the macrocycle; furan oxygen remains uncoordinated.

Fig.74
Template Reactions

Reaction of 2,5-DFF with 3-oxapentane-1,5-diamine in the presence of Ca (II), Sr (II) and Ba (II) leads to either [2 + 2] macrocycle or [1 + 2] open-chain (or 3/4 macrocycle) depending on choice of solvent and metal. In all cases nicely crystalline products were obtained which had no \( \nu_C = 0 \) absorption at ca 1700 cm\(^{-1}\) but instead showed \( \nu_C = N \) at 1620-1630 cm\(^{-1}\). The open-chain forms show \( \nu_{NH_2} \) as a doublet at 3100-3400 and \( \delta_{NH_2} \) at ca 1600 cm\(^{-1}\). Analytical composition and the occurrence of \( P^+ \) at m/e = 384 in the mass spectrum of a compound \([QH][BPh_4]\), obtained by reaction between \([Ag_2Q][ClO_4]\)\(_2\)\(\cdot 2H_2O\) and NaBPh\(_4\) provide further evidence for macrocycle formation.

The electrical conductances given in Table XXV, fall in the ranges expected for 1:2 electrolytes. The \( \nu_3 \) and \( \nu_4 \) i.r modes of ClO\(_4^-\) occuring at 1090 and 625 cm\(^{-1}\) exhibit some degree of splitting in all cases except \([CaQ][ClO_4]\)\(_2\)\(\cdot EtOH\)\(\cdot H_2O\) indicating bonding in order to satisfy the metal's coordination number requirements. The presence of \( \nu_{OH} \) bands around 3420 cm\(^{-1}\) suggest additional coordination of H\(_2O\) and EtOH solvent for the same reason.

The \(^1H\) n.m.r data in CD\(_3\)CN solvent confirm the conclusions relating to the nature of the ligands Q and 3/4 Q; assignments can be found in Table XXVI. All the Ca, Sr, and Ba complexes exhibit furan and imine proton signals at ca 7.0 and 8.2 ppm. In its 3/4 ring form Q shows four sets of triplets one at ca 2.9 ppm corresponding to \( H^F \) adjacent to amine, one at 3.8 ppm due to \( H^C \) adjacent to imine, and two very closely spaced triplets between 3.5 and 3.7 ppm, corresponding to the similar \( H^D \) and \( H^E \) protons which are adjacent to the ether oxygens. In its macrocyclic form \( H^C \) and \( H^D \) appear as a broadened singlet around 3.8 ppm with the required relative intensity for 16 protons.

The complexes \([M(3/4Q)][ClO_4]\)\(_2\)\(\cdot H_2O\) (M = Ca, Sr) are very insoluble in alcoholic solvents and crystallize out within minutes of the mixing of reagents. It was found possible in the case of Ca (II) to convert
this product into the macrocyclic complex $[\text{CaQ}][\text{ClO}_4]_2\cdot\text{H}_2\text{O}$ simply by preventing the $3/4\text{Q}$ complex from crystallizing out. This was achieved by adding 10% (V/V) of acetonitrile to the solution and refluxing. An analogous result was not found in the case of Sr, where only the $3/4$-macrocyclic complex was obtained. Perhaps in this case the amine groups are coordinated in positions too remote to be bridged by incoming 2,5-DFF. Conversely, no $[\text{Ba}(3/4\text{Q})]^{2+}$ complex was isolated, a reflection possibly, of barium's preference for coordination numbers greater than 7.

**Transmetallations**

The non-coordination of furan oxygens in the transmetallated products of $L$ and $L'$, and as will be seen also in Q, means that in contrast to the pyridine-based macrocycles the metal ions are bound to the macrocycle by at least two imine bonds or more if the ether oxygens coordinate. Thus, in the binuclear systems, it should be possible to bind substrate molecules in an East-West bridging fashion between the two metal centres. The binding of axial monodentate ligands can be used to achieve higher coordination numbers, if required.

Transmetallation of $[\text{BaQ}][\text{ClO}_4]_2\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ with Ag (I), Cu (I) and Cu (II) afforded the complexes listed in the latter half of Table XXV. The single di-Ag (I) complex $[\text{Ag}_2\text{Q}][\text{ClO}_4]_2\cdot2\text{H}_2\text{O}$ and its daughter product $[\text{QH}][\text{BPh}_4]$ both behave as expected in their physical properties. Conductivity measurements suggest 1:2 electrolyte behaviour for the former and 1:1 electrolyte behaviour for the latter. I.r and n.m.r data, Tables XXV, XXVI, follow closely those already described for $[\text{MQ}][\text{ClO}_4]_2\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ (M = Ca, Ba).

The coordination environment around each silver is envisaged as 3-coordinate 'N$_2$O', where each silver ion is coordinated to two imines and one water. Whether or not the ether oxygen coordinates is difficult to
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>$\Lambda_{\text{M}}$</th>
<th>$v_{\text{C = N}}$</th>
<th>$v_f$</th>
<th>$v_{\text{NH}_2}$</th>
<th>$v_{\text{NH}_2}$</th>
<th>$v_{\text{ClO}_4}$</th>
<th>OTHER</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ca(3/4Q)][ClO$_4$]$_2 \cdot$H$_2$O</td>
<td>white</td>
<td>320</td>
<td>1643(m)</td>
<td>3118(w)</td>
<td>3355(m)</td>
<td>3300(m)</td>
<td>1600(m)</td>
<td>1090(s,br) 3425(m,br)(H$_2$O)</td>
</tr>
<tr>
<td>[Sr(3/4Q)][ClO$_4$]$_2 \cdot$H$_2$O</td>
<td>white</td>
<td>293</td>
<td>1625(m)</td>
<td>3120(w)</td>
<td>3355(m)</td>
<td>3298(m)</td>
<td>1600(m)</td>
<td>1090(s,br) 3420(br)(H$_2$O)</td>
</tr>
<tr>
<td>[Ba Q][ClO$_4$]$_2 \cdot$EtOH$\cdot$H$_2$O</td>
<td>pink</td>
<td>289</td>
<td>1640(s)</td>
<td>3120(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1100(s,br) 3425(m)(OH)</td>
</tr>
<tr>
<td>[Ca Q][ClO$_4$]$_2 \cdot$EtOH$\cdot$H$_2$O</td>
<td>white</td>
<td>300</td>
<td>1640(s)</td>
<td>3122(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1100(s,br) 3335(m,br)(OH)</td>
</tr>
<tr>
<td>[Ag$_2$Q][ClO$_4$]$_2 \cdot$2H$_2$O</td>
<td>white</td>
<td>227</td>
<td>1636(s)</td>
<td>3095(m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1090(s,br) 3520(m)(H$_2$O)</td>
</tr>
<tr>
<td>[QH][BPh$_4$]</td>
<td>white</td>
<td>114</td>
<td>1638(s)</td>
<td>3100(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3530(m)(OH)</td>
</tr>
<tr>
<td>[Cu$_2$Q][ClO$_4$]$_2 \cdot$3H$_2$O</td>
<td>daffodil yellow</td>
<td>-</td>
<td>1633(s)</td>
<td>3120(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1100(s,br) 3480(s,br)(H$_2$O)</td>
</tr>
<tr>
<td>[Cu$_2$Q][BPh$_4$]$_2 \cdot$2MeCN</td>
<td>orange</td>
<td>-</td>
<td>1628(s)</td>
<td>3120(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2300$\omega$(MeCN)</td>
</tr>
<tr>
<td>[Cu$_2$Q(pdz)$_2$][BPh$_4$]$_2$</td>
<td>red</td>
<td>-</td>
<td>1628(s)</td>
<td>3110(w)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1445(m)(pdz) 1420(m)(pdz)</td>
</tr>
</tbody>
</table>

Cont...
| [Cu$_2$Q(OMe)$_2$(py)$_2$][ClO$_4$]$_2$·2H$_2$O | bright green | 294 | 1628(s) | 3110(m) | - | - | 1090(s,br) | 2,800(m)(OMe) |
| [Cu$_2$Q(OC$_3$)$_2$(py)$_2$][ClO$_4$]$_2$·2H$_2$O | bright green | - | 1628(s) | 3110(m) | - | - | 1090(s,br) | 2045(m)(OC$_3$) |
| [CuQ$^1$][BPh$_4$]$_2$ | aqua-marine | 220 | 1628(s) | 3095(m) | 3280(w) | 1605(w) | - | - |
| 1618(s) | 3182(w) |

a 10$^{-3}$ M in acetonitrile at 20° C.

b pdz = C$_4$H$_4$N$_2$. 

TABLE XXV Continued
TABLE XXVI

\(^1\)H N.M.R DATA FOR THE DIAMAGNETIC COMPLEXES

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G + H(_2)O</th>
<th>BPh(_4)</th>
<th>EtOH</th>
<th>OTHER</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ca(3/4Q)][ClO(_4)](_2)-H(_2)O</td>
<td>7.04(s)[2]</td>
<td>8.27(s)[2]</td>
<td>3.87(t)[4]</td>
<td>3.55-3.69(m)[8]</td>
<td>2.92(t)[4]</td>
<td>2.46(s)[br]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Sr(3/4Q)][ClO(_4)](_2)-H(_2)O</td>
<td>7.02(s)[2]</td>
<td>8.25(s)[2]</td>
<td>3.86(t)[4]</td>
<td>3.65-3.73(m)[8]</td>
<td>2.93(t)[4]</td>
<td>2.40(s)[16]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BaQ][ClO(_4)](_2)-EtOH-H(_2)O</td>
<td>7.03(s)[4]</td>
<td>8.22(s)[4]</td>
<td>3.82(m)[16]</td>
<td></td>
<td></td>
<td></td>
<td>3.53(q), 1.10(t)</td>
<td></td>
<td>2.31(s)[H(_2)O]</td>
<td></td>
</tr>
<tr>
<td>[CaQ][ClO(_4)](_2)-EtOH-H(_2)O</td>
<td>7.13(s)[4]</td>
<td>8.24(s)[4]</td>
<td>3.82(s)[16]</td>
<td></td>
<td></td>
<td></td>
<td>5.5(s), 3.53(q), 1.08(t)</td>
<td></td>
<td>2.20(s)[H(_2)O]</td>
<td></td>
</tr>
<tr>
<td>[Ag(_2)Q][ClO(_4)](_2)-2H(_2)O</td>
<td>7.03(s)[4]</td>
<td>8.16(s)[4]</td>
<td>3.75(s), 3.74(s)[16]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[QH][BPh(_4)]</td>
<td>6.70(s)[4]</td>
<td>7.97(s)[4]</td>
<td>3.67(s)[16]</td>
<td></td>
<td></td>
<td></td>
<td>7.26(m)</td>
<td>6.95(m)</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>[Cu(_2)Q][ClO(_4)](_2)-H(_2)O</td>
<td>6.79(s)[4]</td>
<td>7.84(s)[4]</td>
<td>3.62(s)[16]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu(_2)Q][BPh(_4)](_2)-2MeCN</td>
<td>6.79(s)[4]</td>
<td>7.91(s)[4]</td>
<td>3.66(s)[16]</td>
<td></td>
<td></td>
<td></td>
<td>7.25(m)</td>
<td>6.99(t) [40]</td>
<td>1.95(s)[L(MeCN)]</td>
<td>6.80(t)</td>
</tr>
<tr>
<td>[Cu(_2)Q(pdz)(_2)][BPh(_4)](_2)</td>
<td>6.72(s)[4]</td>
<td>7.91(s)[4]</td>
<td>3.66(s)[16]</td>
<td></td>
<td></td>
<td></td>
<td>7.31-7.24(m)</td>
<td>7.00(t) [40]</td>
<td>9.16(t)[4] pdz)</td>
<td>6.84(t)</td>
</tr>
</tbody>
</table>

CD\(_3\)CN solv; TMS references; Multiplicities in parentheses; \(\delta\) in ppm; Relative intensities in square brackets.

\(^\dagger\) pdz = pyridazine(C\(_4\)H\(_8\)N\(_2\))
ascertain; i.r spectroscopy is unhelpful because of the presence of perchlorate and other strong ligand absorptions in the 1100-1200 cm\(^{-1}\) region. However, experience with other macrocycles \(L\) and \(L'\) containing ether groups, suggests that this is not a good coordinating species to Ag\((I)\) or indeed to transition metals \(^{43,45}\).

Treatment of \([\text{Ag}_2Q][\text{ClO}_4]_2\cdot 2\text{H}_2\text{O}\) with NaBPh\(_4\) in acetonitrile solvent resulted in a precipitate of AgBPh\(_4\) and the isolation of a macromolecular white, crystalline material which is possibly \([QH][\text{BPh}_4]\) exhibiting mass spectral parent ion at m/e = 384. The observation of a medium intensity absorption at 3530 cm\(^{-1}\) would be consistent with protonation on nitrogen.

Three di-Cu\((I)\) complexes were prepared containing various ligating molecules. The coordinating ability of these molecules is reflected in the electronic spectra of the complexes. Thus, as the strength of ligand increases in the series H\(_2\)O, MeCN, pdz \(\text{pyridazine)\},\) the complexes change colour in the sequence yellow + orange + red.

The \(^1\)H n.m.r spectra in CD\(_3\)CN solvent, are in accord with the proposed stoichiometries. The fact that \(^1\)H\(^c\) and \(^1\)H\(^d\) for these complexes, and indeed all the macrocyclic complexes, appears as a singlet at ca 3.7 ppm is somewhat surprising. This seemingly accidental equivalence persists throughout all these complexes and in a recently communicated macrocyclic ligand containing the very same ether linkage.\(^{306}\) The acetonitrile in \([\text{Cu}_2Q][\text{BPh}_4]_2\cdot 2\text{MeCN}\) occurs as a singlet at 1.95 ppm. This acetonitrile is not so apparent in the i.r, probably due to loss of intensity on coordination. The presence of pyridazine \(\text{pdz)\} in [Cu}_2Q(\text{pdz})_2][\text{BPh}_4]_2\) is signified by the observation of new i.r vibrations at 1445 and 1420 cm\(^{-1}\) and also by \(^1\)H n.m.r studies. Pyridazine appears as two widely separated triplets at 9.16 and 7.58 ppm corresponding to the 1,1' and 2,2' protons respectively (see Table XXVI and Fig.75). The separation of ca 1.15 ppm is
larger than observed in the analogous complexes $[\text{Cu}_2\text{L(pdz)}_2][\text{BPh}_4]_2$ (8.13 and 7.68 ppm; $L = 57a, b$) where pdz is coordinated in a bridging configuration. These values are virtually the same as those obtained for free ligand in CD$_2$CN (9.18, 7.56 ppm) and demonstrate that the ligand is dissociating in solution. This conclusion is also apparent from the fact that this fluorescent red complex produces faint yellow coloured solutions in MeCN. The effect is assigned to competitive coordination between pdz and MeCN solvent which being in excess will be the favoured ligand.

The H$_2$O and MeCN-solvated complexes are envisaged as containing 3-coordinate Cu (I), coordinated to two imine and one H$_2$O or MeCN ligand. All but weak interactions with the ether group are ruled out on the basis that an i.r. absorption at 1115 cm$^{-1}$ in the free amine, assigned to the ether group, remains unshifted in the BPh$_4^-$ containing complexes. The argument has been extrapolated to the ClO$_4^-$ complexes because in these cases the strong $\nu_3$ frequency of the counterion interferes.

In the solid state the complex $[\text{Cu}_2\text{Q(pdz)}_2][\text{BPh}_4]_2$ is thought to be 4-coordinate and tetrahedral di-Cu (I) where each Cu (I) ion is coordinated to two imines and one nitrogen from each of two pyridazine ligands which bridge the intermetallic void.

Of the three complexes, $[\text{Cu}_2\text{Q}[\text{ClO}_4]_2\cdot 3\text{H}_2\text{O}$ is the most sensitive to O$_2$. It changes gradually to a green solid in air and much more rapidly in solvent (DMA). $[\text{Cu}_2\text{Q}[\text{BPh}_4]_2\cdot 2\text{MeCN}$ is only slightly sensitive while $[\text{Cu}_2\text{Q(pdz)}_2][\text{BPh}_4]_2$ is insensitive even in DMA solution where pyridazine is not likely to dissociate. Indeed, as will be pointed out later, this complex can be isolated under aerobic conditions by treating a Cu (II) complex with pyridazine. The O$_2$ susceptibilities are yet another reflection of ligating power of the substrate molecules; being weakest in the case of H$_2$O and strongest in the case of pyridazine.
**TABLE XXVII**

ELECTRONIC SPECTRA OF THE Cu (I) COMPLEXES

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>MULL ELECTRONIC SPECTRUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(_2)Q][C(_10)(_4)]_2 (\cdot)XH(_2)O</td>
<td>yellow</td>
<td>29,000(sh), 15,000(sh)</td>
</tr>
<tr>
<td>[Cu(_2)Q(MeCN)(_2)][BPh(_4)]_2</td>
<td>orange</td>
<td>31,600 - 17,000(sh)</td>
</tr>
<tr>
<td>[Cu(_2)Q(pdz)(_2)][BPh(_4)]_2</td>
<td>red</td>
<td>31,000 - 17,000(broad,sh)</td>
</tr>
</tbody>
</table>

**TABLE XXVIII**

MAGNETIC AND ELECTRONIC DATA FOR THE Cu (II) COMPLEXES

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>(\mu_{\text{eff}})</th>
<th>ELECTRONIC SPECTRUM(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293</td>
<td>(MULL)</td>
</tr>
<tr>
<td></td>
<td>93</td>
<td>(SOLUTION)</td>
</tr>
<tr>
<td>[CuQ(_1)][BPh(_4)]_2</td>
<td>1.94</td>
<td>14,700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,700(250)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14,600(sh)</td>
</tr>
<tr>
<td>[Cu(_2)Q(OMe)(_2)(py)(_2)][C(_10)(_4)]_2 (\cdot)2H(_2)O</td>
<td>0.84</td>
<td>17,000(sh)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16,400(240)</td>
</tr>
</tbody>
</table>

\(^a\) \(\varepsilon\) per complex in parenthesis.

\(^b\) Moment per metal ion.
ISOMER SHIFT OF $\nu_{\text{CH}}$ VERSUS $\nu_{\text{CD}}$ IN

$[\text{Cu}_2\text{Q(OMe)}_2(\text{py})_2]\text{[ClO}_4\text{]}_2\text{ 2H}_2\text{O}$

Fig. 76
Preliminary gas uptake studies on the complex \([\text{Cu}_2\text{Q}][\text{ClO}_4]_2\cdot3\text{H}_2\text{O}\) in DMA have been undertaken. Each binuclear molecule binds 0.5 mol. (experimental values 0.51 and 0.56) of dioxygen irreversibly, and \(1.05 \pm 0.03\) mol. at \(293\) (from four uptake measurements) of carbon monoxide reversibly. The stoichiometry of the \(\text{O}_2\) uptake experiments suggests a 4-electron reduction of \(\text{O}_2\). The \(\text{CO}\) uptakes are in accord with an equilibrium reaction between two mols. of \(\text{CO}\) and one mol. of \([\text{Cu}_2\text{Q}]^{2+}\). Variable temperature experiments are planned to confirm this. A similar result of 2\(\text{CO}\) per macrocycle has already been predicted from equilibrium calculation between \([\text{Cu}_2\text{L}(\text{MeCN})_2]^{2+}\) and \(\text{CO}^{46a}\).

Binding of \(\text{CO}\) is accompanied by a red + yellow colour change in DMA solvent. Although reversible the dissociation reaction is \(\text{ca} \times 5\) times slower than the uptake. Further discussion as to the mode of \(\text{CO}\) coordination, viz terminal or bridging, will have to await solution i.r studies.

Of the \(\text{Cu}\) (II) complexes isolated, i.r and conductivity data are to be found in, Table XXV and the magnetic and electronic data in, Table XXVIII.

\([\text{Cu}_2\text{Q}(\text{OMe})_2(\text{py})_2][\text{ClO}_4]_2\cdot2\text{H}_2\text{O}\) is a bright green crystalline compound obtained by exposure of methanolic solutions of \([\text{Cu}_2\text{Q}][\text{ClO}_4]_2\cdot3\text{H}_2\text{O}\) to \(\text{O}_2\) in the presence of pyridine. I.r data indicates retention of the macrocyclic structure by virtue of the presence of \(\nu(C = N)\) at 1628 cm\(^{-1}\). In addition, a medium intensity band at 1605 cm\(^{-1}\) is attributed to coordinated pyridine. A medium intensity band also exists at the lower limit of the aliphatic C-H range at 2800 cm\(^{-1}\). The absence of this band in all the previous complexes and its presence in this complex leads to the assignment of this absorption to \(\nu(C-H)\) of methoxide (\(\text{OMe}^-\)); as implied from elemental analysis. In order to confirm this formulation the preparation was repeated, in small scale, using deuterated methanol (\(\text{CD}_3\text{OD}\)) solvent. As can be seen in, Fig.76, this resulted in shifting the methoxide \(\nu(C-H)\) peak from, 2,800 cm\(^{-1}\) for \(\text{OCH}_3^-\), to 2045 cm\(^{-1}\) for \(\text{OCD}_3^-\) an isomer shift of 755 cm\(^{-1}\). The ratio of \(\frac{\nu_{\text{CH}}}{\nu_{\text{CD}}}=1.4\) is as expected.
The Mull electronic spectrum of this compound shows a main broad signal at 15,000 cm\(^{-1}\) with a high energy shoulder at 17,000 cm\(^{-1}\). All solution measurements, electronic spectra conductivity and e.s.r., indicate that in this phase some structural alteration occurs. Thus the main absorption in solution is seen at 16,400 cm\(^{-1}\), without any high energy shoulder. The complex is a 1:2 electrolyte in MeCN (calculated on the basis of a binuclear structure).

![Diagram of the complex structure](image)

It is suggested that each Cu (II) ion in this compound exists in a 5-coordinate trigonal (possibly trigonal bipyramidal) environment Fig.77. Each Cu (II) would therefore be bonded equatorially to two imines and one bridging methoxide. Analogous structures have been found for closely related complexes \([\text{Cu}_2L^{57\alpha}(\text{OR})_2(\text{NCS})_2]^{210}\) (R = Me, Et, n-Pr). In these complexes antiferromagnetic coupling of the two paramagnetic Cu (II) centres is mediated by the single-atom OR\(^-\) bridge. Coupling is of the order...
2J = -600-700 cm$^{-1}$ and increases along the series Me, Et, n-Pr. In $[\text{Cu}_2\text{Q(OMe)}_2(\text{py})_2\text{ClO}_4]_2\cdot2\text{H}_2\text{O}$ the observed coupling is of similar magnitude; $\mu_{\text{eff}} = 0.84$ BM per metal ion, dropping to 0.44 BM at 93K.

Coupling constants of the order of $2J \gg 700$ cm$^{-1}$ would be required to fit this data. This value is at best approximate. In view of the low moments any residual paramagnetism may be accounted for by paramagnetic impurity. Diamagnetic corrections will also become critical at low susceptibilities. Possibly the strong axial pyridine donors in this complex help push electron density onto the bridges and so enhance the degree of antiferromagnetic interaction. Parallel preparation using EtOH as solvent was unsuccessful in producing an ethoxide bridged complex.

The e.s.r spectrum of the frozen (77K) DMF solution of $[\text{Cu}_2\text{Q(OMe)}_2(\text{py})_2\text{ClO}_4]_2\cdot2\text{H}_2\text{O}$ can be found in Fig.78. It shows an intense four-line pattern which is attributable to mononuclear Cu (II); $A_{11}$ for the first two lines is ca 170 G. This result is in accord with the previous observations that in solution this complex differs significantly from the solid state species. However, addition of successive amounts of MeOH to the solution dramatically reduces the intensity of the signal - much more than expected from simple dilution effects. The observation would be consistent with the reinstatement of the methoxide bridges to produce an e.s.r silent dimeric Cu (II) system. Noticeable also in this e.s.r spectrum is the presence of superhyperfine lines on the 'back' of the $g_\perp$ signal; $A_\perp$ is of the order of 15 G. There appear to be at least nine lines on the high field wing of the $g_\perp$ signal; on expansion ripples can be discerned as extending this pattern into the low-field wing of the $g_\perp$ signal. The occurrence in this case of such superhyperfine lines may be a result of coupling of the unpaired spin on a magnetically independent Cu (II) ion to the nitrogen donors ($I = 1$) in the complex. The nature of this solution species must remain unknown at this stage.
FROZEN SOLUTION E.S.R SPECTRA OF

\[ \left[ \text{Cu}_2Q(\text{OMe})_2(py)_2 \right]\left[ \text{CIO}_4 \right]_2 \cdot 2\text{H}_2\text{O} \]

Fig. 78
E.S.R Spectrum of [CuQ\textsuperscript{1}][BPh\textsubscript{4}]\textsubscript{2}

**Fig. 79**
Finally, a mononuclear complex $[CuQ^1][BPh_4]^2$ was also isolated. The great diversity in the methods of preparation of this compound, which include a Cu (II) templated reaction, indicate high stability and, as will be demonstrated, is a manifestation of the effect of strain within the Q macrocyclic structure.

In the i.r (Table XXV) this complex exhibits a strong, sharply resolved doublet in the $\nu(C = N)$ region at 1628 and 1618 cm$^{-1}$. This would suggest two different types of imine in the complex. Weak $\nu(NH_2)$ absorptions at 3280 and 3182 cm$^{-1}$ together with $\delta(NH_2)$ at 1605(sh) cm$^{-1}$ indicates a non-macrocyclic structure. Elemental analysis implies that one Cu (II), two furan and three amine (NON) moieties are present, while the conductivity in MeCN is within the acceptable range for a 1:2 electrolyte (with allowance for the low ionic mobility of $BPh_4^-$).

Magnetic and electronic spectral measurements, Table XXVIII, are normal for a square-based, non-interacting, mononuclear Cu (II) environment as are the solid and DMF glass e.s.r spectra (4 lines, $A_{11} = 160G$, Fig.79). In order that a reconciliation of this data be achieved, aqua-marine crystals were slowly grown out of acetonitrile solvent and an X-ray structure was performed by Dr MGB Drew of the University of Reading.

The Structure of $[CuQ^1][BPh_4]^2$

As can be seen from, Fig.80, the macrocycle Q has been opened up by the addition of one extra molecule of amine. The copper is bonded to four nitrogens; two cis-amines and two imines. Two uncoordinated imine nitrogens exist within the inner part of the ligand - explaining the doublet character of $\nu(C = N)$ in the i.r spectrum. The Cu (II) exists in a distorted square-plane with angles of $153^\circ$ between trans nitrogens and ca $90^\circ$ between cis nitrogens. Weak interactions exist to three oxygen atoms of the ligand.
The Structure Of $[\text{CuQ}^1]\text{[BPh}_4\text{]}_2$

Fig. 80
TABLE XXIX

Selected Crystallographic Parameters For [CuQ\(^1\)][BPh\(_4\)]\(_2\)

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu .. N(1) 1.912 (23)</td>
<td>N(1) .. Cu .. N(7) 95.2 (9)</td>
</tr>
<tr>
<td>Cu .. N(7) 2.024 (24)</td>
<td>N(1) .. Cu .. N(1)* 90.0 (10)</td>
</tr>
<tr>
<td></td>
<td>N(1) .. Cu .. N(7)* 154.4 (8)</td>
</tr>
<tr>
<td></td>
<td>N(7) .. Cu .. N(7)* 90.8 (10)</td>
</tr>
</tbody>
</table>
A crystallographic two-fold axis bisects the Cu (II) ion and the ether oxygen of the inner part of the ligand. No BPh$_4^-$ interactions with the cation are observed.

Attempts to prepare halide, NCS$^-$, and N$_3^-$ of this complex resulted in the recovery of the starting materials. Similarly, attempts to incorporate a second, heterometal ion into the compound proved unsuccessful, probably because the inner, vacant cavity, where the uncoordinated imines reside, is sterically crowded by the folding of the opened side of the ligand around the metal centre.

The complex bears certain similarities to some mononuclear complexes of compartmental ligands reported by Fenton et al., Fig. 81. In these cases mononuclear Cu (II) complexes are obtained. However, when $R = -(CH_2)_2^-$ or $-(CH_2)_3^-$ the Cu (II) resides in the inner 'N$_2$O$_2$' compartment while $R = -(CH_2)_4^-$, $-(CH_2)_5^-$, $-(CH_2)_2^-$O-(CH$_2$)$_2^-$ or -(CH$_2$)$_2^-$S-(CH$_2$)$_2^-$ results in incorporation of Cu (II) into the outer 'N$_2$O$_2$' compartment. An X-ray structure of the complex containing $R = -(CH_2)_2^-O-(CH_2)_2^-$, the same moiety as exists in Q and Q$^1$, demonstrates this fact.

![Fig. 81](image-url)
Fenton's macrocyclic ligands $L^{58,60}$ (see Chapter 1) bind Cu (II) as a mononuclear square-planar complex $^{202}$. Although in this case $L^{60}$ maintains its macrocyclic integrity, it is similar to $Q^1$ in that it rejects two of the four potentially coordinating imino groups, Fig.39.

Fig.82, outlines the interrelationships between the complexes just described. $[\text{CuQ}][\text{BPh}_4]_2$ occupies a predominant position, however, a ring-closure of this product was achieved against its 'natural grain' by treatment with pyridazine. The reverse di-Cu (I) + di-Cu (II) reaction was exploited in the preparation of $[\text{Cu}_2\text{Q}((\text{OMe})_2\text{(py)})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$ by aerobic oxidation of $[\text{Cu}_2\text{Q}][\text{ClO}_4]_2 \cdot 3\text{H}_2\text{O}$ in the presence of pyridine, (15). Presumably the basicity of the pyridine assists the MeOH $\rightarrow$ MeO$^- + H^+$ ionization. The resultant methoxy bridges then help hold the macrocyclic structure together against its own 'will' to break-up and form mononuclear $[\text{CuQ}^1]^{2+}$.

**Key To Fig.82**

1. Ba (II), Ca (II), EtOH.  
2. Ca (II), Sr (II), MeCN/EtOH.  
3. Cu (II), MeCN.  
4. MeCN, reflux.  
5. Ag (I), MeCN.  
6. NaBPh$_4$, MeCN.  
7. Cu (II), MeCN.  
8. Cu (II), MeCN.  
9. Cu (II), MeCN.  
10. Cu (II), MeCN.  
11. Cu (I), MeOH.  
12. NaBPh$_4$, MeCN  
13. pdz, NaBPh$_4$, MeCN.  
14. CO$_2$, DMA.  
15. Py, O$_2$, MeOH  
16. NaBPh$_4$, MeOH  
17. pdz, MeCN.
The Interrelationships in the Complexes of Q

Fig. 82
Complexes of Schiff-base Acyclic Ligands

The ligands involved in this short section, Fig.83, were prepared directly or in situ by reacting the appropriate amine (in slight excess) with 2,5-DFF. Details of the synthesis and characterization by $^1$H, $^{13}$C n.m.r, i.r and mass spectroscopy are supplied in chapter 2. The presence of $\nu_{\text{C-N}}$ at 1600-1630 cm$^{-1}$ in the i.r of the complexes and free ligand demonstrates retention or successful formation of the Schiff-base functional group.

![Diagram of Schiff-base ligands](image)

Many similarities are borne by the ligand J to the macrocyclic ligand L$^{57a}$, Fig.50. It can present the same number, type (N) and disposition of donors, however the use of a monoprimaray amine in the synthesis has precluded the formation of macrocycle. Instead the reaction halts after a $[1 + 2] \text{[carbonyl + amine]}$ condensation has occurred. The resultant acyclic ligand (or 3/4 macrocycle) will therefore be more flexible than the macrocyclic version. It was of interest to see how this superior flexibility would affect the stereochemistry of the binuclear complexes.

In total five analytically acceptable binuclear Cu (I) and Cu (II) and one polynuclear Cu (I) compound were obtained; their properties are collated in, Tables XXX and XXXI.
The two Cu (I) complexes both contain potentially bridging anions. Information regarding the structure of these compounds is scant and relies heavily on analogy with structurally characterized analogues.

For [(CuI)$_4$J] information about coordination mode I$^-$ is not available since all Cu-I absorptions in i.r., whether terminal or bridging would be expected to lie below 200 cm$^{-1}$ - just outside the normal i.r range. In the case of [Cu$_2$J(NCS)$_2$] a strong absorption occurs at 2083 cm$^{-1}$. This position is at the high end of the N-terminal NCS$^-$ range (see chapter 1) and is below the S-terminal range normally observed with transition metals, however single-atom S-only bridging would appear possible because it is not far from the frequency of the only known example of S-only bridging which is structurally related to this ligand.

Electronic spectra, run as nujol mulls for both these insoluble complexes can be found in Table XXX and, Fig.84. [Cu$_2$J(NCS)$_2$] appears red because of a broad absorption (30,000 - 13,000 cm$^{-1}$) which stretches out of blue and green and tails into yellow. The orange [(CuI)$_4$J] has a much more narrow absorption (30,000 - 20,000 cm$^{-1}$) which allows transmittance of yellow and red light. These high absorptions are attributed to ligand (I$^-$, NCS$^-$)-to-metal charge-transfer.

Possible structures for these complexes are drawn in, Fig.85. The stoichiometry of [(CuI)$_4$J] would suggest a 'cubane'-type structure for the (CuI)$_4$ moiety, tetradentate J could then occupy the fourth, tetrahedral site on each Cu (I) ion. 'Cubane' structures such as these are common among Cu (I)-halide complexes$^{312,315}$ Ag(I) analogous are also known$^{317}$ It is possible that the rarely observed single-atom S-bridging structure exists in [Cu$_2$J(NCS)$_2$]. This type of bonding is found in [Cu$_2$L$^{57a}$ (NCS)$_2$]$^{220}$ where L$^{57a}$ could be thought of as the macrocyclic version of J. As has already
Mull electronic spectra

Fig. 84
been discussed in Chapter 1 \( \nu_{as} \) (NCS) in this compound occurs just above 2100 cm\(^{-1}\), \( \nu_{as} \) (NCSe) is found at 2100 cm\(^{-1}\) in the selenocyanate derivative where Se-only bridging is proposed. The ligand J can twist its terminal NMe\(_2\) groups out of the plane to give one long bridge (as suggested later in an azide complex) but two bridges are probably going to be short. It would seem likely that given the soft nature of the metal centre viz Cu(I), that some type of S-bonding will occur. S-bridging is tentatively proposed in this compound on the basis that it would keep each Cu(I) ion in its favoured tetrahedral environment and by the fact that it resembles \([\text{Cu}_2\text{L}(\text{NCS})_2]\) in colour, solubility and i.r. However S-terminal NCS cannot be totally discounted since the open-chain nature of this ligand would allow twisting of chelating side-amines to achieve such a configuration. This is not possible in the macrocyclic case.

It should be stressed that both these proposals are at best tentative; further progress would require X-ray crystallographic studies.

The series of binuclear Cu(II) complexes all contain potentially bridging species; in each case these may be identified by characteristic i.r. frequencies, Table XXX. The preparation of \([\text{Cu}_2\text{J(OH)}_2][\text{ClO}_4]_2\) differs from the rest in that it could only be prepared using \([\text{Cu(MeCN)}_4](\text{ClO}_4)\) starting material and then allowing the solution to oxidize — much the same technique employed in the preparation of \([\text{Cu}_2\text{Q(OMe)}_2(py)_2][\text{ClO}_4]_2^2\cdot2\text{H}_2\text{O}\) in the previous section.

The ligand field spectra, Table XXX, show that all the complexes (except an azide derivative) absorb around 15,000 cm\(^{-1}\) typical of a tetragonal type of coordination. The brown \([\text{Cu}_2\text{J(N}_3)_3][\text{ClO}_4]\) has its d-d absorption centred at 13,000 cm\(^{-1}\) and is intense (\(\epsilon = 790\) mol.\(^{-1}\) cm\(^{-1}\) per molecule). Fig.85 compares the electronic spectra of the typically tetragonal \([\text{Cu}_2\text{J(OH)}_2][\text{ClO}_4]_2\) with that of \([\text{Cu}_2\text{J(N}_3)_3][\text{ClO}_4]\). The intense
Electronic spectra: $10^{-3}$ M in MeCN

Fig. 85
N$_3$-to-metal charge-transfer in the 25,000-17,000 cm$^{-1}$ region is obvious and is responsible for this compound appearing to be brown rather than the green or blue colours usually associated with Cu (II). The intensity of the d-d transition presumably is due to mixing-in of p-character with the d-orbitals as a result of distortions from square-based to tetrahedral geometry. Electronic solution and mull spectra and conductivity studies in all cases are in accord with retention of the bridging moieties in solution.

\[
[(\text{CuI})_4\text{J}] \quad \left[\begin{array}{c}
\text{N} \\
\text{Cu} \\
\text{NMe}_2
\end{array}\right]
\]

\[
[\text{Cu}_2\text{J(NCS)}_2] \quad \left[\begin{array}{c}
\text{N} \\
\text{Cu} \\
\text{NMe}_2
\end{array}\right]
\]
<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>ELECTRONIC SPECTRA</th>
<th>(\lambda_{M})</th>
<th>(\nu_{C=N})</th>
<th>(\nu_{F})</th>
<th>OTHER (\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{CuI}]_4\text{J})</td>
<td>orange</td>
<td>27,000 (sh)</td>
<td>-</td>
<td>Insol</td>
<td>1614 (s)</td>
<td>3100</td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(NCS)}]_2)</td>
<td>red</td>
<td>25,000 (br, sh)</td>
<td>-</td>
<td>Insol</td>
<td>1606 (s)</td>
<td>3107 (m) 2080 (s)</td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(OH)}]_2[\text{ClO}_4]_2)</td>
<td>blue-green</td>
<td>15,000</td>
<td>25,200 (sh) 15,000 (275)</td>
<td>289</td>
<td>1625 (s) 3125 (m)</td>
<td>3542 (v, s) 3570 (sh) 1090 (s, br) 625 (m)</td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(OAc)}]_2[\text{BPh}_4]_2\ 2\text{H}_2\text{O})</td>
<td>green</td>
<td>14,800</td>
<td>14,600 (245) 267</td>
<td>1625 (s) 3115 (m)</td>
<td>1582 (s, br)</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(OMe)}]_2[\text{BPh}_4]_2\  \text{MeCN H}_2\text{O})</td>
<td>green</td>
<td>15,000</td>
<td>15,000 (296) 250</td>
<td>1623 (s) 3105 (w)</td>
<td>2240 (w) 3570 2255 (w) 2290 (w)</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(N}_3)_3][\text{ClO}_4])</td>
<td>brown</td>
<td>11,800 9,600 (sh) 13,000 (790) 11,900 (sh) 177</td>
<td>1627 (s) 3117 (m)</td>
<td>1627 (s) 3117 (m)</td>
<td>2052 (s) 2090 (s) 1095 (s, br) 625 (m)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE XXXXI</th>
<th></th>
<th>(\mu_{\text{eff}}^b)</th>
<th>293K</th>
<th>93K</th>
<th>(\theta^{(0)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu}_2\text{J(OH)}]_2[\text{ClO}_4]_2)</td>
<td></td>
<td>2.00</td>
<td>1.98</td>
<td>-8</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(OAc)}]_2[\text{BPh}_4]_2\ 2\text{H}_2\text{O})</td>
<td></td>
<td>2.02</td>
<td>1.82</td>
<td>-20</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(OMe)}]_2[\text{BPh}_4]_2\  \text{MeCN H}_2\text{O})</td>
<td></td>
<td>1.81</td>
<td>1.34</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}_2\text{J(N}_3)_3][\text{ClO}_4])</td>
<td></td>
<td>2.10</td>
<td>1.73</td>
<td>a</td>
<td></td>
</tr>
</tbody>
</table>

a does not obey Currie-Weiss Law. b in B.M. per metal ion.
The magnetic data, Table XXXI, suggests weak antiferromagnetic behaviour in all but one case. The fact that the magnetic moment of 
\[ \text{[Cu}_2\text{J(OH)}_2]\text{[ClO}_4\text{]}_2 \] is virtually temperature independent is surprising. That the di-\(\mu\)-hydroxo structure is present is almost certain from the element analysis, conductivity and in particular the presence in the i.r of a very strong and sharp absorption at 3540 cm\(^{-1}\). In the appendix to this thesis antiferromagnetic interaction in Cu (II) dimers is briefly outlined. Illustrated (Fig. A) is the dependance of \(J\) on \(\phi\) (the bridging Cu-O-Cu angle). Ferromagnetic interactions are obtained at low \(\phi\) values and antiferromagnetic interaction and high values of \(\phi\). It could be that in \(\text{[Cu}_2\text{J(OH)}_2]\text{[ClO}_4\text{]}_2\) \(\phi\) is close to ca 97\(^{\circ}\) where \(J = 0\) as the straight line of \(J\) versus \(\phi\) crosses over from ferro- to antiferromagnetic behaviour.

In the remaining complexes coupling of the unpaired spins is greatest when the methoxide bridged species where \(\mu\text{eff}\) falls below the spin-only value of 1.72 BM. The weakest interaction occurs with \(\text{[Cu}_2\text{J(OAc)}_2]\text{[BPh}_4\text{]}_2\cdot2\text{H}_2\text{O}\) where the acetate group may be envisaged as bridging in one of the two versions illustrated in, Fig. 86.
The suggested structure of $[\text{Cu}_2\text{J(N}_3\text{)}_3]^2^+\text{, Fig.87,}$ involves a single 3-atom bridge and two terminal $\text{N}_3^-$. Evidence for the two kinds of $\text{N}_3^-$ present is apparent from the strong 2052 and 2090 cm$^{-1}$ i.r bands. Unlike NCS$^-$, i.r correlations with bonding mode $\text{N}_3^-$ are not reliable. However since the 2090 cm$^{-1}$ absorption is the more intense it is cautiously assigned to the coordinated $\text{N}_3^-$. The remaining 2090 cm$^{-1}$ frequency may therefore correspond to the $\mu$-1,3-azido species. Adoption of the long bridge rather than $\mu$-1,1-azido is consistent with the observed weak antiferromagnetic activity of this compound; $\mu$-1,1-azido bridges are expected to exhibit ferromagnetic exchange.

The e.s.r spectrum (D.M.S.O/MeOH glass) can be found in, Fig.88. The pattern is complex and difficult to interpret. However the complexity does suggest a triplet species. The solid room temperature spectrum, Fig.87, appears as a normal mononuclear Cu (II) ion. This is surprising although it may be that at $293\text{K}$(where $\mu_{\text{eff}} = 1.81\text{ BM}$) the degree of interaction is insufficient to affect the spectrum. Whereas the glass spectrum was recorded at 77K where the moment lies below 1.34 BM. Both the acetate and hydroxo derivative give non-interacting signals: $g_{11} = 2.27$, $g_\perp = 2.13$; $\Delta = 158 G$, OH$^-$: $g_{11} = 2.32$, $g_\perp = 2.08$, $A_{11}^\perp = 150$. E.s.r data on $[\text{Cu}_2\text{J(N}_3\text{)}_3][\text{ClO}_4^-]$ has not been obtained due to instrumental difficulties.

![Fig.87](image)

No potentially catalytically active complexes where obtained. The only di-Cu (I) complexes isolated contained bridging or bridgehead ligands NCS$^-$ and I$^-$ respectively. The effect of these coordinating anions was not only to block substrate receptor sites but also to make the complexes too insoluble to work with.
Given the insolubility of [Pd$_2$(EDAAF)Cl$_4$], the only complex of EDAAF, there are few physical probes available to characterize this compound. In the i.r spectrum of the free ligand (Chapter 2) a strong absorption occurs at 1637 cm$^{-1}$ where both $\nu$(C = N) and $\nu$(CH = CH$_2$) are coincident. On coordination this signal shifts to 1628 cm$^{-1}$ with a shoulder at 1635 cm$^{-1}$. Previous studies on Pd (II) complexes of a related Schiff-base ligand containing pendant olefinic groups have shown Pd (II)'s preference for the imine donors. It would seem possible that a similar situation exists in the present case, Fig. 88a. A medium intensity i.r band at 330 cm$^{-1}$ suggests terminal chloride in this case.
The ligands, Fig. 89, were prepared by the methods described in the experimental section. The molecules are capable of forming a 5-membered ring chelates in a variety of ways. They may use (a) both nitrogen atoms; (b) both X groups; or (c) one nitrogen and one X. Modification of the group X allows the introduction of soft ligating groups like sulphur, which may be the preferred donor in complexes of softer metal ions. Previous studies on these and closely related ligands with first row transition metals have shown that they prefer to chelate in bidentate fashion via the α-di-imine groups.

It was of interest also to study any catalytic or gas uptake (O₂, CO) properties that these compounds may possess.

<table>
<thead>
<tr>
<th>X</th>
<th>LIGAND</th>
<th>ABBR.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>2,2- bi-4,5-dihydroimidazine</td>
<td>biz</td>
<td>3</td>
</tr>
<tr>
<td>S</td>
<td>2,2- bi-4,5-dihydrothiazine</td>
<td>btz</td>
<td>3</td>
</tr>
<tr>
<td>O</td>
<td>2,2- bi-2-oxazoline</td>
<td>bo</td>
<td>2</td>
</tr>
<tr>
<td>NH</td>
<td>2,2- bi-2-imidazoline</td>
<td>bi</td>
<td>2</td>
</tr>
<tr>
<td>S</td>
<td>2,2- bi-2-thiazoline</td>
<td>bt</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 89
The Copper (I) Complexes of btz, bt and bo.

The complexes prepared are listed in Table XXXV, together with their physical data. All the complexes are diamagnetic and stable to air in the solid state, while the solutions, where solubility permits, slowly turn green on exposure to air.

The i.r. spectra of the closely related btz and bt ligands show a strong $\nu(C = N)$ absorption at 1614 cm\(^{-1}\) and 1590 cm\(^{-1}\) respectively, accompanied by strong bands in the 800-1200 cm\(^{-1}\) region; corresponding to skeletal vibrations of the heterocyclic rings. Weak-to-medium intensity bands at 650-660 cm\(^{-1}\) in both ligands be due to the $\nu(C-S)$ vibration. The slightly different bo ligand exhibits $\nu(C = N)$ at 1663 cm\(^{-1}\). Marked changes in the i.r spectra occur on coordination to Cu (I). These are best discussed in retrospect the crystal structures which were determined for the two complexes [Cu(btz)\(_2\)][BPh\(_4\)] and [Cu\(_2\)(bt)\(_4\)][ClO\(_4\)]\(_2\) by Dr M. G. B. Drew and T. R. Pearson of the University of Reading.

X-ray Crystal Structures

(a) [Cu(btz)\(_2\)][BPh\(_4\)]

Refinement was obtained to a final R value of 0.061. The cation Cu(btz)\(_2\)\(^+\) has a crystallographic C\(_2\) symmetry with the Cu (I) atom positioned on the 2-fold axis. The Cu is bonded to two btz ligands via the $\alpha$-di-imine moieties (Cu - N bond lengths 2.010(6) and 2.024(6)\(^\AA\)). The two 'CuN\(_2\)' planes intersect at a dihedral angle of 68.9° giving the cation a severely distorted (flattened) tetrahedron. Several $\alpha$-di-imine complexes have been known to show this kind of distortion, Table XXXII. The dihedral angle of 68.9° of the title complex is among the smallest known.

[Cu(tmp)\(_2\)][ClO\(_4\)]\(_2\) has a smaller dihedral angle of 67.6°. This distortion towards square-planar occurs despite the fact that unfavourable steric
The Structure of $[\text{Cu(btz)}_2]^+$

Fig. 90

**TABLE XXXIII**

SELECTED CRYSTALLOGRAPHIC DATA FOR $[\text{Cu(btz)}_2]^+$

<table>
<thead>
<tr>
<th>BOND DISTANCES ($\text{Å}$)</th>
<th>BOND ANGLES ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–N(1) 2.010(6)</td>
<td>N(1)–Cu–N(12) 91.48(23)</td>
</tr>
<tr>
<td>Cu–N(12) 2.024(6)</td>
<td>N(1)–Cu–N(1*) 118.73(24)</td>
</tr>
<tr>
<td>N(1)...(12) 2.63</td>
<td>N(1)–Cu–N(12*) 136.41(24)</td>
</tr>
<tr>
<td></td>
<td>Cu–N(1)–C(6) 113.9(4)</td>
</tr>
<tr>
<td></td>
<td>Cu–N(12)–C(7) 112.8(4)</td>
</tr>
<tr>
<td></td>
<td>N(1)–6(6)–C(7) 115.1(5)</td>
</tr>
<tr>
<td></td>
<td>N(12)–(17)–(16) 115.2(5)</td>
</tr>
</tbody>
</table>
Table XXXII
DIHEDRAL IN Cu (1)-α- DI-IMINE LIGANDS

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>DIHEDRAL ANGLE</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(dmp)₂][NO₃] 2H₂O</td>
<td>85.4°</td>
<td>323</td>
</tr>
<tr>
<td>[Cu(dmp)₂][ClO₄]</td>
<td>81.8</td>
<td>324</td>
</tr>
<tr>
<td>[Cu(dmbp)₂][BF₄]</td>
<td>80.9</td>
<td>325</td>
</tr>
<tr>
<td>[Cu(dmbp)₂][NO₃]</td>
<td>80.0</td>
<td>326</td>
</tr>
<tr>
<td>[Cu(tmbp)₂][ClO₄]</td>
<td>67.6</td>
<td>327</td>
</tr>
<tr>
<td>[Cu(btz)₂][BPh₄]</td>
<td>68.9</td>
<td></td>
</tr>
</tbody>
</table>

**dmp:** 2,9-dimethyl-1,10-phenanthroline

**dmbp:** 6,6'-dimethyl-2,2'-bipyridine

**tmbp:** 4,4',6,6'-tetramethyl-2,2'-bipyridine
Interactions occur between the 6,6-methyl groups in the planar configuration.

In the coordinated btz molecule five of the atoms of the 6-membered hetercyclic ring are planar. There is a small twist around the C(6) - C(7) bond connecting the two 6-membered rings (torsion angle of N(1) - C(6) - C(7) - N(12) is 13.9°). No contacts exist between cation and anion less than 3.5Å. More detailed crystallographic discussion can be found in Ref. 328.

The reason for the large deviation of 90° for the dihedral angle between the two 'CuN₂' units is unclear. Stereochemical crowding around the Cu(I) does not exist and intermolecular packing effects seem inadequate in explaining such a large (21°) divergence from ideal tetrahedral geometry. Moreover, the observation of dihedral angles ranging from 68-85° in all the Cu(I) α-di-imine structures known seems to suggest that the distortion may have an intrinsic electronic origin. Possibly there is some mixing of the exited state, formally a planar Cu(II) complex with a ligand radical anion, with the ground state. Alternatively, flattening of the tetrahedron towards square-planar would result in a more efficient d_π - p_π* overlap.

The Structure of [Cu₂(bt)₄][ClO₄]₂ (Fig. 91)

In the [Cu₂(bt)₄]²⁺ cation each Cu(I) is bonded to two nitrogen atoms of one ligand (A) (Cu - N, 2.277(6), 1.995(5)Å) and is also strongly bonded to one nitrogen N(IB) of a second ligand molecule (B) (Cu - N 1.961(5)Å). This ligand (B) is in the trans configuration with S(10B) cis to N(IB); N(IB) being coordinated while S(10B) remains remote at 3.039(2)Å from the metal centre. The Cu(I) is also strongly bonded (2.428(2)Å) to a sulphur, S(10B*), of a centrosymmetrically related 'Cu(bt)₂' unit. The geometry is best
THE STRUCTURE OF $[\text{Cu}_2(\text{bt})_4]^{2+}$

**Fig. 91**

**TABLE XXXIV**

SELECTED CRYSTALLOGRAPHIC DATA FOR $[\text{Cu}_2(\text{bt})_4]^{2+}$

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (1) – Cu (2)</td>
<td>N(1A)–Cu(1)–N(7A) 78.36(22)</td>
</tr>
<tr>
<td>Cu (1) – N(1A)</td>
<td>N(1A)–Cu(1)–N(1B) 110.39(2)</td>
</tr>
<tr>
<td>Cu (1) – N(7A)</td>
<td>N(7A)–Cu(1)–S(10B) 102.82(21)</td>
</tr>
<tr>
<td>Cu (1) – N(1B)</td>
<td>N(1B)–Cu(1)–S(10B) 102.66(21)</td>
</tr>
<tr>
<td>Cu (1) – S(10B*)</td>
<td>N(1B)–Cu(1)–S(10B) 102.66(21)</td>
</tr>
<tr>
<td>Cu (1) – S(10B)</td>
<td>N(7A)–Cu(1)–N(1B) 144.64(22)</td>
</tr>
<tr>
<td>N (1) – N(7)</td>
<td></td>
</tr>
</tbody>
</table>
described as a very distorted tetrahedron comprising N(1A), N(7A), N(1B) and S(10B) if the weak (3.039(2)\AA) interaction between Cu (1) and S(10B) is discounted. The Cu \ldots Cu separation is 3.65\AA and no clear interactions are observed within the dimer or between cation and anion. More detailed crystallographic description can be found in Ref.328.

The widely different structures of the two complexes is unexpected. Previous studies with these ligands and Fe (II) had established that both bt and btz coordinate via the α-di-imine group. On the other hand Cu (I) is known to have an affinity for sulphur but it is far from obvious why these two ligands should behave differently towards the same metal ion. We think the answer lies in the difference in the heterocyclic ring-size for bt and btz.

In the planar btz chelate 'Cu-N₂C₂' ring the N \ldots N separation is 2.63\AA, both atoms subtending an angle of 81.5° at the metal, Fig.92. In contrast the smaller 5-membered ring of bt pulls the two imine nitrogens further apart (N \ldots N in coordinated bt is 2.71\AA) so that the lone pairs converge on the metal centre at greater distances and subtend a smaller angle (78.3°), Fig.92. The net result is a distorted chelate ring.

\begin{center}
\includegraphics[width=0.8\textwidth]{fig92.png}
\end{center}

THE DIFFERENT 'BITES' OF btz and bt.

Fig.92
It would therefore appear that the α-di-imine group of 
$[\text{Cu(btz)}_2]^+$ is better suited for chelation. Whatever the advantage in the 'bite' of btz compared to bt, the effect must be small enough not to influence critically the coordinating properties of the α-di-imine group towards Fe (II) where both ligands generate a field strong enough to cause spin-pairing. Possibly, when coordinating to Cu (I), the softer nature of this metal ion combined with the soft donor qualities of sulphur, results in a delicate balance between coordination of α-di-imine and sulphur with the result that both occur in the same molecule.

Given that sulphur coordination is 'elected' in the case of bt, the trans configuration used to bring this about may well be expected to be inferior to the cis configuration since the sulphur lone-pairs will not lie in the same plane as the nitrogen lone-pair. Thus the Cu atom prefers to bond strongly with the sulphur of another ligand molecule of an adjacent 'Cu(bt$_2$)' unit.

With the coordination modes of the btz and bt ligands now established the physical properties, Table.XXXV of these two complexes can be more easily explained.

For the complex $[\text{Cu(btz)}_2][\text{BPh}_4]_2$ Fig.93, occurs as a single medium band at 1530 cm$^{-1}$; a shift of -84 cm$^{-1}$ relative to free btz ligand. The tentatively assigned $\nu(C-N)$ band at 660 cm$^{-1}$ in free btz has suffered a reduction in intensity and a smaller coordination shift (see Fig.2 for a full i.r. spectrum). Such large coordination shifts to lower energies together with the alteration in intensity is indicative of strong coupling between vibration modes within the Cu(N=C-C=N) chelate ring 329 330. This would arise from metal d$\rightarrow$to-ligand P* back coordination. Effects similar to these have already been observed in low-spin Fe (II) complexes of the α-di-imines 322 330. Significantly in the complexes $[\text{Cu(btz)}_3][\text{ClO}_4]_2$ and $[\text{Cu(bt)}_2][\text{ClO}_4]_2$, where little metal-to-ligand charge-transfer is expected, $\nu(C-N)$ is shifted to lower frequencies only by 46 and 5 cm$^{-1}$ respectively and without appreciable loss in intensity.
TABLE XXXV

PHYSICAL DATA FOR THE COPPER (I) COMPLEXES OF btz, bt AND bo

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>$\lambda_{M} , ^a$ (Scm mol$^{-1}$)</th>
<th>$\nu(C=N)$</th>
<th>$\Delta\nu(C=N) , ^b$</th>
<th>$\nu(C-S)$</th>
<th>$\Delta\nu(C-S) , ^b$</th>
<th>ELECTRONIC SPECTRA $^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(btz)$_2$][BPh$_4$]</td>
<td>dark brown</td>
<td>102</td>
<td>1530(m)</td>
<td>-84</td>
<td>670(w)</td>
<td>+20</td>
<td>26.0(sh)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.7(1640)(s,b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.9(sh)</td>
</tr>
<tr>
<td>[Cu(btz)I]$_2$</td>
<td>burgundy-brown</td>
<td>INSOL</td>
<td>1578</td>
<td>-36</td>
<td>660(v,w)</td>
<td>+10</td>
<td>23.0$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1541</td>
<td>-11</td>
<td></td>
<td></td>
<td>20.0(sh)</td>
</tr>
<tr>
<td>[Cu$_2$(bt)$_4$][ClO$_4$]$_2$</td>
<td>red-orange</td>
<td>162</td>
<td>1600(m)</td>
<td>+10</td>
<td>652(w)</td>
<td>0</td>
<td>25.2$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1572(m)</td>
<td>-18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1552(m)</td>
<td>-38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CuI)$_2$bt$]$</td>
<td>orange</td>
<td>INSOL</td>
<td>1590</td>
<td>0</td>
<td></td>
<td></td>
<td>22.6$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1568</td>
<td>-22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu(bo)$_2$][ClO$_4$]</td>
<td>yellow-orange</td>
<td>-</td>
<td>1650(m)</td>
<td>-13</td>
<td></td>
<td></td>
<td>25.6(sh)$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23.6</td>
</tr>
<tr>
<td>[(CuI)$_2$bo]</td>
<td>bright-yellow</td>
<td>INSOL</td>
<td>1655</td>
<td>-8</td>
<td></td>
<td></td>
<td>24.0$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1635</td>
<td>-28</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $10^{-3}$ M in acetonitrile at 20° C; $^b$ shift relative to free ligand; $^d$ mull; $^e$ band maxima in 10$^{5}$ cm$^{-1}$, $\epsilon/\lambda$ mol$^{-1}$ cm$^{-1}$, in parenthesis.
[Cu$_2$(bt)$_n$][ClO$_4$]$_2$ or empirically [Cu(bt)$_2$][ClO$_4$] behaves in a more complex manner. The single free ligand v(C = N) occurring at 1500 cm$^{-1}$ is replaced by three medium intensity bands at 1600, 1572 and 1552 cm$^{-1}$. The 1500-1600 cm$^{-1}$ pattern is complicated while v(C=S) at 652 cm$^{-1}$ is much reduced in intensity and occurs with several other bands in the region, Fig. 94. This can be rationalized by reference to the three different types of imine found in the crystal structure viz uncoordinated (1600 cm$^{-1}$); coordinated and chelating (1552 cm$^{-1}$) and coordinated and bridging (1572 cm$^{-1}$), Table XXXV.

The electronic spectra refer to Cu (I)-to-ligand charge-transfer transitions. The different energies of each system reflect the different coordination environments of the metal ion in the complexes. Low energy charge-transfer may be taken as an indication of good π-accepting capacity of the α-diimine group. Thus [Cu(btz)$_2$][BPh$_4$] exhibits the most efficient d$^0$-$p^*$ charge-transfer by virtue of its low absorption, is in accord with the observed flattened of the tetrahedral structure, which would serve to enhance the effect. The very different spectrum obtained from the relatively insoluble (in C$_2$H$_4$Cl$_2$) complex corresponds with the known difference in structure of this complex. Marked deviations from Beer's Law were found for the acetonitrile solutions of both compounds. This effect was more pronounced in the latter case. The effect of adding free ligand to the solutions was to partially restore the spectrum of the btz complex, while even large excesses of bt failed to produce measurable spectra. This behaviour precludes worthwhile n.m.r studies since several species are likely to be present in solution.

Using the infrared electronic spectral criteria established by comparison of [Cu$_2$(bt)$_4$]$^{2+}$ and [Cu(btz)$_2$]$^+$, structures can be proposed for the remaining complexes.
Proposed Structure of [Cu(btz)I]₂

For [Cu(btz)I]₂ the structure in, Fig.95, is proposed, on the basis that (a) btz has always, even with Cu (I), has been observed to coordinate in the N₂, α-di-imine fashion; (b) the Cu (I) ion most frequently occurs in a tetrahedral environment; (c) the electronic spectrum of the complex is similar to that of [Cu(btz)₂] [BPh₄]; (d) large i.r coordination shifts support this view. The ν(C=N) splitting may represent either some distortion of the ligand or low solid state symmetry for the complex.

The stoichiometries and physical properties of [(CuI)₂L]ₙ (L = bo; bt) suggest equivalent structures for these complexes. Splitting ν(C=N) in the i.r would be consistent with the trans configuration of the ligands which the X-ray crystal structure of [Cu₂(bt)₄]²⁺ has shown to be possible. Coordination shifts are in any case smaller for these complexes than in [Cu₂(bt)₄]²⁺ but in all cases there is a virtually unshifted component of ν(C=N). Presumably the small shifts, 20-30 cm⁻¹ only result from restricted delocalization and tie-up with the higher energy charge-transfer bands. The unshifted band may indicate non-chelation, while the low solubility of the complexes suggest polymerization. On this evidence it is impossible to go beyond proposing some type of trans polymeric structure.

The structure of [Cu(bo)₂][ClO₄] is thought to be similar to that of [Cu(btz)₂][BPh₄] given the correspondence of the data in, Table XXXV.
The Cu (II) Complexes of biz and bi

The complexes prepared are listed in Table XXXVI. The yellow Cu (I) complexes proved too oxygen sensitive to handle. For the Cu (II) complexes magnetic and e.s.r data, as collated in Table XXXVII, are all normal but are structurally uninformative. The conductivities obtained in all cases suggest 1:2 electrolytes, making allowance for the lower values obtained for complexes containing the relatively bulky BPh₄⁻ anion.

Depending on the preparation, two different solid state isomers of [Cu(bi)₂][ClO₄]₂ have been found; form (B) the blue isomer and form (P) the purple isomer. Both forms are interconvertible by the methods described in the experimental section. The differences between (B) and (P) are quantitatively expressed in the solid state (mull) electronic spectra and i.r. spectra. Complex (B) exhibits a strong, broad band with maximum at 16,900 cm⁻¹ while complex (P) displays its maximum d-d absorption at 17,600 cm⁻¹. Both are consistent with tetragonal Cu (II). The fact that the complexes give new and identical electronic spectra in acetonitrile solution serves to illustrate that the differences originate in the solid-state structure.

The differences are most noticeable in the i.r. spectra of the complexes. Figs.96,97. (B) contains a very broad v(N - H) extending from 3.400 to 2,500 cm⁻¹ and centred at 3145 cm⁻¹. A sharp, medium intensity band appears 'growing' out of this 'background' at 3365 cm⁻¹. The perchlorate v₄ absorption is split into three medium intensity signals at 640, 630 and
TABLE XXXVI
MAGNETIC AND ESR DATA FOR THE COPPER (II) COMPLEX OF biz and bi

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$\mu_{\text{eff}}$ 293</th>
<th>93</th>
<th>ESR $^a$</th>
<th>$^b$</th>
<th>$^c$</th>
<th>$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[Cu(biz)$_2$][ClO}_4^-$]$_2$</td>
<td>1.82 1.82</td>
<td></td>
<td>2.11$^c$</td>
<td>2.24$^c$</td>
<td>172$^c$</td>
<td></td>
</tr>
<tr>
<td>$\text{[Cu(biz)$_2$][BPh}_4^-$]$_2$</td>
<td>1.91 1.89</td>
<td></td>
<td>[2.07$^b$]</td>
<td>2.29$^b$</td>
<td>[180$^b$]</td>
<td></td>
</tr>
<tr>
<td>$\text{[Cu(bi)$_2$][ClO}_4^-$]$_2$(P)</td>
<td>1.98 1.89</td>
<td></td>
<td>2.06$^c$</td>
<td>2.24$^c$</td>
<td>173$^c$</td>
<td></td>
</tr>
<tr>
<td>$\text{[Cu(bi)$_2$][ClO}_4^-$]$_2$(B)</td>
<td>2.11 1.91</td>
<td></td>
<td>2.06$^c$</td>
<td>2.24$^c$</td>
<td>180$^c$</td>
<td></td>
</tr>
<tr>
<td>$\text{[Cu(bi)$_2$][BPh}_4^-$]$_2$</td>
<td>2.10 1.98</td>
<td></td>
<td>[2.05$^b$]</td>
<td>2.29$^b$</td>
<td>200$^b$</td>
<td></td>
</tr>
<tr>
<td>$\text{[Cu(bi)$_2$(MeCN)$_2$][BPh}_4^-$]$_2$</td>
<td>2.18 1.95</td>
<td></td>
<td>[2.07$^c$]</td>
<td>2.24$^c$</td>
<td>180$^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ moments in B.M. per mole.

$^b$ solid state.

$^c$ D.M.F. glass.

$^d$moments in B.M. per mole.

625 cm$^{-1}$, suggesting coordination of the anion.

The i.r. of complex (P), in contrast to (B), contains a single sharp $v_{(N-H)}$ absorption at 3325 cm$^{-1}$, while splitting of $v_3$ and $v_4$ perchlorate frequencies is apparent, although not to the same complicated extent as occurs in (B).

In the absence of crystal structures all that can be said at this stage is that two solid state isomers exist differing in coordination geometry around Cu (II) and in H-bonding from the ligand NH.

The green complexes $\text{[Cu(bi)$_2$][BPh}_4^-$]$_2$ and $\text{[Cu(bi)$_2$][BPh}_4^-$]$_2$·2MeCN are somewhat anomalous. If a tetragonal arrangement exists in these compounds then the expected colour would be blue or purple as previously.

$\text{[Cu(bi)$_2$][BPh}_4^-$]$_2$ differs only in counterion to (B) or (P). The green colours
### TABLE XXXVII

**PHYSICAL DATA FOR THE COPPER (II) COMPLEXES OF biz and bi**

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>COLOUR</th>
<th>$\Lambda_M^a$ (Scm mol$^{-1}$)</th>
<th>ELECTRONIC SPECTRA $^b$</th>
<th>INFRARED DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MULL</td>
<td>MeCN SOLUTION</td>
<td>$\nu$(C = N)</td>
</tr>
<tr>
<td>[Cu(biz)$_2$][ClO$_4$]$_2$</td>
<td>prussian-blue</td>
<td>320</td>
<td>16.600</td>
<td>15,000(170)</td>
</tr>
<tr>
<td>[Cu(biz)$_2$][BPh$_4$]$_2$</td>
<td>grey-blue</td>
<td>267</td>
<td>16.600</td>
<td>15,000(170)</td>
</tr>
<tr>
<td>[Cu(bi)$_2$][ClO$_4$]$_2$(P)</td>
<td>purple</td>
<td>352</td>
<td>17,600</td>
<td>15,600(80)</td>
</tr>
<tr>
<td>[Cu(bi)$_2$][ClO$_4$]$_2$(B)</td>
<td>blue</td>
<td>352</td>
<td>16,900</td>
<td>15,600(80)</td>
</tr>
<tr>
<td>[Cu(bi)$_2$][BPh$_4$]$_2$</td>
<td>pastel green</td>
<td>284</td>
<td>16,400</td>
<td>15,600(80)</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BMeCN%7D$">Cu(bi)$_2$</a>$_2$[BPh$_4$]$_2$</td>
<td>dark green</td>
<td>284</td>
<td>18,600(sh)</td>
<td>15,600(80)</td>
</tr>
</tbody>
</table>

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$^a$ $10^{-3}$M in acetonitrile at 20$^\circ$C; $^b$ frequency in cm$^{-1}$, $\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$; in parenthesis.
suggest some type of interaction with the Cu (II) ion which absorbs blue light in addition the the normal d-d absorptions thereby making the complexes appear green. This raises the question of whether or not some type of tetraphenylborate interaction is present of the type reported by Floricni et al. However further rationalization is beyond the available evidence.

The two biz complexes \([\text{Cu(biz)}_2][\text{BPh}_4]_2\) and \([\text{Cu(biz)}_2][\text{ClO}_4]_2\), both behave in a more expected manner. All physical data are consistent with the existence of Cu (II) in a square-planar environment in both complexes. There is no sign of coordination where perchlorate is the counterion, nor of any tetraphenylborate interaction causing green complexes.

The biz complexes have unusually high \((X2)\) extinction coefficients when compared with their counterparts. This discrepancy may be explained if distortions from square-planar towards tetrahedral symmetry were to occur in these complexes. Such a suggestion would seem reasonable since in the ideal square-plane the protons \(\alpha-\) to the imine group would be close to the \(\alpha-\)protons of the second biz ligand. This effect would be expected to be more pronounced for the larger 6-membered ring biz than it would be for bi - thus the more intense signals. Distortions of this sort, towards tetrahedral introduce p-character to the d-orbitals allow slight relaxations of the Laporte selection rules for d-d transitions.

The e.s.r data, Table XXXVI, at first sight, appears quite normal for tetragonal mononuclear Cu (II) however there does exist, surprisingly, a 7-line \(M = 2\) signal in the D.M.F. glasses of all the complexes. This would be possible if there was some sort of aggregation of the mononuclear moieties, held together by weak interactions of the uncoordinated \(>\text{NH}\) of the ligand with neighbouring mononuclear species; this interaction being too weak to affect the magnetic measurements. Closer examination of the \(g_\perp\) signal reveals (though lost on the reduction in Fig.97a) at least twelve superhyptine lines attributable to superimposition of the Cu (II) and nitrogen hyperfine patterns \((A_\perp \sim 15 \text{ G})\).
FIG 97a: ESR SPECTRA OF [Cu(bi)$_2$][ClO$_4$]$_2$ (P)
Oxidation Studies of a Binuclear Copper (I) Complex

The binuclear Cu (I) complex used herein was prepared and characterized as described by Dr. V. McKee and isolated as a yellow diamagnetic solid with formula Cu₂(MeRV)(ClO₄)₂. Previous studies have shown that each mol. of binuclear macrocycle consumed 3 moles. of O₂ irreversibly in oxidizing to a green product. However, uptake of the first mol. of O₂ was accompanied by development of an absorption band at 15,300 cm⁻¹ (ε ca 2550 dm³ mol⁻¹ cm⁻¹) which did not intensify on further oxidation and was consistent with the formation of a μ-peroxo-di-Cu (II) species. Fig. 98. Subsequent consumption of 2 moles. of O₂ was traced to beyond oxidation.

Although reversible O₂ binding was not found in this case other transition metals have been known to behave as oxygen carriers. Busch's Laccunar Fe and Co complexes were mentioned earlier; McAuliffe et al. have reported Mn (II)/phosphine systems which will reversibly bind O₂. Recent independent work has served to confirm this behaviour.

It would be useful if the ligand oxidation could be circumvented and the oxidizing potential redirected towards the substrate in a catalytic manner. To this end the system was supplied with oxidisable substrates eg catechols, substituted phenols and thiols.

MeRV:

![Diagram of MeRV molecule]

Fig. 98
The reactions were followed by \( \text{O}_2 \) uptake in DMF solution at 30\( ^\circ \text{C} \) under one atmosphere of \( \text{O}_2 \). (Using equipment described in the appendix). The DMF was dried over \( \text{CuSO}_4 \) and distilled under vacuum at 30-40\( ^\circ \text{C} \). The types of oxidations observed are illustrated in Fig. 99, and the results are summarized in Table XXXVII.

The irreversible consumption of 0.92 and 0.90 moles of \( \text{O}_2 \) per \([\text{Cu}_2(\text{MeRV})] (\text{ClO}_4)_2\) required several minutes for completion. In the absence of added substrate this result prompts comparisons to the 1:1 \( \text{O}_2:\text{Cu}_2 \) stoichiometries found for haemocyanin and tyrosinase, the suggestion being that each \( \text{O}_2 \) molecule is associated, intramolecularly with the two copper ions in each macrocycle. This is in contrast to the 0.5:1, \( \text{O}_2:\text{Cu}_2 \) stoichiometry for the same reaction with the smaller macrocycles \( Q \) and \( L \) where short-lived bimolecular intermediates are proposed in a process which generates a \( \mu \)-oxo-bridged \( \text{Cu} \) (II) species.

**Oxidation of substrate**

3,5-di-tert-butylcatechol (3,5-DTBC), 2,6-di-tert-butylphenol (2,6-DTBP), 2,4-di-tert-butylphenol (2,4-DTBP), thiophenol (PhSH) and ascorbic acid were studied.

3,5-DTBC and 2,6-DTBP are oxidized to the corresponding diquinones. Evidence for this was gained by the isolation of red crystalline product from the catalytic reaction mixtures. The solution containing 3,5-DTBC gave a material with the following physical properties: \( \lambda_{\text{max}} = 25,000 \text{ cm}^{-1} \) (in DMF) m. pt. = 111\( ^\circ \text{C} \); mass spectrum m/e = 220; i.r. 3058(m), 2957(s), 1658(m), 1242(m), 890(m); \( ^1\text{H} \) n.m.r. (ppm) 1.23(s), 1.28(s), 7.23(s). Characterization was confirmed by preparation of 3,5-di-tert-butylquinone (3,5-DTBQ) by an alternative route; namely oxidation of catechol with \( \text{Ag}_2\text{O} \). The properties of this sample were identical to the former.

The experimentally obtained value of ca 0.85 moles \( \text{O}_2 \) per mole. 3,5-DTBC is not that expected (0.5) if the reaction were solely oxidation.
\[
(1) \quad \text{substrate} \quad + \quad \frac{1}{2} \text{O}_2 \quad \rightarrow \quad \text{product} \quad + \quad \text{H}_2\text{O}
\]

\[
(2) \quad 2 \quad \text{substrate} \quad + \quad \text{O}_2 \quad \rightarrow \quad \text{product} \quad + \quad 2\text{H}_2\text{O}
\]

\[
(3) \quad \text{PhSH} \quad + \quad \frac{1}{2} \text{O}_2 \quad \rightarrow \quad \text{product} \quad + \quad \text{H}_2\text{O}
\]

**Fig. 99**

**TABLE XXXVII**

<table>
<thead>
<tr>
<th>SUBSTRATE</th>
<th>O(_2) : SUBSTRATE</th>
<th>SUBSTRATE : Cu(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,5-Di-tert-butylcatechol</td>
<td>0.88, 0.86, 0.83, 0.80</td>
<td>15, 13, 19, 19</td>
</tr>
<tr>
<td>2,6-Di-tert-butylphenol</td>
<td>0.3</td>
<td>18</td>
</tr>
<tr>
<td>2,4-Di-tert-butylphenol</td>
<td>0.13</td>
<td>21</td>
</tr>
<tr>
<td>PhSH</td>
<td>0.25</td>
<td>167</td>
</tr>
<tr>
<td>PhC ≡ CH</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>Ascorbic Acid</td>
<td>a</td>
<td></td>
</tr>
</tbody>
</table>

a Cu/MeRV Ineffective as catalyst.
to 3,5-DTBQ. This suggests that a mixture of coupled and polymeric products may have been obtained. This is the situation described in Chapter 1.

The value of 0.3 moles. O\textsubscript{2} obtained for the 2,6-DTBP experiment is less than the theoretical value of 0.5 mole O\textsubscript{2} required for its oxidation. The stoichiometry suggests competing oxidations which require consumption of less than 0.5 moles of O\textsubscript{2} per mole substrate. In this case the red crystalline needles isolated have an i.r. spectrum: 3000(w), 2958(m), 1602(s), 1360(r), 1090(m), 899(m) - consistent with the proposal that the product is the quinone of Fig. 99.

2,4-DTBP was studied in the hope that it would be possible to follow an oxidation through to the same 3,5-DTBQ, already established as the major product of the oxidation of 3,5-DTBC. This reaction would have involved oxygen incorporation but in the event the reaction proved non-catalytic and only small quantities (0.13 mole.) O\textsubscript{2} were consumed. Non-catalytic activity was also confirmed with the substrates phenylacetylene and ascorbic acid.

The thiophenol experiment produced the exact ratio of 0.25 moles. O\textsubscript{2} per mole. PhSH required for the coupling reaction shown (3) - Fig. 99. Although no product was isolated in this case, a similar experiment using Cu\textsubscript{2}(RN)(BPh\textsubscript{4})\textsubscript{2}, where RN, as can be seen from Fig. 100, is very similar to MeRV. The product was characterized by mass spectroscopy; m/e = 218, m.p.t. = 57\textdegree C, chemical analysis: 65.4\% C, 4.7\% H and i.r.: 3062(w), 3045(w), 1570(s), 1470(m), 1435(m), 1070(m), 987(m), 740(s), 688(s), 463(m)

\[ \nu s-s = 450-500 \text{ cm}^{-1} \]

\[ \nu s \]

Fig. 100
Work in this laboratory by Dr A. Lavery using Cu(ClO₄)₂·6H₂O in DMF on these substrates has shown that this salt will catalyse the oxidation of 3,5-DTBC in ca 15 mins with consumption of ca 0.5 moles of O₂ per substrate molecule, while oxidation of 2,6-DTBP is extremely slow and that of thiophenol undetectable. Thus while oxidation of 3,5-DTBC may be as efficient as that of Cu₂(MeRV)(ClO₄)₂, the MeRV complex is much more efficient at catalysing 2,6-DTBP and thiophenol as in reactions 2 and 3 of Fig. 99. This presumably demonstrates the importance of inherent binuclearity.

Fig. 101
While the mechanism of catechol oxidation remains uncertain, possible routes have been suggested by Ochai and Solomon, Fig. 101.

Similar studies in acetonitrile solvent showed a repressed activity. Acetonitrile acts like a poison, probably because it is capable of coordinating to the diCu (I) species thus stabilizing it and occupying sites otherwise reserved for incoming substrate. It was for these reasons that DMF was the favoured reaction medium. In addition this solvent affords high solubility of both substrate and catalyst.
General Conclusions

The major objectives as perceived at the outset of this work were:

(1) to synthesize and structurally characterize potentially binucleating macrocycles;

(2) to prepare the transition metal complexes;

(3) to look at the binding of small molecules and ions as bridges;

(4) to observe and rationalize any magnetic interactions and

(5) to study the possibility of activation of bridging ligand to reaction with other available substrates.

To a large extent these objectives have been achieved.

In a macrocyclic complex, the coordination requirements of the metal ion may dictate ligand conformation or alternatively the steric properties of the ligand may enforce unusual coordination geometries upon the metal ion. Complexes of the series of ligands L (Chapter 1) nicely illustrate these effects. The ligands 33N and 33NMe and to a lesser extent P and H, being large and flexible form complexes of the first category. Thus the 28-membered 33N and 33NMe and 26 and 24-membered H and P macrocycles will form binuclear complexes with the relatively small transition metal ions and the intermediate-sized Pb (II) (33N, 33NMe, P, H) and Ag (I) (33N, 33NMe) ions. The macrocycles 33N and 33NMe are more versatile by virtue of their larger ring-size and in the presence of an amino functional group. The increased flexibility of the larger ring allows 33NMe to form the mononuclear Co (II), Ni (II) and Fe (II) the amino functional group permits 33N to accommodate the larger group (II) metal ions Ca (II) and Sr (II) by a ring contraction mechanism, involving addition of one >NH across the adjacent imine bond, to adapt the macrocyclic cavity to the size of these particular metal ions.
The macrocycle Q and the acyclic J and EDAAF belong to different family of Schiff-base ligands. Nevertheless their binucleating potential (in and east-west relationship) has been realized with Cu (I) (Q,J), Cu (II) (Q,J), Ag (I) (Q) and Pd (II) (EDAAF). There is some indication of strain in the di-Cu (II) complexes of Q which will readily open to form a mononuclear species - ligand-controlled chemistry. However the importance of metal-ion control is also demonstrated in this system by formation of the 3/4-macrocyclic Sr (II) and Ca (II) products and by the fact that a binuclear entity such as \([\text{Cu}_2(\text{OMe})_2(\text{py})_2]^{2+}\) is capable of holding the macrocyclic structure intact, albeit only in the solid state, despite the ligand-controlled tendency to form ring-opened products.

The heterocyclic ligands display a chemistry which is mainly determined by the nature of Cu ion centre. In this way Cu (I) chemistry is prevalent in the S-containing ligands btz and bt while Cu (II) chemistry applies to bi and biz. The severely distorted \([\text{Cu} \text{(btz)}_2]^{+}\) structure and the unexpected binuclear structure \([\text{Cu}_2(\text{bt})_4]^{2+}\) are traced to preference of the Cu (I) metal centre for geometries approaching tetrahedral.

In a great many bimetallic complexes the metal ions share a common bridging donor e.g. NCS\(^-\) which controls the distance between the metals. For 33N and 33NMe no evidence was found to indicate this using thiocyanate. The distances of \(\gamma R\) observed for the extended macrocycles could accommodate a lengthwise thiocyanate bridge between the metals were there is no steric constraints in the macrocycle. However, NCS\(^-\) is prevented from functioning as an 'equatorial' bridge by the presence of four macrocyclic N-donors arranged around each metal in approximate planar geometry. Thiocyanate appears to function only as an 'axial' bridge producing the dimeric tetranuclear assemblies \([\text{Co}_4 \text{L} \text{(NCS)}_2]^{6+}\) (L = 33N, 33NMe).
There are available 'equatorial' sites in the ligands H, P and J and here at least four and possibly five fundamental terminal and bridging modes of NCS⁻ have been found, including the rare N-only bridging mode of NCS⁻ in some di-Pb (II) complexes of the macrocycles P and H. A direct correlation is apparent between this bonding mode and the occurrence in the i.r of $\nu_{as}(\text{NCS}) < 2000 \text{ cm}^{-1}$.

The observation of $\nu_{as}(\text{NCS})$ below 2000 cm⁻¹ in $[\text{Cu}_2(33N-2H)(\text{HNCS})_2]^2^+$ was assigned, on the basis of X-ray structural data, to the presence of coordinated thiocyanic acid and not to N-only bridging NCS⁻. The complex is the first of its type.

Metal-ion control of the mode of coordination is evident in the structure of the heterobinuclear $[\text{PbMnP(NCS)}_4]$ where the S-donors of both the 3-atom bridging thiocyanates are directed towards Pb (II) while the N-donors are both directed towards Mn (II).

The di-Cu (II) complexes of 33N, 33NMe and P, Q and J exhibit a wide range of antiferromagnetic coupling $2 J \approx -20$ and $-700 \text{ cm}^{-1}$. The weak antiferromagnetic behaviour of 33N, 33NMe and P are consistent with the known (from X-ray) large metal ... metal separations. Interactions are of a dipolar nature through space in the former and through the 3-atom bridging NCS⁻ in the latter. On the basis of zero-splitting in e.s.r (33N: $D = 30$ G; P: $D = 79$ G) P displays the larger interaction as expected for the smaller ring size.

When bridging occurs through single atom such as OMe⁻, the observed coupling is higher and demonstrably so in the case of the e.s.r silent $[\text{Cu}_2\text{Q(OMe)}_2(\text{py})_2][\text{ClO}_4]_2\cdot 2\text{H}_2\text{O}$.

The Cu (I) complexes obtained in the course of the above studies proved inadequate for use as organic oxidation catalysts. $[(\text{CuI})_4\text{J}]$ and $[\text{Cu}_2\text{J(NCS)}_2]$ proved too insoluble and in any case the presence of coordinating anions serves to block access to labile Cu (I) active sites.
[Cu(btz)$_2$][BPh$_4$] and [Cu$_2$(bt)$_4$][ClO$_4$]$_2$ are too labile at low concentration for CO studies and too stable for O$_2$ studies. The activity of the complex [Cu$_2$(MeR)-V][ClO$_4$]$_2$ in the oxidation of substrates such as substituted catechols, phenols and thiols has demonstrated the importance of the built-in binuclear site. The recently prepared [Cu$_2$Q][ClO$_4$]$_2$·3H$_2$O also shows some promise in CO and O$_2$ activation. Its irreversible O$_2$ and reversible CO activity has been highlighted in Chapter 3. There is scope here for further development particularly as to the nature of CO binding (terminal or bridging) and the possibility of oxidation of organic substrates.
Appendix

Infrared spectra were recorded in the range 400-200 cm\(^{-1}\) as KBr discs or nujol mulls using a Perkin-Elmer 577 or 598 grating spectrometer. Electronic spectra were recorded using Pye-Unicam SP 700, SP8000 or Perkin-Elmer 402 spectrometers. The solid state spectra were recorded on the SP700 instrument and are the transmittance spectra of nujol mulls.

A conductivity cell with a cell constant 0.0352, constructed from bright platinum electrodes, in conjunction with a conventional resistance/capacitance bridge was used for electrical conductance measurements.

\[ K = \frac{0.0352}{R} \] (where R = resistance reading)

\[ K_{corr} = K - K_s \quad (K_s = \frac{0.0352}{\text{resistance of MeCN}}) \]

Molar conductivity \[ \Lambda_M = 1000K_{corr}/c \] (where c = molar concentration)

Ranges in MeCN:

1:1 electrolyte \[ 120-160 \ \Omega^{-1}\text{cm mol}^{-1} \] (92-199)
1:2 electrolyte \[ 220-300 \] " (145-336)
1:3 electrolyte \[ 340-420 \] " (variable)

Mass spectra were recorded using either the A.EI. Ms902 mass spectrometers, at an ionizing voltage of 70eV. \(^1\)H N.M.R spectra were measured using a Joel JNP-PM X 60 MHz or a Bruker WH90 or a Bruker WM250 MHz Fourier transform N.M.R spectrometer. The \(^13\)C N.M.R spectra were recorded on Bruker WH 22.6 MHz or Bruker WM 62.9 MHz spectrometers.

Magnetic measurements were carried out by the Gouy method using Newport Instruments variable temperature (93-300K) magnetic balance. E.s.r spectra were obtained as undiluted powders or as frozen solutions, using a Varian E9 instrument.

Mossbauer spectra were recorded at room temperature using a Harwell constant acceleration spectrometer and a \(^{57}\)Co in Pd source. The equipment was calibrated with an iron foil standard at 293K. Absorber thickness were not more than 50 mg. cm\(^{-2}\). Isomer shifts and quadrupole splittings were determined by visual inspection to + 0.02 mm s\(^{-1}\).
**Intramolecular Antiferromagnetism**

Magnetically dilute Cu (II) complexes have effective magnetic moments in the range 1.75 to 2.20 BM regardless of stereochemistry and virtually independent of temperature.

For binuclear Cu (II) complexes (excluding M-M bonding) there exists the possibility of a magnetic interaction between the two paramagnetic centres. This interaction may be of a dipolar nature through space, in which case the interaction is small. Alternatively, a bridging ligand may provide a superexchange pathway. Antiferromagnetic coupling has the effect of lowering the energy gap (2J) between the diamagnetic singlet and paramagnetic triplet states, where 2J is the exchange integral defined by the Hamiltonian operator \( \hat{H} = -2JS_1 S_2 \). \( S_1 \) and \( S_2 \) are the spins of the two coupling nuclei. \( J \) is negative for antiferromagnetic and positive for ferromagnetic coupling. Fig.A, shows how magnetic susceptibility varies with temperature as a function of \(-J \chi A\) is calculated from the Bleaney Bowers equation as shown.

The extent of the exchange interaction between the two coupled Cu (II) centres depends largely on the magnitude of the overlap between the magnetic orbitals. Studies on di-\( \mu \)-hydroxo bridged Cu (II) complexes have shown a linear correlation between 2J and \( \phi \), the bridging angle, Fig.B. Note that when \( \phi = 97.6^\circ \) \( J = 0 \) and that \( \phi \) can cause ferromagnetic(F) or antiferromagnetic coupling: (F) \( 97.6 < \phi < 97.6 \) (AF).

**E.S.R.**

In the electron spin resonance experiment (e.s.r) unpaired electrons will normally 'line-up' along the direction (z) of an applied field (H) and this lifts the degeneracy of the \( \pm 1/2 \) spin states of the electron (Zeeman Effect). The energy difference between these two states (microwave for e.s.r) is proportional to the applied field. Thus

\[ \Delta E = h\nu = g\beta H \]
Fig. A

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

\( \mu_{\text{eff}} = 2.84 (\chi_A \cdot T)^{\frac{1}{2}} \)

Fig. B

PLOT OF \( 2J \) versus \( \phi \)
Hypothetical, isotropic hyperfine coupling for mono, [C], and binuclear Cu (II), [D], without zero-field splitting.
Typical first derivative e.s.r. spectrum for 1 pair weakly interacting $S = \frac{1}{2}$ complexes having $I = 0$ and $g_\parallel < g_\perp$.

**FIG E**

Idealized energy level scheme and e.s.r. spectrum for two interacting $S = \frac{1}{2}$ systems – showing zero-field splitting and exchange coupling.
g is the gyromagnetic ratio and \( g \) the Bohr Magneton. If the electron spin is the only source of magnetism then \( g_e = 2.0023 \). The \( g \) value is a unique property of the molecule as a whole and is independent of any hyperfine interactions (see below) that may be present. If however the electron is associated with a nucleus possessing spin the Nuclear Zeeman Effect provides various nuclear spin states for the electron to couple to; selection rules for transition are \( \Delta M_s = \pm 1 \) and \( \Delta M_I = 0 \). Thus mononuclear Cu (II) will show four equally intense lines, Fig.C. When the electron can see two equivalent nuclei - as in magnetically coupled Cu (II) dimers seven lines become possible with intensity ratios 1:2:3:4:3:2:1, (Fig.D). In general \( 2nI + 1 \) transitions occur (\( n = \) number of equivalent nuclei) and the intensity ratios are given by the coefficients of the binomial expansion of \( (1 + X)^n \). These patterns are referred to as hyperfine structure and their separations as the hyperfine coupling constant, \( A \). Since in the dimer, the electron spends only half its time on a given nucleus, the hyperfine constant is usually half that of a corresponding magnetically dilute mononuclear Cu (II).

The unpaired electron in Cu (II) resides a d-orbital, where there is formally no electron density at the nucleus. Any interaction with the nucleus is via spin polarization mechanisms and is therefore small. The hyperfine will also be anisotropic and may be resolved into three unique directions \( \hat{x}, \hat{y} \) and \( \hat{z} \). In solution random tumbling averages \( A_{\text{aniso}} \) to zero so only \( A_{\text{iso}} \) (isotropic) is observed, Fig.D. In solids or frozen solutions \( g_{||} \) and \( g_{\perp} \) signals are obtained. Since in a situation of axial symmetry the \( \perp \) axes are doubly degenerate the probability of transition is twice that in \( || \) hence the observed greater (\( \sim X 2 \)) intensity of the \( g_{\perp} \) signal. Hyperfine structure is usually resolved for \( g_{||} (A_{||}) \) and not for \( g_{\perp} (A_{\perp}) \). John-Teller distortion in tetragonal or square-
planar Cu (II) leads to $d_{z^2}$ stabilization and the unpaired electron resides in the $d_{x^2-y^2}$ orbital. In such cases $g_{||} > g_{\perp} > 2$. Less commonly, the $d_{z^2}$ ground state is found in trigonal bipyramidal and pentagonal bipyramidal Cu (II) in which case $g_{\perp} > g_{||} \approx 2$.

Where there is appreciable interaction between metals this leads to zero-field splitting $D$, Fig.E,F. This is usually quite anisotropic and will result in splitting of the 11 and 1 (at least) into two pairs of signals, (Fig.F). As a result of interaction several transition arise of which (i) (ii) and (v) are forbidden. Transition (ii) refers to a $\Delta M_S = 2, g = 4$ process. This 'half-band' signal as it is known can usually be resolved into its 7-line pattern. Transitions (i) and (v) correspond to direct singlet - triplet transitions, observation of these is very rare.

Sometimes hyperfine coupling to 'in-plane' ligand nuclei occurs. For a square-planar complex e.g. Cu phthalocyianin all four nitrogens are equivalent and show their maximum coupling along the $x, y$ (1) directions. The empirical $2nI + 1$ formula will again give the number of lines. Hyperfine constants are smaller than metal-electron interactions and the pattern is usually seen superimposed onto the main signal (superhyperfine).

**Measurement of the gas-uptake**

The gas-uptakes for O$_2$ and CO were monitored by the pressure change ($\Delta P$) in a thermostatted reaction vessel with a volume of 18.97 ml. and containing 5.10 ml. of the complex solution. The pressure in the reaction vessel was recorded automatically using a standard Langhan-Thompson transducer (type UP4) and referred to a standard reference pressure of $2/3$ atmospheres.
The equilibrium constant for the gas in the reaction vessel with the solvent is given by,

$$K_{\text{solvent}} = \left[ \frac{(V_{\text{tot}} - V_1)}{V_1} \right] \left[ \frac{(\Delta P)}{P_i - \Delta P} \right]$$

where $V_{\text{tot}}$ = total volume of the reaction vessel and the transducer, $V_1$ = volume of solvent and $P_i$ = initial gas pressure in the reaction vessel.

No. of moles of gas consumed = $$\frac{\Delta P}{6.321 \times 10^4} \left[ \frac{(V_{\text{R.V.}} - V_1)}{T_{\text{R.V.}}} + \frac{2.22 + \frac{K V_1}{T_{\text{Room}}}}{T_{\text{R.V.}}} \right]$$

where $T_{\text{R.V.}}$ is the temperature in the reaction vessel, and $V_{\text{R.V.}}$ is the volume of the glass reaction vessel. The catalytic oxidations were carried out in a larger reaction vessel of total volume 36.2 ml. and a solvent volume of $\sim$ 10 ml.
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