REACTIONS OF MULTIDENTATE-LIGAND COPPER(I) COMPLEXES WITH DIOXYGEN

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Lastly, I thank Henriette Wymar for typing this thesis, and whoever left this poem in the Caltech computer:

CATSUP BOTTLE,
CATSUP BOTTLE,
NONE'LL COME
AND THEN A LOT'LL.

O. NASH
END X-RAY

Reactions of Multidentate-Ligand Copper(I) Complexes with Dioxygen

Abstract:

Syntheses, isolation, and characterization of several copper(I) complexes with multidentate ligands (including macrocycles), and their reactions with dioxygen are reported. A binuclear dioxygen complex was obtained from 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxo-cyclotetradeca-3,5,10,12-tetraenato copper(I) in dichloromethane solution at -79° C. In the absence of excess dioxygen up to 40% of regenerated copper(I) has been observed upon warming. At room temperature the stoichiometry O_2/Cu is greater than 1.0 and increases with solvent basicity. At large triphenylphosphine to copper ratios the uptake is decreased and at low ratios the uptake is enhanced. The macrocyclic complex 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene copper(I) perchlorate in the solid state or in dichloromethane solution at -79° C is ketonated in either of two positions. The 3,5,7,7,10,12,14,14-octamethyl derivative is ketonated in only one position. Similar reactions are observed for the 4,11-diene copper(I) complexes as well as partial oxidative dehydrogenation.

Reactions of Multidentate-Ligand Copper(I) Complexes with Dioxygen

Table of Contents Page

Table of Contents (continued) Page

Table of Contents (continued) Page

Proposals

Chapter One. Introduction

Chapter One. Introduction.

As early as 1880, Bertholet observed that cuprous salts in solution react with atmospheric oxygen.[1]

> A peine filtrées, ces dissolutions se troublent aussitôt, en déposant un précipité... En effet, il résulte de l'absorption de l'oxygène de l'air; il continue à se former tant que la liqueur renferme de chlorure cuivreux.

Of course, biological systems have utilized the interaction of copper with dioxygen for much longer than chemists have studied it. Copper is an essential element for most life forms since copper-containing protein and enzyme systems[2, 3] are prominent in the use and activation of molecular dioxygen.[4, 5]

This chapter will first examine what little is known about the interaction of dioxygen with copper in copper-containing proteins. The results of others' kinetic studies of copper(I) autoxidation follow. These studies indicate copper dioxygen species exist at least as intermediates in small molecules as well. The attempts by chemists to synthesize copper dioxygen complexes are then discussed. These have been a qualified failure, with few systems adequately studied and the oxidized products obtained not well characterized. The more successful syntheses of cobalt(II) and iron(II) dioxygen complexes are then examined. In particular, the strategies used to successfully study dioxygen complexes, such as steric control and low temperatures, as well as choice of solvent and redox potential effects are summarized. Lastly, since macrocyclic ligands will be used and copper(I) is known to activate dioxygen for substrate oxidations, the known macrocyclic ligand oxidation reactions will be discussed. The first chapter is intended to provide the background needed to place the results reported in the following chapters in perspective. Chapter Two will examine our initial studies with multidentate ligands which indicate macrocyclic systems must be used for these labile copper complexes. Chapter Three will report studies of a low temperature, binuclear copper dioxygen complex in solution, as well as ketonation of a macrocyclic ligand by copper dioxygen activation.

Copper-Containing Proteins and Dioxygen

Copper-containing protein and enzyme systems are prominent in the use and activation of molecular dioxygen. In humans copper is the third most abundant metal, after iron and zinc. Cytochrome c oxidase, containing both iron and copper, is vital in the respiratory process in reducing dioxygen to water, and as such is responsible for 90% of the oxygen consumption of the biosphere.[6] In arthropods and molluscs, the oxygen transport protein hemocyanin utilizes copper.[7] The blue copper enzymes laccase, ascorbate oxidase, and ceruloplasmin mediate substrate oxidation coupled with reduction of dioxygen to water.[8,9] The copper-containing amine oxidases and galactose oxidase respectively oxidize primary amines and alcohols to aldehydes, coupled with the reduction of oxygen to peroxide.[9] Tyrosinase and dopamine-β-hydroxylase are monooxygenases which add one of the atoms of dioxygen to their respective substrates.[10] The above important copper proteins have one thing in common; all presumably involve dioxygen coordinated to copper, but little is known about the interaction or even the nature or structure of the copper binding site.

None of the above mentioned copper proteins has been studied crystallographically although plastocyanin[11] (an electron carrier blue copper protein) and superoxide dismutase[12,13] (which contains both copper and zinc) have been examined. Plastocyanin shows imidazole nitrogen coordination from histidine residues as well as the sulfur coordination expected for a blue copper protein. Superoxide dismutase contains copper coordinated to four imidazole nitrogen atoms, one of which is deprotonated and also coordinated to the zinc atom. Coordination of at least some histidine nitrogen atoms as found for these copper proteins is postulated for most of the others on the basis of electron paramagnetic resonance nitrogen superhyperfine splittings as well as titration evidence.

Of special interest are the copper proteins which reversibly bind dioxygen: hemocyanin which functions biologically as an oxygen carrier, and the enzyme tyrosinase which functions biologically to activate oxygen for substrate incorporation. In hemocyanin, subunits of two copper(I) atoms reversibly bind one dioxygen molecule.[6] Oxyhemocyanin is diamagnetic; electron paramagnetic resonance[14] and magnetic measurements[15,16] indicate strong antiferromagnetic coupling between pairs of copper(II) ions. Resonance Raman study of hemocyanin[17-19] shows a new band at 749 cm^{-1} indicating a peroxo complex upon addition of $^{16}O_2$. The band appears at 708 cm^{-1} for $^{18}O_2$. Use of unsymmetrically labeled dioxygen shows both oxygen atoms to be equivalent.[19] A second resonance Raman band at 267 cm^{-1} which does not shift with oxygen isotope labeling is assigned to a copper(II) imidazole vibration.[18] Titration evidence also indicates imidazole coordination.[20] The monooxygenase tyrosinase very likely has a similar coordination environment. Treatment with one hydrogen peroxide per two copper atoms reduces the copper and gives a form which can then reversibly bind oxygen.[21,22] The visible spectrum[21,22] of oxytyrosinase is very similar to that of oxyhemocyanin, as are the electron paramagnetic resonance spectra[23,24] of the nitric oxide derivatives. Additionally tyrosinase shows a two-electron reduction with E = +0.36 V (pH 7.0) for the enzyme but not for the apoenzyme.[25] Note that the similar "soft" nitrogen ligand environments of hemocyanin and tyrosinase give both reversible oxygenation and activation of oxygen for incorporation into substrates. Application of these criteria to the choice of copper(I) complexes studied here has resulted in the use of soft nitrogen imine and pyridine groups to coordinate the metal.

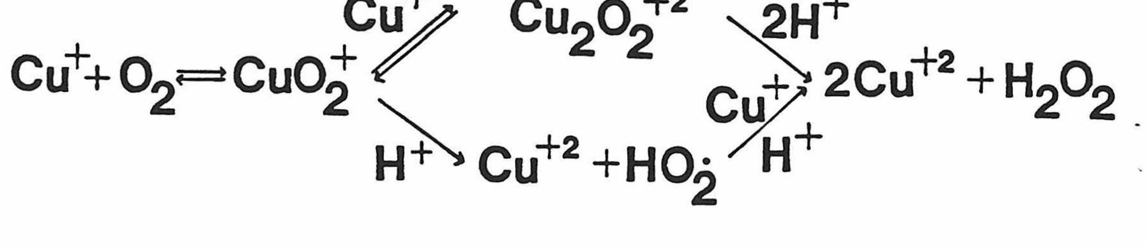
The use of oxygen by the copper proteins shows that given the correct ligand environment, copper dioxygen complexes can be synthesized and specific and useful substrate oxidations can be achieved. Kinetic studies of autoxidation of small molecule copper(I) compounds are examined next. Copper dioxygen complexes exist for these small molecules too, if only as fleeting intermediates.

Kinetic Studies of Copper(I) Autoxidation

Few kinetic studies of the autoxidation of copper(I) complexes in non-aqueous solvents have been carried out. The autoxidation of copper(I) chloride in glacial acetic acid,[26] tetrakis(acetonitrile) copper(I)perchlorate in dimethylsulfoxide,[27] and various substituted copper(I) bis-phenanthroline perchlorate complexes in nitromethane,[28, 29] was studied and all were found to follow the rate law $k[Cu(I)]^2[O_2]$. Such a rate law implies a binuclear transition state, $Cu^+ + O_2 \overset{\text{fast}}{\rightleftharpoons} CuO_2^+ \overset{Cu^+}{\rightleftharpoons} Cu_2O_2^{++} \xrightarrow{\text{fast}}$ products, and the two-electron reduction of O_2 to H_2O_2.

In contrast, most aqueous acetonitrile systems[30-38] follow a rate law $k[Cu(I)][O_2]$. Such a rate law could imply a mononuclear transition state, $Cu^+ + O_2 \rightleftharpoons CuO_2^+ \xrightarrow{\text{fast}}$ products, and the stepwise one-electron reduction of O_2. However, the rate law is equally well accounted for[37] by the binuclear mechanism if a steady state approximation is applied to CuO_2^+ and $k_{-1} \ll k_2[Cu^+]$. The experimental observation of the two-electron oxygen reduction product (H_2O_2) rather than the one-electron reduction product ($HO_2\cdot$) is also inconclusive since the reaction of aqueous Cu(I) with $HO_2\cdot$ is nearly diffusion controlled.[39] The best evidence for the binuclear mechanism in aqueous solution has been obtained with a series of substituted copper(I) imidazole complexes, whose autoxidation kinetics indicate both paths being followed simultaneously.[40, 41] Whether the reduction of O_2 occurs in one- or two-electron steps, the measured reaction stoichiometries are found to be two copper atoms per one dioxygen as shown in scheme I-1.

Scheme I-1



In general, further reactions with H_2O_2 are not observed or are determined to proceed at a much slower rate, and the products in water are not isolated.

Claims of Small Molecule Dioxygen Complexes

Although kinetic data demonstrate the transient formation of dioxygen containing copper complexes, none has been well characterized. Even the oxidized products have not been well characterized in general. For example, addition of dioxane to autoxidized dimethylsulfoxide solutions of tetrakis(acetonitrile) copper(I)tetrafluoroborate is reported to result in a precipitate analyzing (C, H, S, Cu) for an oxo species, $Cu_2O(DMSO)_4(dioxane)(BF_4)_2$, that is stable for several days at room temperature.[42] The only reported clean dioxygen reactions of copper(I) are those of the substituted bis-phenanthroline complexes in nitromethane which yield stable copper(II) coordinated-nitromethanide anion bis-phenanthroline complexes.[43] Published claims of actual non-protein copper dioxygen complexes are based on partially reversible[44,45] or irreversible[46,47] oxygen uptakes and color changes,[48-52] elemental analysis,[46] or changes in the infrared spectrum upon exposure to oxygen.[47,53-55] Both superoxo (1083 cm^{-1}, 1109 cm^{-1})[53,54] and peroxo (856 cm^{-1}, 845 and 885 cm^{-1})[47,55] type complexes have been claimed solely on the basis of new infrared peaks.

The best studied complex is that reported by Wilson (Fig. I-1).[44] Solutions of the complex absorb one dioxygen per two copper atoms in dimethylsulfoxide, acetonitrile, dimethylformamide, pyridine, and 2,6-lutidine. After heating (40° C) and degassing (N_2) the green solution

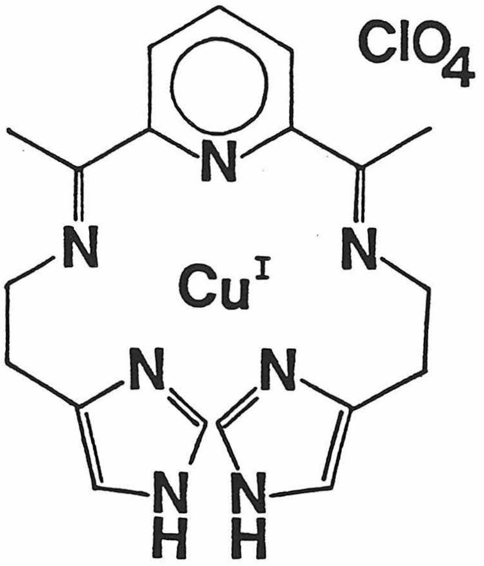


Fig. I-1. Wilson's complex[44]

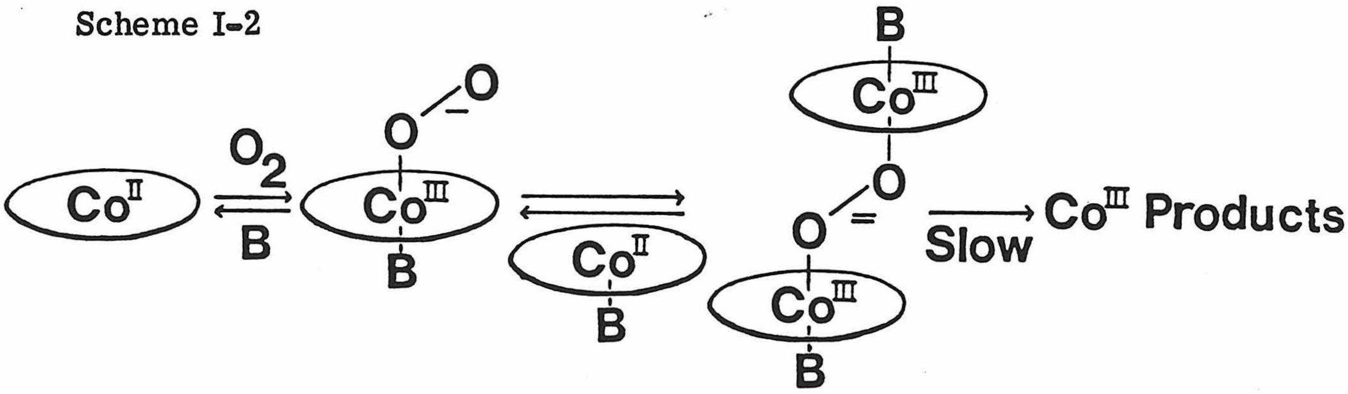
to remove coordinated dioxygen, the complex is capable of reabsorbing 0.8 dioxygen per two copper atoms. Integration of the electron paramagnetic resonance spectrum of the oxygenated solution accounts for only 20% of the available copper and the signal is probably due to the irreversibly oxygenated component. The apparent dioxygen complex is presumably diamagnetic. The red compound in the solid state also absorbs dioxygen and turns green.

In general, metal complexes are often irreversibly oxidized by dioxygen without forming isolable dioxygen complexes. In some cases the metal is oxidized and in others the ligand may be oxidized. Destructive oxidation is also common. In most, if not all, of these reactions peroxo and hydroperoxo intermediates are involved.[56] No small molecule copper dioxygen complex has been isolated as a pure solid. Identification of the products of oxygen reactions with copper(I) complexes, other than that they contain copper(II), has rarely been done successfully. However, cobalt(II) and iron(II) dioxygen complexes have successfully been prepared. Examined next are the kinds of products obtained and the techniques that were successful in studying them.

Dioxygen Complexes of Cobalt(II) and Iron(II)

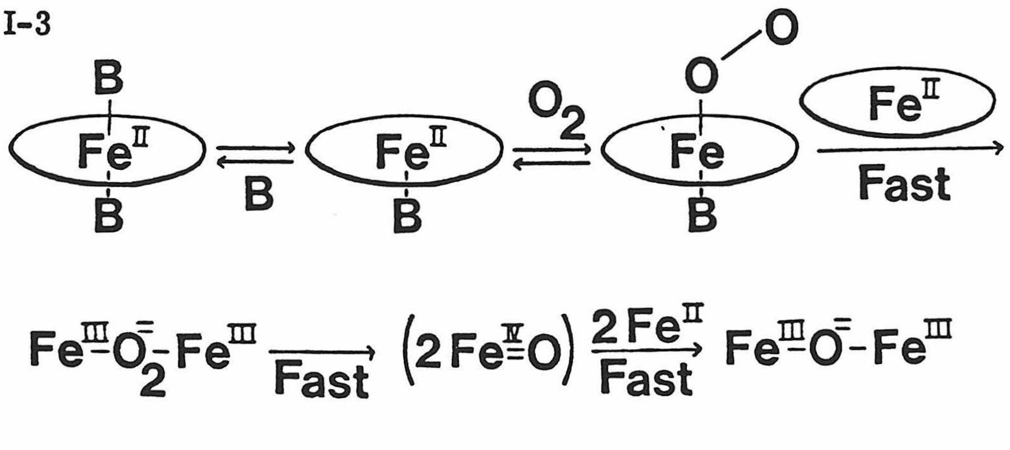
The air oxidation of cobalt(II) to cobalt(III) is often used to synthesize cobalt(III) compounds. By the choice of suitable ligands such as Salen[57, 58] or Acacen[59] and the proper conditions, the intermediate mononuclear peroxo and binuclear superoxo species (Scheme I-2) may be reversibly formed and/or isolated.

Scheme I-2



The air oxidation of iron(II) complexes typically gives irreversible iron(III) μ-oxo species (Scheme I-3). By choice of the proper conditions

Scheme I-3



and/or a suitably modified porphyrin ligand, the reaction can be stopped (or the subsequent steps slowed) at the mononuclear reversible dioxygen complex. Such is the case for hemoglobin and myoglobin.

The "suitable" conditions are of particular interest[60-63] since some of the strategies used to obtain the cobalt and iron dioxygen complexes are applicable to the study of the copper(I) dioxygen interaction. Factors found to be important in previous studies of dioxygen complexes include steric prevention of reaction with a second metal atom as well as temperature, solvent, and redox potential effects.

Strategies for Study of Dioxygen Complexes

One strategy used for the iron complexes is to prevent the approach of a second iron atom. Hemoglobin and myoglobin contain isolated iron(II) porphyrins which cannot readily meet. Such is also true of a 1-(2-phenylethyl)imidazole carbonmonoxy heme complex in a polystyrene film prepared by Wang[64] in 1958. After removal of the CO the material bound dioxygen reversibly. (This experiment has been confirmed more recently).[65, 66] A similar approach used successfully to obtain reversible oxygenation involves preparation of an imidazole modified silica gel to coordinate an iron porphyrin.[67]

To accomplish the same in solution requires some elegant synthetic organic chemistry. Collman's picket fence porphyrins[68-70] and Baldwin's capped porphyrins[71] sterically block one side of the porphyrin to decrease or prevent binding of the axial base to that side. Dioxygen then binds almost exclusively on the bulky side where close approach of a second bulky iron porphyrin is prevented. The mononuclear dioxygen complexes with these modified porphyrins are stable at room temperature in solution for several hours. A non-porphyrin macrocycle utilizing a similar idea also shows increased stability over the non-bulky macrocycle.[72]

A last possible way to prevent dimer formation is by reaction of the solid state complexes with dioxygen. If the metal atoms are far enough apart in the crystalline material, if there is a vacant coordination site, and if the solid is permeable to dioxygen, such a procedure should work. Solid imidazole proto- and mesohemes do combine reversibly with molecular oxygen.[73] Evaporated carbonyl solutions of an iron porphyrin with attached imidazole reversibly bind dioxygen upon removal of the CO.[65] Dioxygen 1-methylimidazole complexes of iron picket fence porphyrin lose dioxygen under vacuum. Upon exposure to oxygen the reaction is reversed.[61,74] While several cobalt(II) Salen complexes react in the solid state reversibly with dioxygen,[57] iron(II) Salen complexes react in the solid state to give the μ-oxo compounds.[75] In applying these steric strategies to copper(I), synthesis of modified polymers and blocking one side of a macrocycle by organic groups were not considered, due to the difficulties in synthesizing plain macrocyclic complexes. Reaction of dioxygen with solid complexes has been investigated, but for most compounds reported here either no reaction occurs in the solid state or the same stoichiometry is determined as in solution at -79°. The solution studies are generally easier since the extent of reaction of the solid is difficult to monitor.

Lowering the temperature has been found to increase the likelihood of obtaining dioxygen adducts. Dioxygen binding to transition metals is generally exothermic, so both enthalpy and entropy effects increase the thermodynamic binding at low temperature. The activation energy for O–O bond cleavage is fairly high, so lower temperatures slow μ-oxo formation. Even for the bis(1-methyl-imidazole)iron(II) complexes of tetraphenylporphyrin[76] and mesoporphyrin IX dimethyl ester,[77] reversible oxygenation has been observed in dichloromethane at low temperature (-79° and -50° respectively). Many other non-hindered axial base iron porphyrin complexes also give reversible dioxygen complexes in various solvents at low temperatures.[78-81] The cobalt(II) Acacen complexes in dimethylformamide give reversible oxygen chemistry at -20° C, but at room temperature a continuous slow uptake of oxygen over a period of days is observed indicating oxidation of the ligand.[59] Use of the low temperature strategy to examine manganese(II) tetraphenylporphyrin complexes has successfully resulted in the observation of reversible manganese dioxygen complexes at -79°.[82-85] Application of the low temperature strategy to copper(I) has proved to be helpful and in one case resulted in stabilization of a binuclear copper-dioxygen complex in solution (see Chapter Three).

To reduce chances of irreversible oxidation, aprotic solvents are usually used and ligands with easily lost protons avoided. Such solvents simulate the hydrophobic environment of the proteins. Although all heme-dioxygen complexes seem more sensitive to oxidation in hydroxylic solvents and in acids than in aprotic media, no thorough study has been made.[86] Protons presumably result in the reaction, $M\text{-}O_2 \xrightarrow{H^+} M(III) + HO_2 \rightarrow$ further products. The presence of easily lost protons on unsubstituted imidazole may be the cause of the much greater stability of the 1-methylimidazole porphyrin dioxygen complexes.

Tetraphenylporphyrinbis(imidazole)iron(II) reacts instantaneously and irreversibly (0.21 ± 0.05 O_2/Fe) even at -78° in toluene,[77] but the 1-methylimidazole complexes give reversible adducts.[76] Similarly iron(II) complexes of mesoporphyrin IX dimethyl ester reversibly bind oxygen at -50° in dichloromethane in the presence of 1-methylimidazole, but are irreversibly oxidized if imidazole is used.[77] Even the capped iron porphyrins, which have a five-hour half life at room temperature with 1-methylimidazole in benzene, are oxidized instantaneously if imidazole is used instead.[71] Cobalt porphyrin complexes behave similarly, giving mononuclear dioxygen complexes with 1-methylimidazole that are stable for several days at room temperature, but decomposing irreversibly and instantaneously with imidazole.[87] While it has not yet been proven that imidazole acts as an acid to effect these drastic stability changes, such an effect seems reasonable and it is generally agreed that easily dissociable protons should be avoided when studying dioxygen complexes. The application of the aprotic solvent strategy to the copper (I) complexes studied herein is of even greater importance. In hydroxylic solvents copper(I) disproportionates to copper(II) and copper(0). In nitromethane the somewhat easily lost solvent proton from nitromethane would appear to account for the observed 0.25 O_2/Cu stoichiometry (see Chapter Three).

Another solvent effect is the enhancement of dioxygen binding by more polar solvents. While methylimidazole cobalt(II) protoporphyrin IX dimethyl ester in toluene requires an oxygen pressure of 417 Torr for half oxygenation at -23°, only 12.6 Torr are required in dimethylformamide.[88] (O_2 is also more soluble in toluene than dimethylformamide.)[88] A similar effect is observed for bis(pyridine)iron(II) tetraphenylporphyrin in solution at -78°. Under one atmosphere of dioxygen complete adduct formation occurs in dichloromethane, only a small amount of adduct is formed in toluene, and the amount in diethyl ether is intermediate.[76] Thus the observed effect is that the polar dioxygen complexes are more favored in higher dielectric constant media.

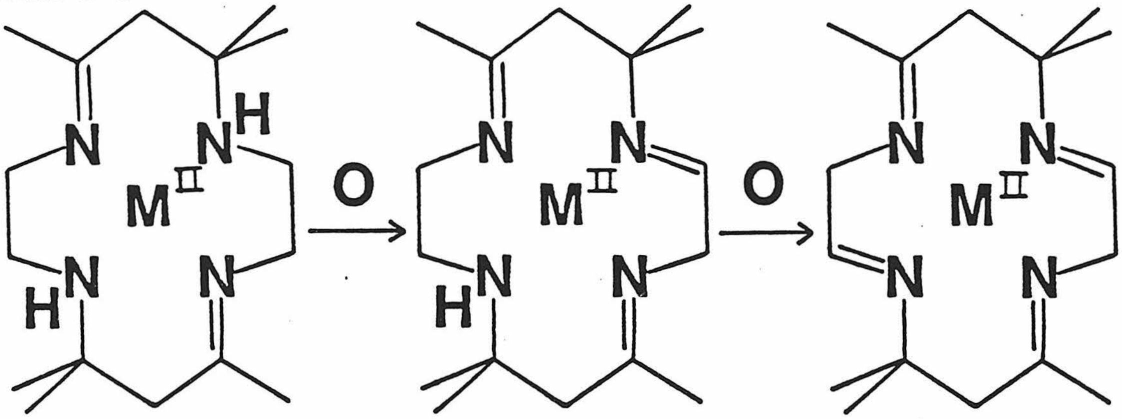
In agreement with electron transfer from metal to dioxygen[89] to give Co(III)-O_2^- is the observation that the binding constants are proportional to the cobalt(II) to cobalt(III) oxidation potential.[90,91] Thus the easier it is for cobalt(II) to be oxidized to cobalt(III), the stronger the bond in Co(III)-O_2^-. Very positive reduction potentials may result in lack of reactivity, such as found for cobalt(II) porphyrins at 25°. Very negative reduction potentials could give outer sphere electron transfer or irreversible adduct formation. An example of the latter is provided by pyridine chromium(II) tetraphenylporphyrin. The chromium(III) oxidation state is so favored (reduction of chromium chloride tetraphenylporphyrin in dimethylsulfoxide is at -0.86 V vs SCE) that the binding of dioxygen is irreversible.[92] The most stable copper(I) complex reported here (highest Cu(II) to Cu(I) reduction potential) fails to react with dioxygen and may be an example of the opposite extreme (Chapter Three). Presumably there is an ideal potential range for reversible adduct formation for each metal. The reduction potential of copper in tyrosinase, which forms reversible dioxygen adducts, is +0.36 V.

In addition to oxygen adducts, reaction with dioxygen can lead to ligand oxidation. Examined next are the oxidations macrocyclic compounds have been found to undergo. An advantage of macrocyclic ligands is that they tend to stay intact and coordinated to the metal after oxidation.

Known Macrocycle Oxidations

Oxidative dehydrogenation of coordinated amine ligands to form imine linkages is a common macrocyclic response to oxidizing agents in general.[93] For example, the diimine shown in Scheme I-4, is successively oxidized to the triimine and then the tetraimine.

Scheme I-4



The strength of oxidizing agent necessary depends on the metal ion. With the above macrocycle, the iron(II) complex is oxidized by O_2,[94] the nickel(II) complex is oxidized by HNO_3,[95,96] and the copper(II) complex, reported for the first time here (see Chapter Three), requires a perchloric acid permanganate treatment. Many other amine-containing macrocycles, including several nickel(II) species in the presence of dioxygen, undergo oxidative dehydrogenation. Fig. I-2 shows an example where a further aromatization has occurred after oxidative dehydrogenation.[97]

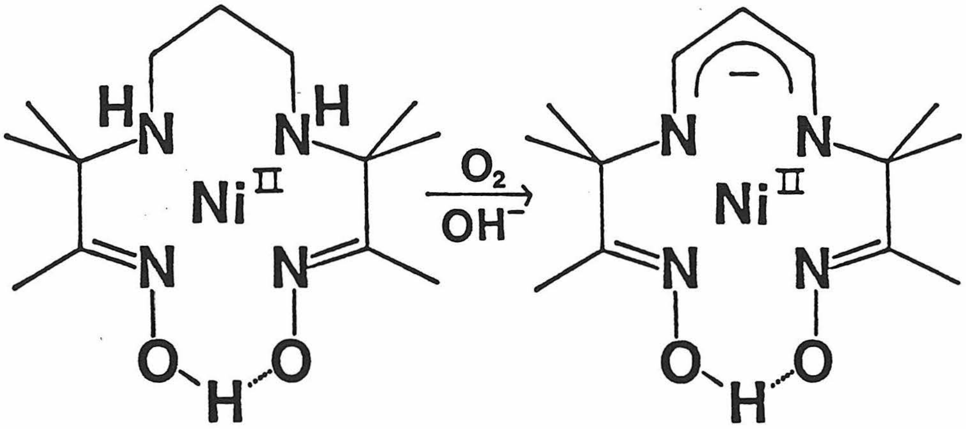


Fig. I-2. Oxidative dehydrogenation of a Ni(II) complex in the presence of base. The reaction stoichiometry is 1.0 O_2/Ni(II).

The mechanism for the oxidative dehydrogenation presumably involves higher oxidation states of the metal. Initial conversion of the M(II) to M(III), and subsequent electron abstraction from an N-H bond would yield a M(II) ligand radical species. This could then be oxidized to yield the observed product. Such a mechanism is supported by the decomposition of M(III) complexes in solution.[94,98,99]

A second type of ligand reaction, which has been observed occasionally upon oxygenation of macrocyclic complexes, is ketonation (Fig. I-3). In Fig. I-3C the ligand, of course, has also undergone oxidative dehydrogenation. While the product in Fig. I-3A could be identified by spectroscopic means ($\nu_{C=0}$ = 1670 cm^{-1}), the product in Fig. I-3B required crystallographic analysis as the carbonyl and imine vibrational frequencies appear to be degenerate (1678 cm^{-1}). Ligand modification of B by adding a methyl group at the ketonation position blocks the reaction as expected, and only the slow reaction to cobalt(III) occurs. Ketonation of a copper(I) macrocycle has been observed here and is reported in Chapter Three, as well as blockage of that ketonation by a methyl group substitution.

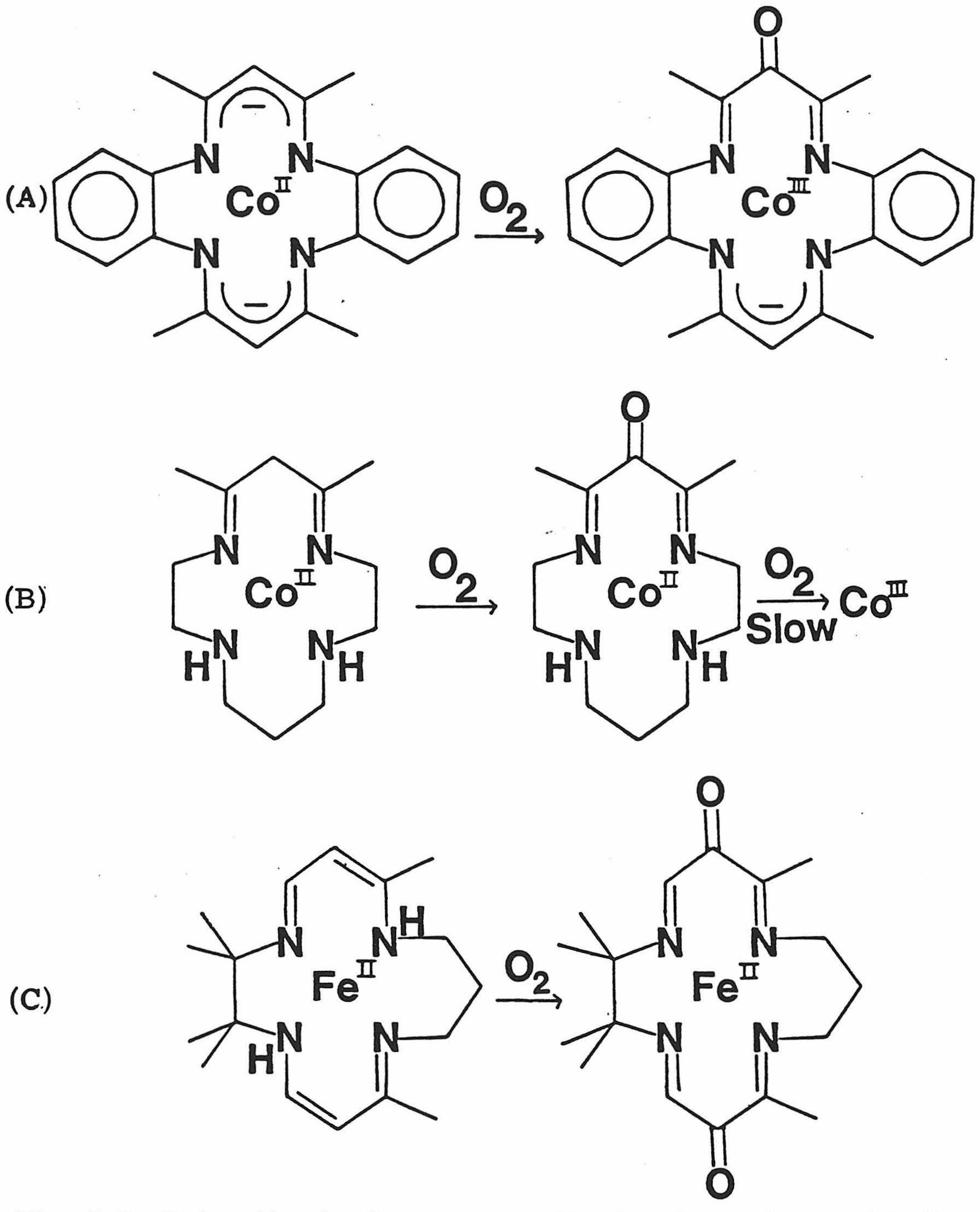
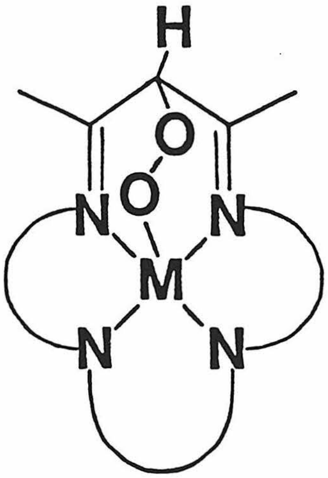


Fig. I-3. Ketonation by dioxygen reaction has been observed in these three macrocycles: (A), reference 100; (B), reference 101; (C) reference 102.

The proposed mechanism[100] involves the intermediate shown in Fig. I-4. Similar addition at the central carbon has been observed[100,103,104] for nitriles and acetylenes giving products like those in Fig. I-5, and making the proposed intermediate more plausible. The common structural feature of the macrocyclic ligands undergoing ketonation is the β-diimine unit, $-N{=}CR{-}CH_2{-}CR{=}N-$. Copper(II) has also been observed to catalyze ketonation of non-macrocyclic β-diimines.[105,106]

Fig. I-4. Presumed intermediate in the ketonation reaction of β- diimines.



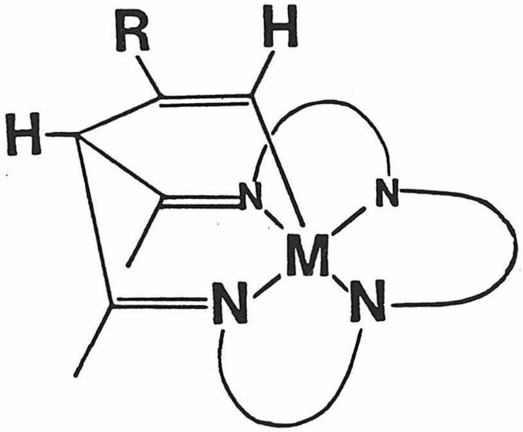


Fig. I-5. Nitrile and acetylene adducts of β -diimines.

Summary

Formation of dioxygen complexes and/or activation of dioxygen for substrate oxidation occurs for some copper-containing proteins. Kinetic studies indicate copper dioxygen complexes exist for small molecules too, although so far only as intermediates. Few products have been identified from reactions of dioxygen with copper(I). The present study involves the dioxygen reactions of multidentate, flexible, soft nitrogen ligand copper complexes. The aim was to adjust the ligand characteristics and reaction conditions such that interaction of dioxygen with copper was favored. If a copper dioxygen adduct could not be isolated, possible ligand oxidation was investigated since the enzyme reactions indicate that copper is capable of activating dioxygen toward substrate reactions. Chapter Two will discuss our early work on multidentate systems, beginning with a discussion of the choice of optimal ligands for this study of copper(I) complexes and dioxygen.

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Chapter Two. Dioxygen Reactions of Two Copper(I) Multidentate Ligand Systems

Chapter Two. Dioxygen Reactions of Two Copper(I) Multidentate Ligand Systems

Extreme lability, facile disproportionation, and air sensitivity are difficulties which must be overcome when studying reactions of copper(I) complexes. The first two govern the choice of suitable ligands; the last simply requires Schlenck, vacuum-line, and inert atmosphere glove box techniques.

Choice of Ligands

Both copper(I) and copper(II) are substitution labile. Complexes of monodentate and even bidentate ligands lead to solutions containing several species. Use of polydentate ligands, including macrocycles, inhibits these multiple equilibria and increases the chance of correlation between solution and solid state structures. The composition of the active species is an important question that is difficult to answer for copper oxidation catalysts in general. Polydentate ligands are expected to stay coordinated to the copper even after oxidation has occurred, thus simplifying the problem of copper lability.

Many copper(I) complexes disproportionate rapidly to copper(II) and copper(0).[1] Ligand environments having "hard" saturated amines and/or an enforced square planar coordination environment are known to destabilize copper(I) with respect to copper(II), as shown by electrochemical studies.[2,3] Soft ligands, including sulphur, phosphorous, aromatic amines (pyridine, pyrazolate) and imines tend to favor copper(I). The imidazole ligands found for copper in hemocyanin and tyrosinase, as well as the positive reduction potential for copper(II) to copper(I) in tyrosinase, suggest that soft nitrogen ligands and flexible geometries will favor the desired reactions with dioxygen as well as reduce the tendency toward disproportionation.

Prior to the start of this study, few multidentate nitrogen ligand copper(I) complexes had been isolated,[4,5] except for the substituted 1,10-phenanthroline,[5] 2,2'-bipyridyl,[5] and hydrotris(1-pyrazolyl)-borate complexes.[6-9] Only one nitrogen donor copper(I) macrocyclic complex had been isolated.[2,10] The oxygenation studies thus required synthesis of new copper(I) multidentate nitrogen ligand complexes.

This chapter discusses the dioxygen reactions of two related multidentate ligand complexes. One is mononculear and the other binuclear (Fig. II-1).

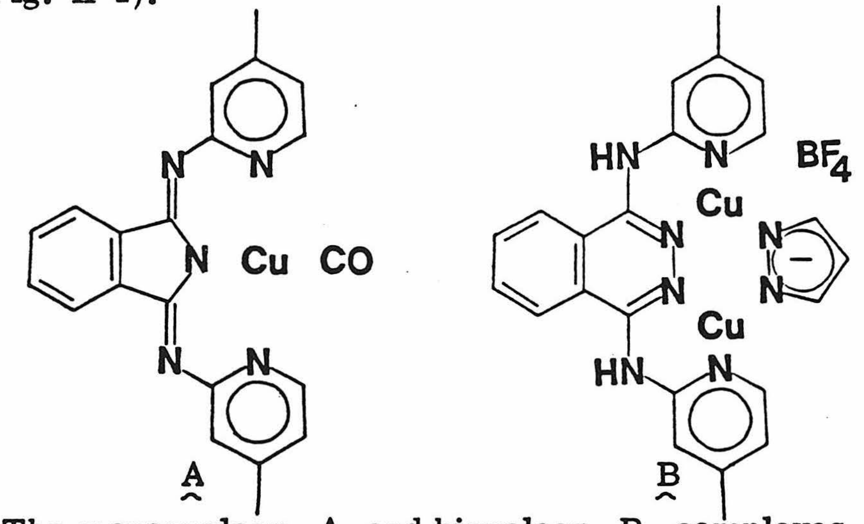


Fig. II-1. The mononuclear, A, and binuclear, B, complexes whose oxygen reactions are examined in this chapter.

Multidentate Mononuclear Copper(I) Complex A

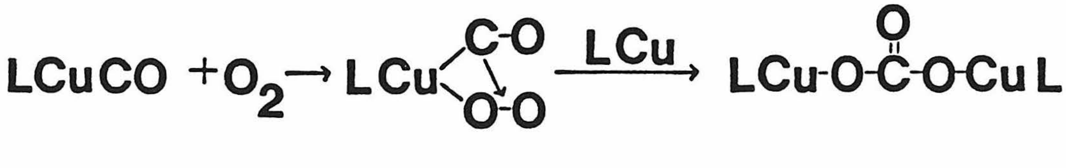
The mononuclear compound, A, is the copper(I) carbonyl complex of 1,3-bis(4-methyl-2-pyridylimino)isoindoline. This tridentate ligand is prepared by the condensation of 1,2-dicyanobenzene with 2-amino-4-

methylpyridine.[11] The synthesis and dioxygen reactions of this compound have appeared elsewhere (Ref. 12 included as Appendix 1), but are summarized here. The three coordinate copper(I) complex could not be isolated from solution. Several attempts to incorporate fourth ligands other than carbon monoxide were unsuccessful. Upon exposure to dioxygen, light-yellow suspensions of the carbonyl complex in benzene gradually turn brown. Crystals of the oxygenation products were obtained by slow evaporation.

The stoichiometry measured in benzene on a vacuum line indicates 0.5 ± 0.1 dioxygen consumed and 0.91 ± 0.05 carbon monoxide evolved per copper atom. This stoichiometry is consistent with the formation of a dioxygen bridged dimer, $2Cu(L)CO + O_2 \rightarrow (CuL)_2O_2 + CO$. Further examination indicates the reaction is much more complicated. Crystallographically identified products include a carbonate-bridged dimer (Fig. II-2) and a hydroxy-bridged tetramer (Fig. II-3) in which one-quarter of the ligand molecules have been oxidized to phenolate anions. Large amounts of non-crystalline material have not been identified.

Although no dioxygen compounds have been isolated, it is likely that they are involved as intermediates. A plausible mechanism for the formation of the bridging carbonate involves intramolecular insertion of coordinated carbon monoxide into coordinated dioxygen (Scheme II-1). Formation of the tetrameric species

Scheme II-1



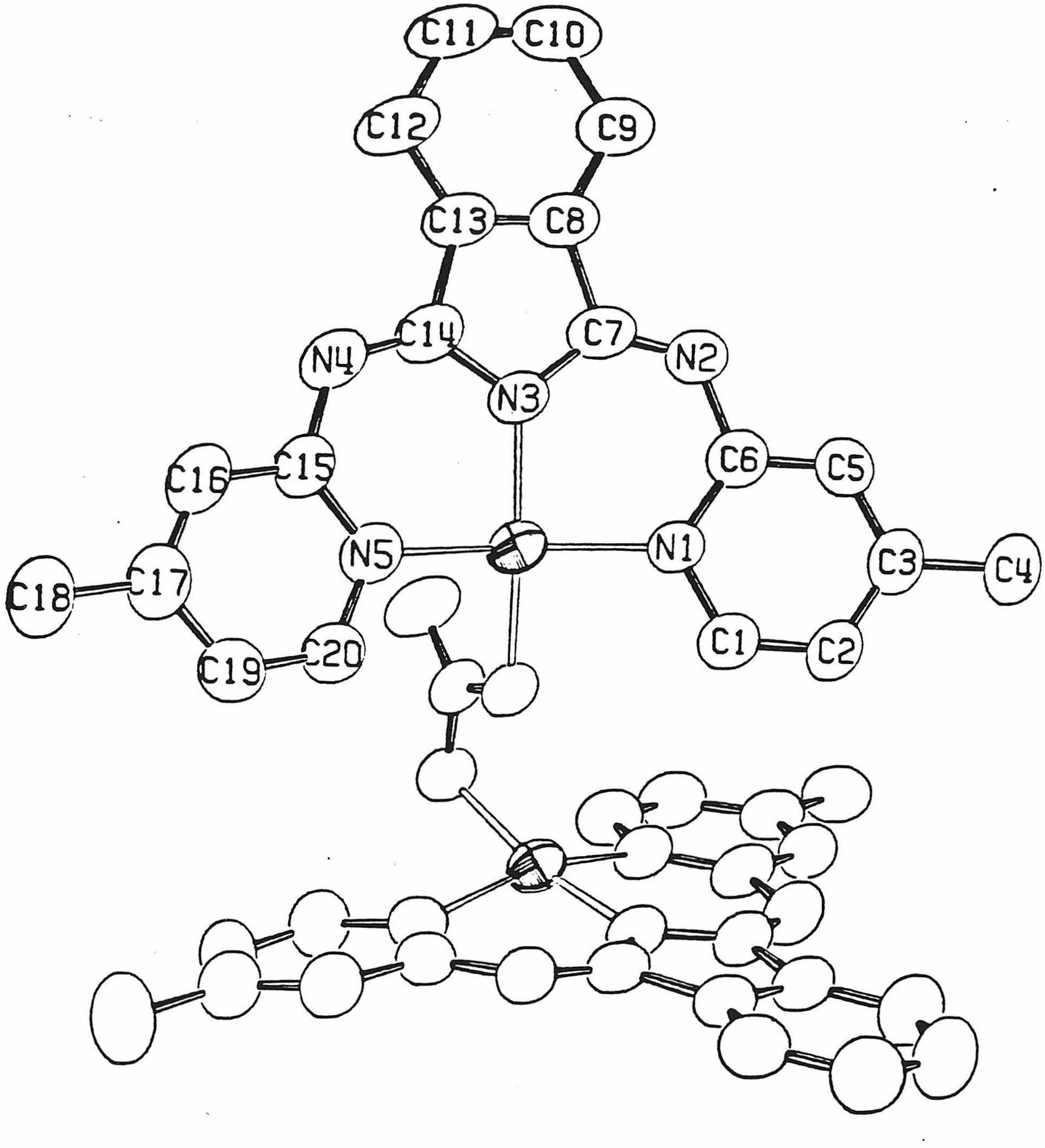


Fig. II-2. The carbonate-bridged dimer from oxygenation of $\hat{A}$.

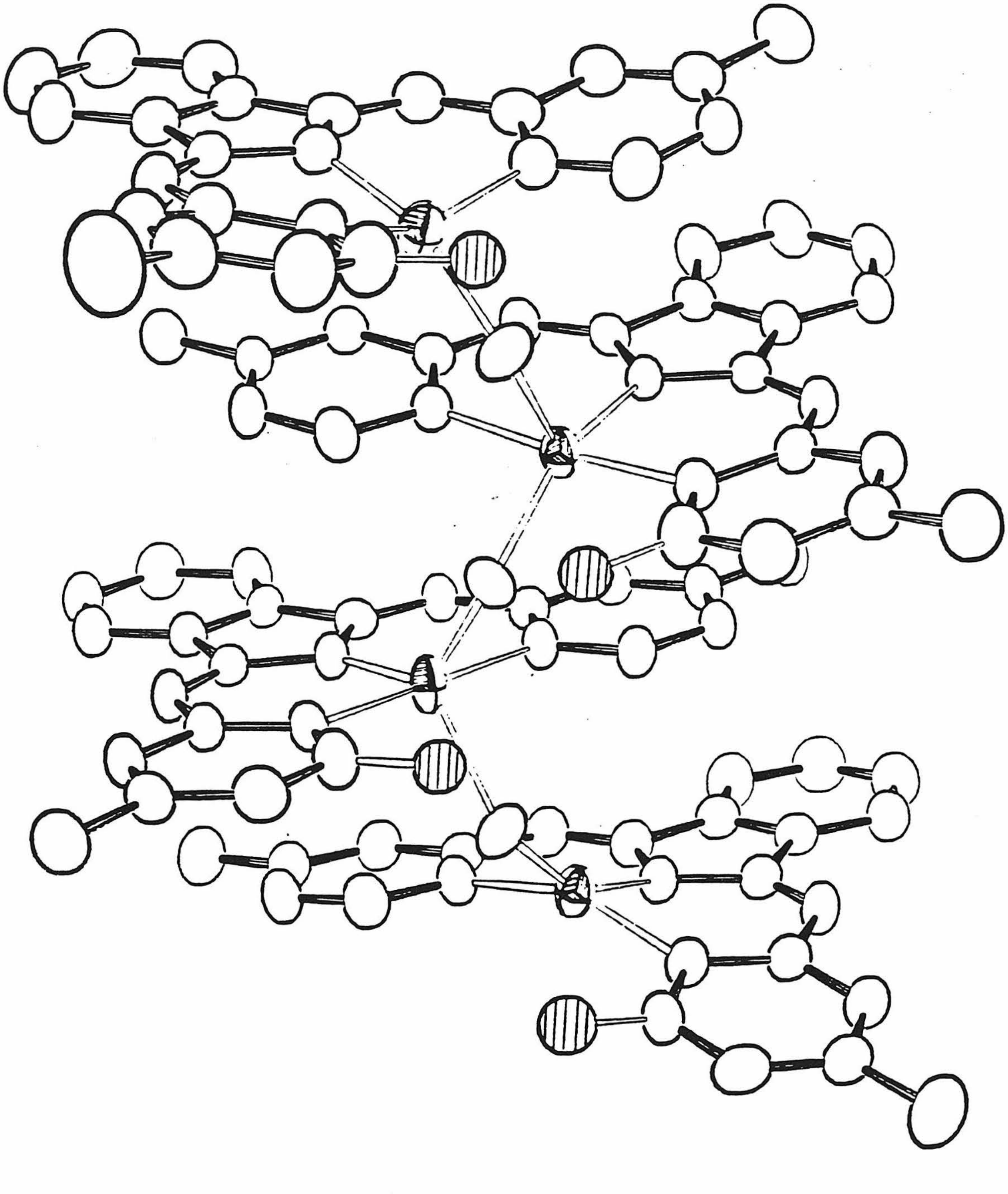
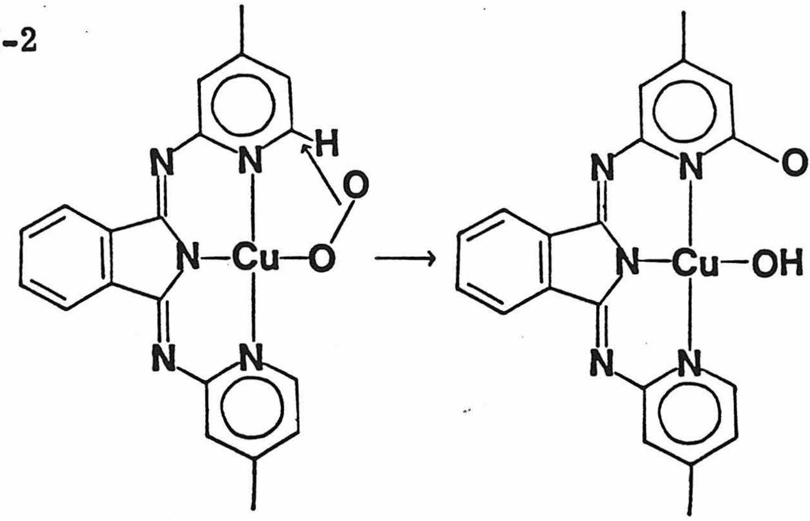


Fig. II-3. The hydroxy-bridged dimer from oxygenation of A; the partial occupancies of the four phenolate anions shaded in the figure sum to one.

$(CuL)_3(CuLO)(\mu\text{-}OH)_3$ may also involve a dioxygen intermediate, with copper promoted activation of coordinated dioxygen leading to ligand hydroxylation (Scheme II-2).

Scheme II-2



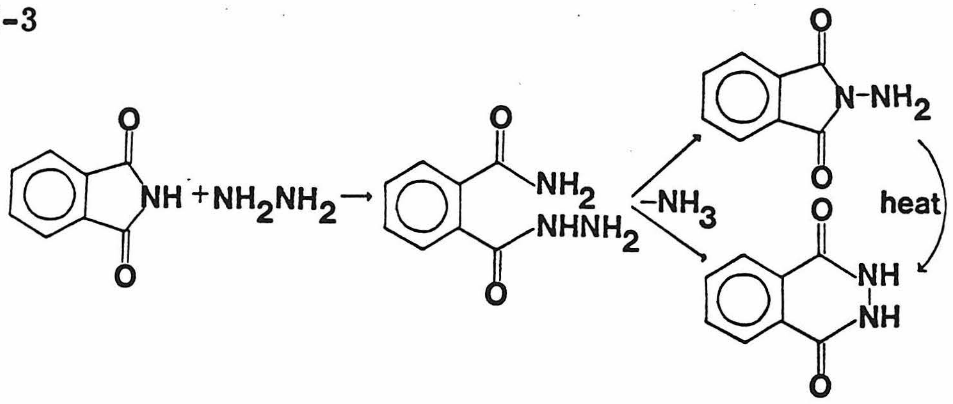
Several important observations concerning this system may be summarized. 1) Stoichiometry measurements indicated possible dioxygen complex formation but such was not observed crystallographically. 2) Copper(I) can reduce dioxygen by four electrons resulting in O–O bond cleavage, even in an aprotic solvent like benzene. O–O bond fission had not been crystallographically shown previously for any copper(I) dioxygen reaction. 3) This work is the first structural characterization of any copper(I) autoxidation product.

Binuclear Dicopper(I) Complex B

A binucleating version of 1,3-bis(4-methyl-2-pyridylimino) isoindoline can be synthesized by treatment with hydrazine, yielding 1,4-bis(4-methyl-2-pyridylamino)phthalazine. The intermediates of the reaction are probably similar to those observed for phthalimide[13]

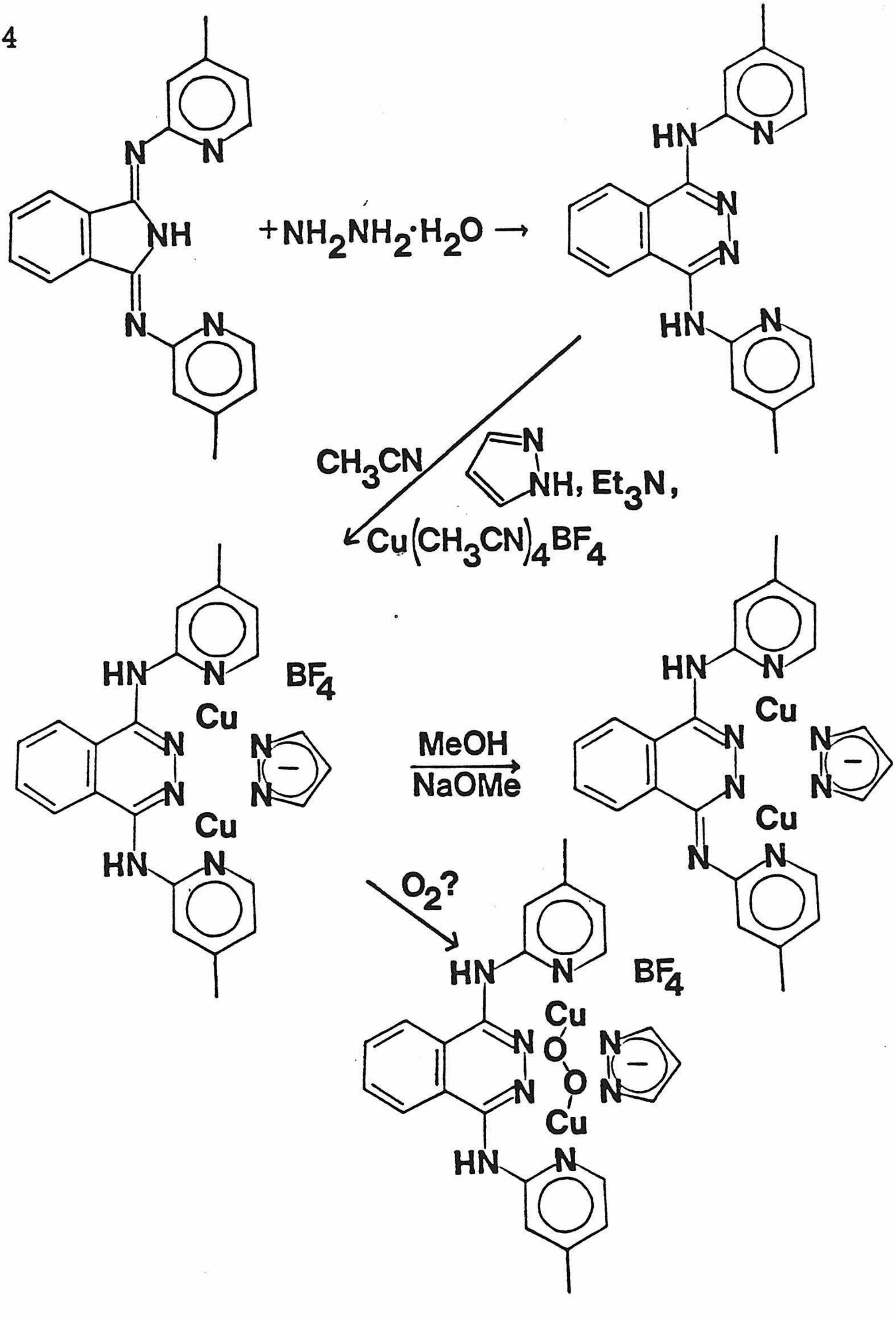
(Scheme II-3). The much less soluble binucleating ligand without the methyl substituents has been used to form binuclear copper(II), cobalt(II) and recently, nickel(II) complexes.[14-16] In these cases the metal may be four, five, or six coordinate with bridging and terminal halides, hydroxides, or waters completing the coordination. The present ligand coordinates two copper(I) atoms and a product, B, can be isolated by addition of pyrazolate anion (Scheme II-4). Pyrazole was chosen to complete the coordination environment both to stabilize the copper(I) oxidation state and because binuclear copper(I) complexes with a bridging pyrazole had recently been observed to be three-coordinate.[17] Molecular models show that the three-coordinate dicopper(I) complex provides a good fit for dioxygen in a binuclear cis geometry. X-ray structural characterization of the dicopper(I) complex is in progress by R. E. Marsh.

Scheme II-3



Oxygen stoichiometries determined at room temperature give 0.25 ± 0.01 dioxygen taken up per copper(I) atom. The techniques used were stoichiometry in dichloromethane by difference using a Toepler

Scheme II-4


NH
N
+NH2NH2·H2O →
HN
CH3CN
NH, Et3N,
Cu(CH3CN)4BF4
BF4
Cu
MeOH
NaOMe
O2?
O

pump, in propylene carbonate using a Warburg manometer, and in the solid state (again by difference with a Toepler pump). The solution uptakes were rapid (see Fig. II-4) and presumably controlled by the dissolution of dioxygen. Uptakes were performed in quadruplicate.

A stoichiometry of 0.25 dioxygen per copper atom corresponds to simple oxidation of copper(I) to copper(II) with the reduction of dioxygen to water, hydroxide or oxo species. With such a stoichiometry there can be no ligand oxidation and no dioxygen complex isolated. The infrared spectra show few changes upon oxygenation and the $^{18}O_2$ and $^{16}O_2$ products are identical. Magnetic susceptibility of the oxygenated solid, $\mu_{corr} = 1.60\ \beta M.$ per copper (25°, Faraday balance), indicates a copper(II) product as expected.

If a dioxygen complex is involved, it could be more stable at low temperature (see Chapter One). Thus the stoichiometry was measured in dichloromethane at -78° C. By difference using a Toepler pump no reaction could be detected. The same solutions then gave the expected uptake at room temperature. Since such an observation is also consistent with a reversible reaction at low temperature, a constant pressure measurement in dichloromethane at -78° was undertaken. Again no uptake was observed, indicating lack of oxygen reactivity at low temperature.

One explanation for this lack of reactivity involves the pyrazolate ligand. Not only would dioxygen binding be expected to be enhanced at low temperature, but so would the pyrazolate binding. If the first step of the dioxygen reaction involves dissociation of the pyrazolate, low temperatures could shut off the dioxygen reaction.

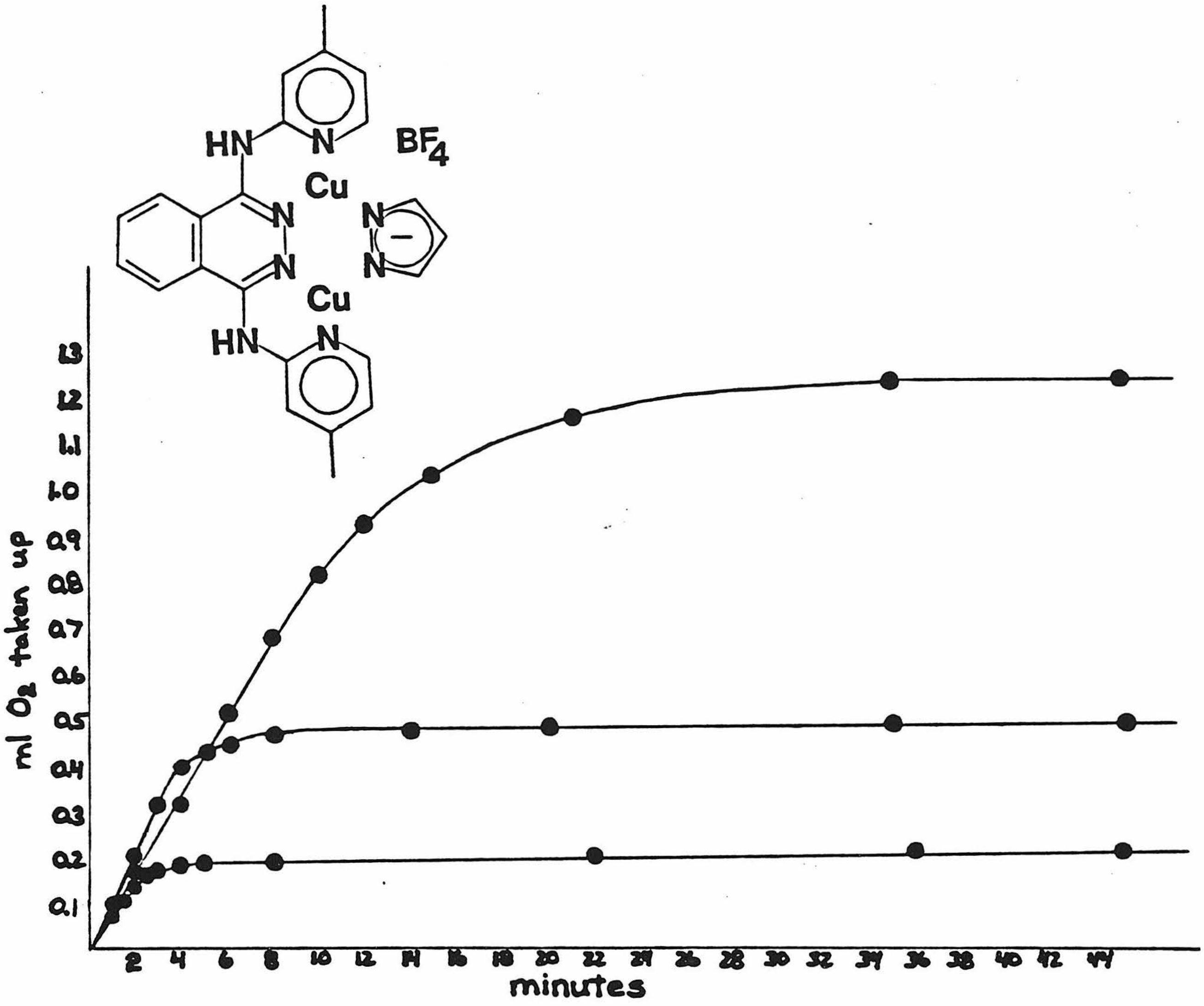


Fig. II-4. Dioxygen uptakes of propylene carbonate solutions of B at constant pressure (atmospheric) as a function of time. Three concentrations are shown; all took up 0.25 O_2/Cu.

The reduction of dioxygen to water or hydroxide requires a proton source. That proton source could be the ligand itself. Consequently the dicopper(I) binucleating ligand pyrazolate tetrafluoroborate complex was treated with sodium methoxide to give the anion of the binucleating ligand and loss of the tetrafluoroborate anion, **C** (Scheme II-4). The stoichiometry determined in propylene carbonate at constant pressure is unchanged (0.26 ± 0.02 O_2/Cu). In dichloromethane, the deprotonated compound was much less soluble. However the original slurry dissolved rapidly upon addition of dioxygen and the uptake as measured by difference was 0.30 ± 0.05 O_2/Cu.

In summary, it should be noted that, 1) this binuclear system apparently effects the four-electron reduction of dioxygen, and 2) dissociation of the pyrazolate appears to be necessary for the reaction to occur. Both the mononucleating and binucleating systems have been complicated by having even one dissociable ligand. A more ideal system would have no dissociable ligands and a vacant coordination site. Macrocyclic complexes which meet these requirements are discussed in the next chapter.

Experimental: Synthesis and Characterization of **B**

1,4-bis(4-methyl-2-pyridylamino)phthalazine. 1,3-bis(4-methyl-2-pyridylimino)isoindoline (17.0 g) prepared by the method of Siegl,[11] was dissolved in methanol (300 ml) with heating. Hydrazine hydrate (10 ml, Aldrich) was added, and the solution refluxed for ten minutes. After sitting at room temperature overnight, the solution was reheated for one hour during which time the precipitate redissolved, the solution got darker, and additional ammonia was driven off. Upon cooling to room temperature the yellow needles were isolated by filtration. Yield: 11.7 g, 66%. Anal. Calcd. for $C_{20}H_{18}N_6$: C, 70.16; H, 5.30; N, 24.54. Found: C, 69.90; H, 5.25; N, 24.95.

There are at least two isomers of the free ligand. The melting point of the product was usually 98-99 °C but occasionally material with melting point 174-175° was obtained by the same procedure. Above the melting point of the lower melting isomer the compound resolidifies and then remelts at the higher melting point. Curiously, heating the product above the higher melting point and then cooling results in the lower melting isomer. This cycle can be repeated several times with no obvious degradation. The two isomers have slightly different infrared spectra. At the mass spectrum probe temperature both are converted to the same isomer and the mass spectra obtained are identical with large peaks at 341.1 and 342.1 mass units. (The ligand has mass 342.16). Which isomer reacts with copper(I) to give the complex is not determinable since they interconvert in solution and the equilibrium would continually produce more of the reacting isomer until the reaction went to completion. (The copper complexation is somewhat slow). Starting with either isomer gave identical products with copper(I) and pyrazolate. The proton magnetic resonance spectra of the starting mononucleating ligand and the expanded binucleating ligand are compared in Fig. II-5.

Dicopper(I) 1,4-bis(4-methyl-2-pyridylamino)phthalazine pyrazolate tetrafluoroborate. 1,4-bis(4-methyl-2-pyridylamino)phthalazine (2.00 g, 5.8 mmol) and pyrazole (0.40 g, 5.8 mmol) were dissolved

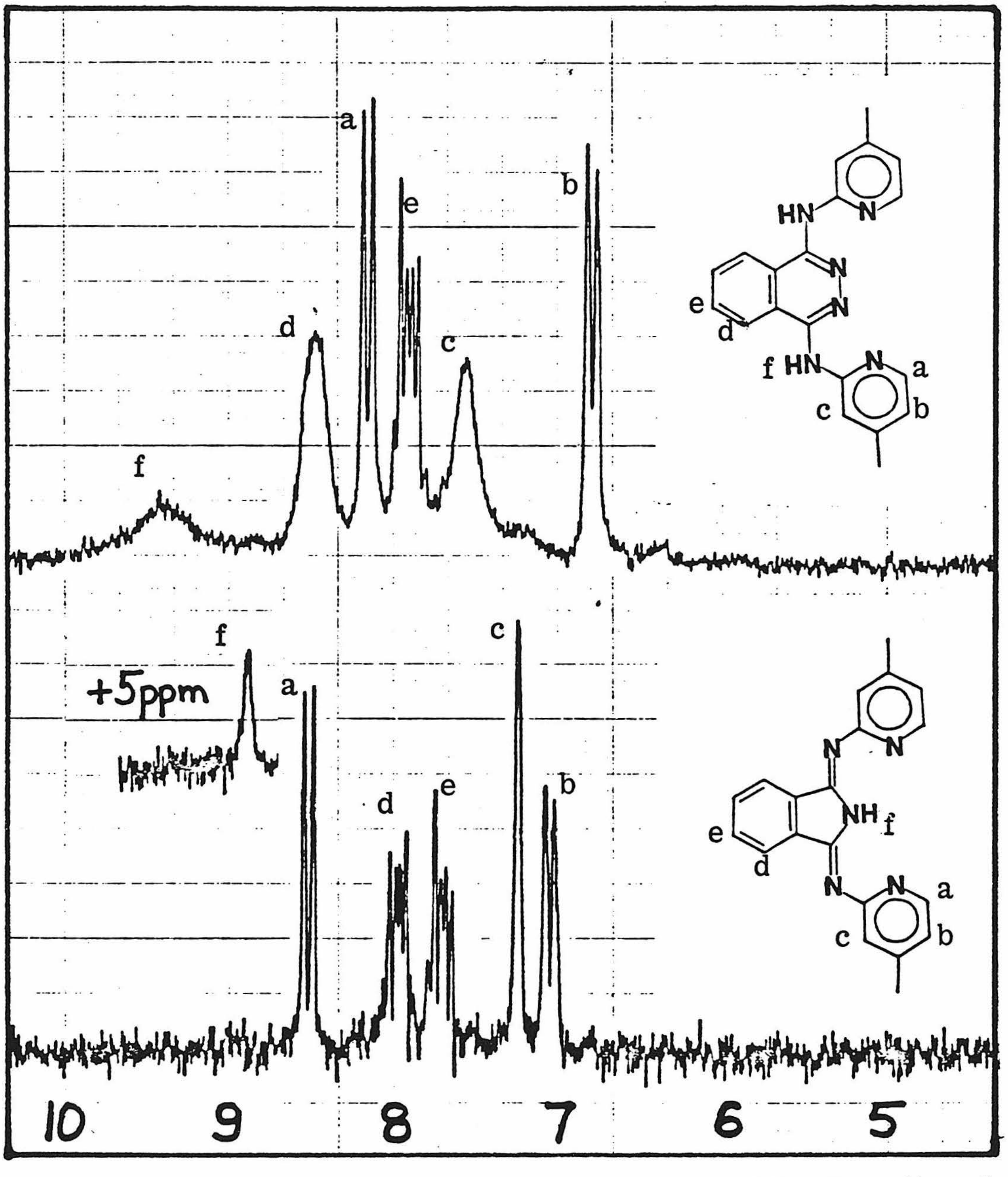


Fig. II-5. Proton magnetic resonance spectra of the free ligands of A and B in dimethylsulfoxide-d_6. Assignments are as indicated and chemical shifts are downfield from TMS. All peaks shown integrate as 2 except the half-size peak f in the bottom spectrum (the methyl group signals are not shown and integrate as 6H).

in hot acetonitrile (150 ml) in an oxygen-free glove box. Upon addition of $Cu(CH_3CN)_4BF_4$ (3.68g, 1.17 mmol) prepared by the published method,[18] the solution turned a dark red. Addition of triethylamine (2 ml) to deprotonate the pyrazole resulted in the formation of an orange precipitate over a period of an hour. The solution was allowed to cool slowly to room temperature after which the product was isolated by suction filtration (3.29 g, 90% yield). Anal. Calcd. for $C_{23}H_{21}N_8Cu_2BF_4$: C, 44.32; H, 3.40; N, 17.98. Found: C, 44.75; H, 3.45; N, 18.25. The infrared spectrum shows vibrations of the BF_4^- group (1050 to 1100 cm^{-1}) and conductivity measurements in acetonitrile indicate at 1:1 electrolyte.

Dicopper(I) 1-(4-methyl-2-pyridyl amino)-4-(4-methyl-2-pyridylamino) phthalazine anion pyrazolate. A slurry of dicopper(I) 1,4-bis-(4-methyl-2-pyridyl amino)phthalazine pyrazolate tetrafluoroborate (1.0 g) was stirred overnight in methanol (200 ml) in an oxygen-free glove box in the presence of an excess of sodium methoxide. The deprotonated ligand complex was recovered by filtration and washed with methanol. Yield: 0.63 g, 73%. The infrared spectrum of the product shows no vibration that can be assigned to the tetrafluoroborate anion and conductivity measurements in acetonitrile indicate a neutral compound. The proton magnetic resonance spectra of the free ligand and both copper complexes are compared in Fig. II-6.

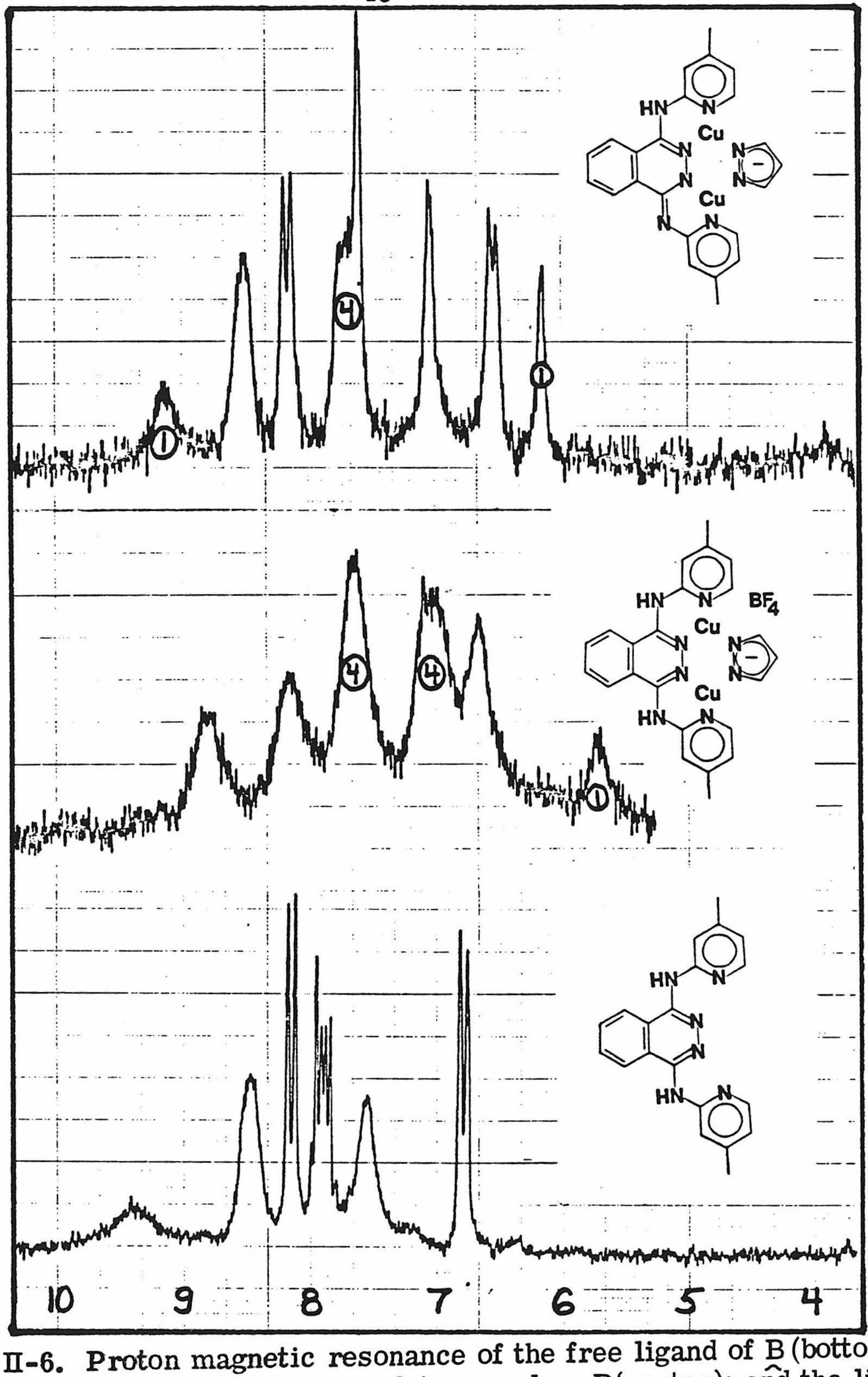


Fig. II-6. Proton magnetic resonance of the free ligand of B (bottom); the ligand dicopper(I) BF$_4$ pyrazolate complex, B(center); and the ligand anion dicopper (I) pyrazolate complex, C (top). All peaks shown integrate as two protons except those otherwise marked. The solvent is dimethylsulfoxide-d$_6$, the methyl groups are not shown (integration 6H), and the chemical shift is downfield from TMS.

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Chapter Three. Dioxygen Reactions with Copper(I) Tetraazamacrocyclic Complexes

Chapter Three. Dioxygen Reactions with Copper(I) Tetraazamacrocyclic Complexes

While both of the ligands in Chapter Two were multidentate, it was necessary to add an additional ligand in order to isolate a copper(I) complex. Dissociation of this additional ligand either because of lability or the requirement for a vacant coordination site complicated the results and led to a variety of products.

Tetradentate N_4-macrocyclic complexes can solve the problem of dissociable ligands but only one such copper(I) complex had previously been isolated.[1] The reactions of dioxygen with several new macrocyclic complexes (Fig. III-1) are reported herein. Of particular importance are $CuLBF_2$, 1 and $Cu(I)Me_8$tetraene(ClO_4), 10. $CuLBF_2$, 1, forms a binuclear dioxygen complex (Fig. III-2) at -79° in CH_2Cl_2 solution. $Cu(I)Me_8$tetraene(ClO_4), 10, undergoes relatively clean ligand oxidation at -79° in dichloromethane to precipitate a ketonated copper(II) complex (Fig. III-3). The dioxygen reactions of the remainder of the macro-

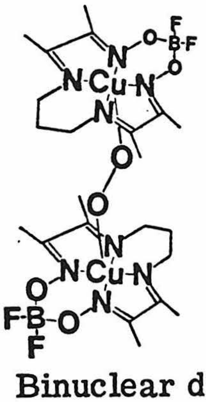


Fig. III-2. Binuclear dioxygen complex of $CuLBF_2$, 1.

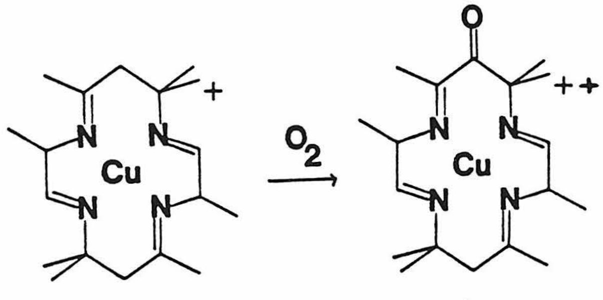
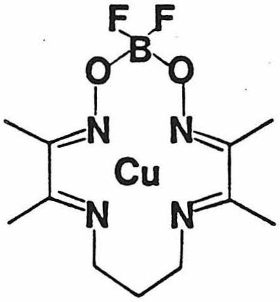


Fig. III-3. Ketonation of $CuMe_8$-tetraene(ClO_4), 10.



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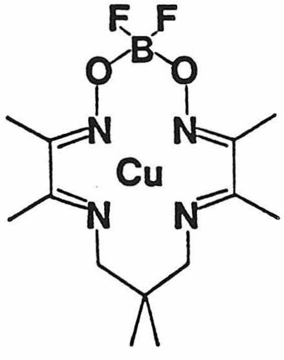

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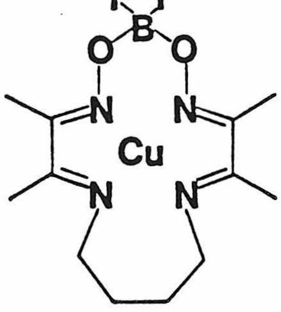

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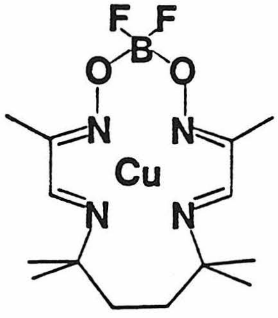

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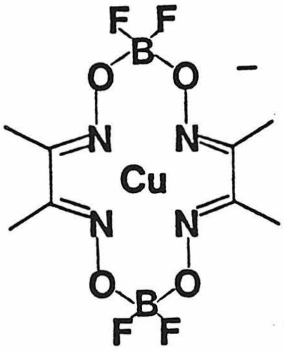

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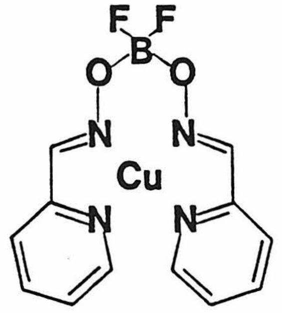

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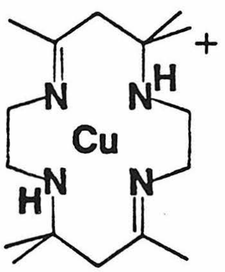

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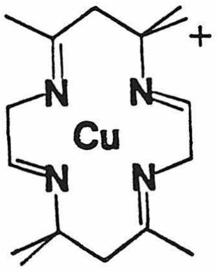

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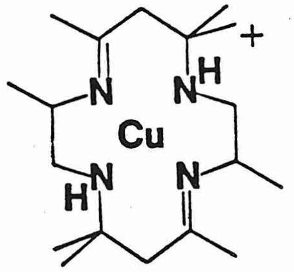

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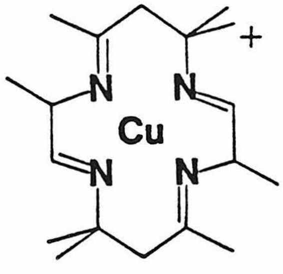

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Fig. III-1. Copper(I) tetraaza macrocycles whose oxygen reactions are examined in this chapter.

cycles in Fig. III-1 are discussed here in relation to the dioxygen reactions of $CuLBF_2$, **1**, and Cu(I)Me_8tetraene(ClO_4), **10**.

$CuLBF_2$, **1**

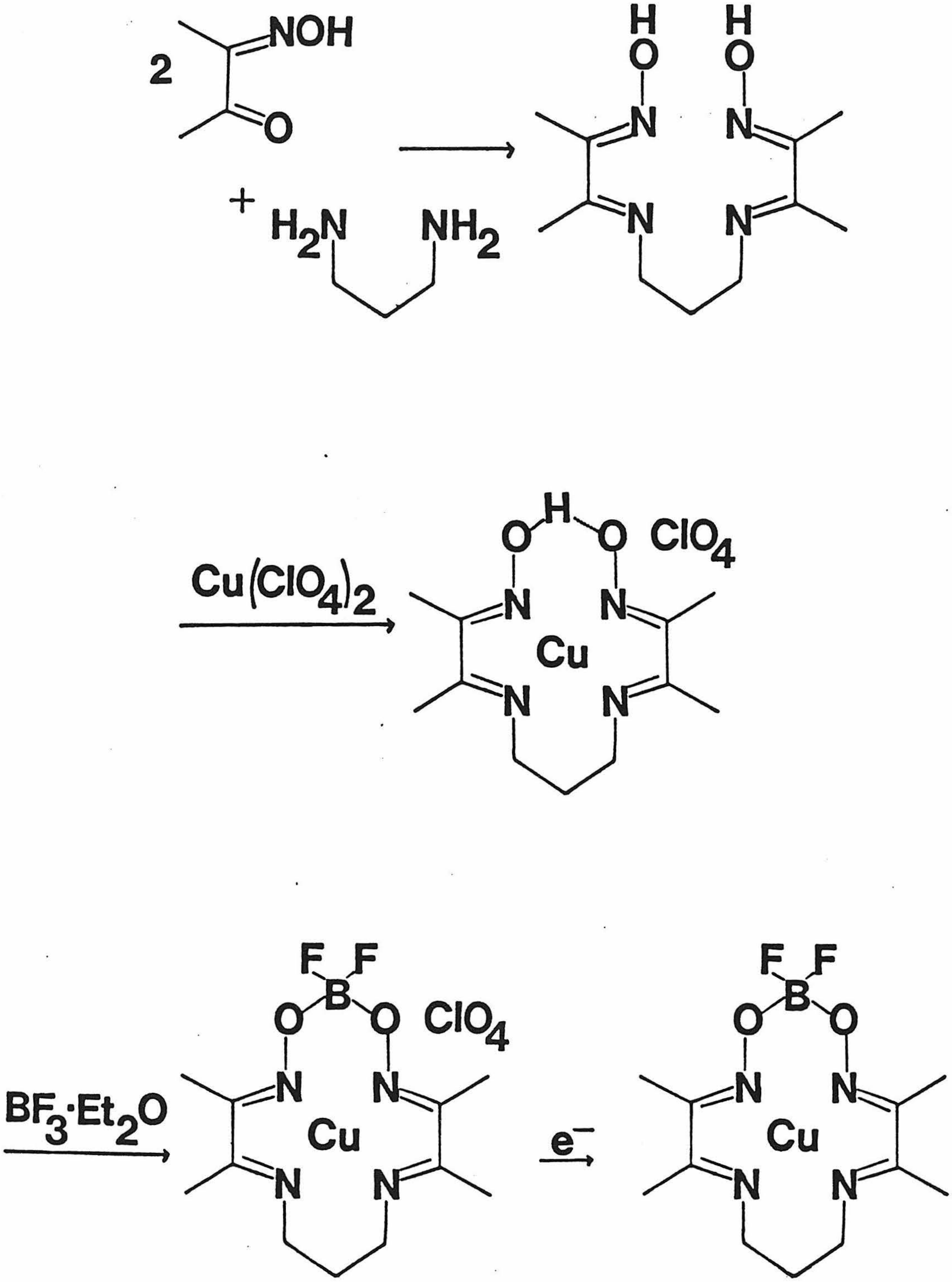
The corresponding copper(II) complex was synthesized by the Schiff base condensation of 2,3-butanedionemonoxime with 1,3-propanediamine, followed by treatment with copper(II) and boron trifluoride etherate (Scheme III-1).[2,3] The copper(II) was then reduced electrochemically to copper(I). Electrochemical reduction was found to be both specific and practical and was used to prepare all copper(I) complexes discussed in this chapter and shown in Fig. III-1. $CuLBF_2$, **1**, precipitated from acetone solution upon reduction and was isolated by filtration.

An important question is whether upon reduction the electron goes into the copper atom or into the ligand. Suffice it to say that the metal atom reacts like copper(I) with both carbon monoxide and dioxygen. This question is discussed further in Appendix Two.

$CuLBF_2$, **1**, is coordinatively unsaturated and reacts with a variety of fifth ligands. Both the four-coordinate nature of the reduced species and the five-coordinate nature of the carbonyl adduct have been verified by crystallographic analysis (Fig. III-4).[3,4] $CuLBF_2$, **1**, is thus a good candidate for study of copper(I) dioxygen reactions, being both a macrocycle with no labile ligands and coordinatively unsaturated.

The four-coordinate $CuLBF_2$, **1**, complex reacts readily with dioxygen in dichloromethane solution at room temperature, changing color from deep blue ($\epsilon = 10,000$ at 677 nm in acetone)[3] to brown. Immediate purging with nitrogen gas or immediate freeze pump thawing

Scheme III-1



CuLBF$_2$, 1

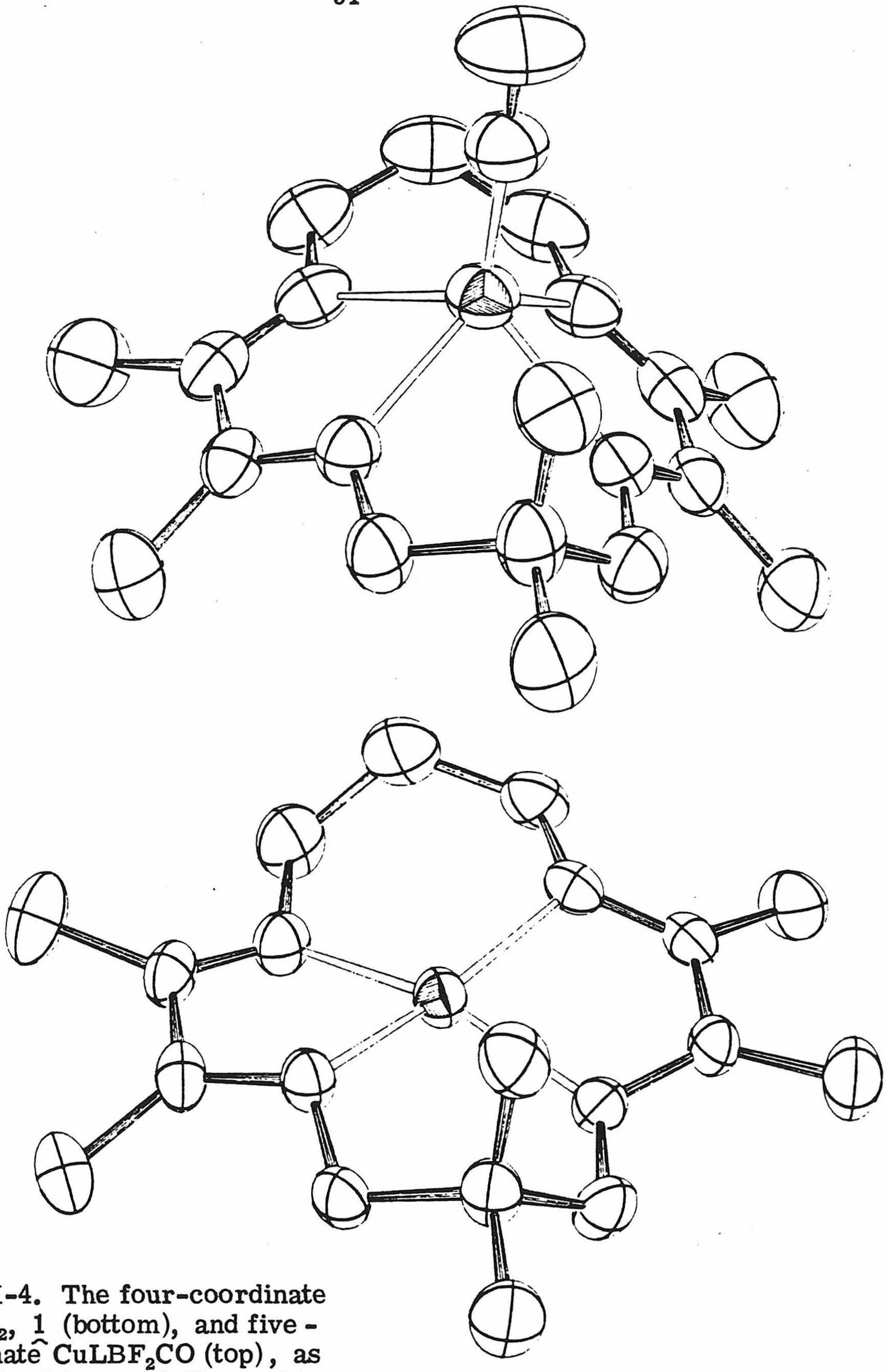


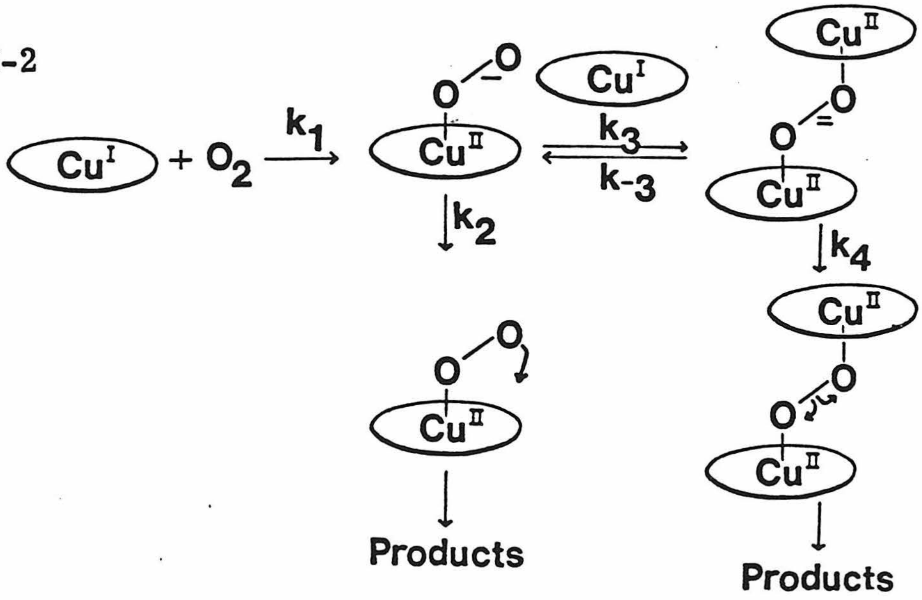
Fig. III-4. The four-coordinate CuLBF$_2$, **1** (bottom), and five-coordinate CuLBF$_2$CO (top), as determined by crystallographic analysis.

restores some but not all of the original color to give a dirty blue solution. While this observation is consistent with reversible dioxygen adduct formation, further investigation indicates such is not the case.

$CuLBF_2$, 1, Reaction with Dioxygen at -79°

$CuLBF_2$, 1, forms a binuclear dioxygen complex (Fig. III-2) at -79° in dichloromethane. The mechanism in Scheme III-2 is supported by the following observations. 1) Stoichiometry determinations by difference using the Toepler pump find 0.50 ± 0.06 dioxygen taken up per copper atom at -79° in dichloromethane solution. At low temperatures, reaction k_3 in Scheme III-2 predominates. 2) Reaction of deep-blue dichloromethane solutions of $CuLBF_2$, 1, with dioxygen at -79° gives a brown solution. If any excess dioxygen present is removed before warming to room temperature, the blue color reappears upon warming (Fig. III-5). As much as 40% of the original amount of $CuLBF_2$ has been quantitatively observed by visible absorption spectroscopy (684 nm in dichloromethane). Infrared spectra of the material so

Scheme III-2



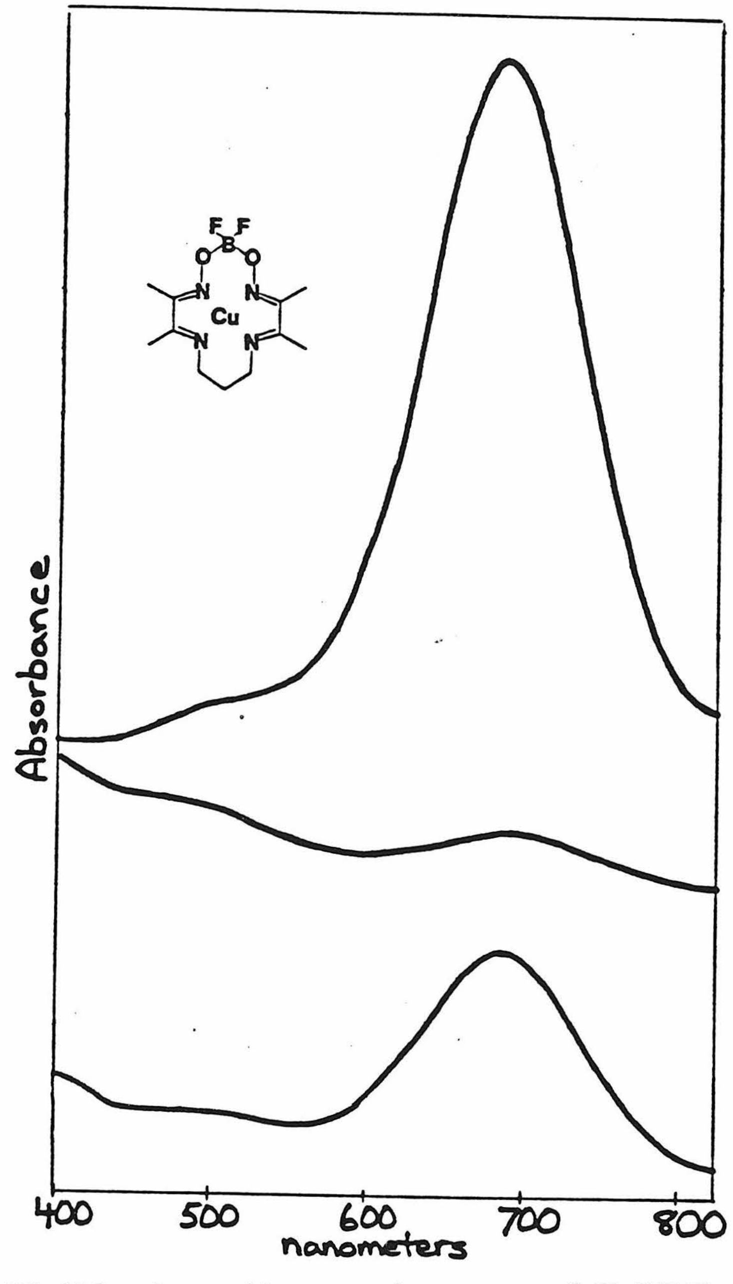


Fig. III-5. Visible absorption spectroscopy of $CuLBF_2$, 1, in dichloromethane. All samples are the same concentration in the same cell. Top: $CuLBF_2$, 1. Center: $CuLBF_2$, 1, in the presence of dioxygen, spectrum obtained at approximately 200° K. Bottom: $CuLBF_2$, 1, treated with dioxygen at 200°K, excess dioxygen removed, and sample warmed to 25°.

treated verify $CuLBF_2$, **1**, as a major component. The extent of reaction k_4 in Scheme III-2 must be small as it does not fit the experimental observation of regeneration of $CuLBF_2$, **1**. At room temperature, reaction k_{-3} followed by k_2 in Scheme III-2 becomes important. 3) No gas is released as the solution warms and regains its blue color. Reaction k_{-1} in Scheme III-2 is not observed. 4) The electron paramagnetic resonance signal obtained in frozen solution following reaction of $CuLBF_2$, **1**, with dioxygen at -79° in dichloromethane, or by quick freezing soon after addition of dioxygen at room temperature, does not account for the majority of the copper present (Fig. III-6). The binuclear complex $(LBF_2)Cu\text{-}O_2\text{-}Cu(LBF_2)$ proposed in Scheme III-2 as the major species present at -79° should be diamagnetic by analogy with oxyhemocyanin (see Chapter One), and is in agreement with the observed electron paramagnetic resonance signal. 5) Observation of reversible color changes and small electron paramagnetic resonance signals immediately after dioxygen introduction at room temperature indicate that rate of reaction k_3 in Scheme III-2 is competitive with k_2 at room temperature.

A sample of $CuLBF_2$ oxygenated at -79° in dichloromethane was filtered in a cooled Schlenck apparatus and the recovered solid dried in vacuo at low temperature. The room temperature infrared spectrum of this material is identical with that obtained from room temperature reaction products. If the product at low temperature was different from that at room temperature, it has decomposed on warming as a solid. Magnetic susceptibility measurements (25°, Faraday method)

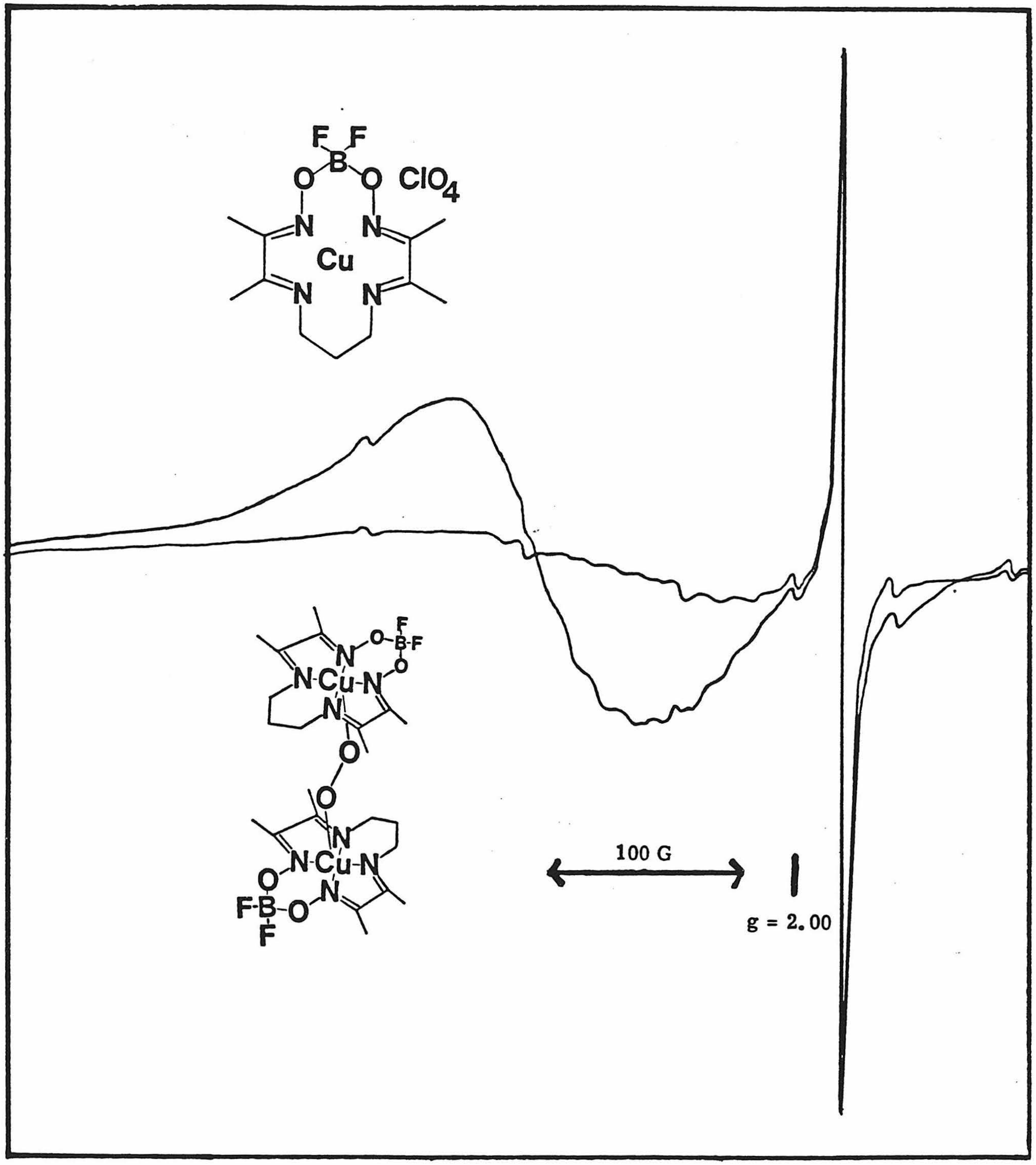


Fig. III-6. Electron paramagnetic resonance spectra in frozen solution. The samples contained the same internal capillary tube filled with a dilute octahedral chromium oxide sample in KCl. Large signal: 2.3 mM Cu(II) LBF_2ClO_4 in EtOH. Small signal: 1.8 mM Cu(I) LBF_2 in CH_2Cl_2 after reaction with dioxygen at -79°C.

indicate a copper(II) product with $\mu = 1.88\ \beta.M.$.

While the observations at low temperature were encouraging, the decomposition of the solid on warming implies the chance of isolating a dioxygen complex with this ligand is small. Investigation of the room temperature product was undertaken in hopes of identifying the decomposition products so that the ligand could be modified in such a way as to prevent decomposition.

CuLBF$_2$, $\underset{\sim}{1}$, Reaction with Dioxygen at 25°

The room temperature stoichiometry of the CuLBF$_2$, $\underset{\sim}{1}$, dioxygen reaction was measured in a variety of aprotic solvents. The values determined fall into four groups (Fig. III-7). There is no correlation of solvent dielectric constant or dipole moment with stoichiometry. Excluding dichloromethane the groups are acidic, neutral, and basic aprotic solvents.[5]

The reaction in nitromethane is much simpler than in the other solvents. In nitromethane, the room temperature stoichiometry is 0.25 dioxygen per copper atom. Copper(I) has been oxidized to copper(II) and the four-electron reduction of dioxygen to water, hydroxide, or oxo species has occurred. No ligand oxidation has taken place. The infrared spectrum of the product is that of CuLBF$_2$ClO$_4$ minus the perchlorate bands plus a very strong band at 1550 cm^{-1}. This absorption is assigned to the nitromethanide anion as found in autoxidation studies in nitromethane (see Chapter One), although an expected[7] additional strong band at 1270 cm^{-1} is not observed. Addition of a tenfold excess of tertiary amines increases the stoichio-

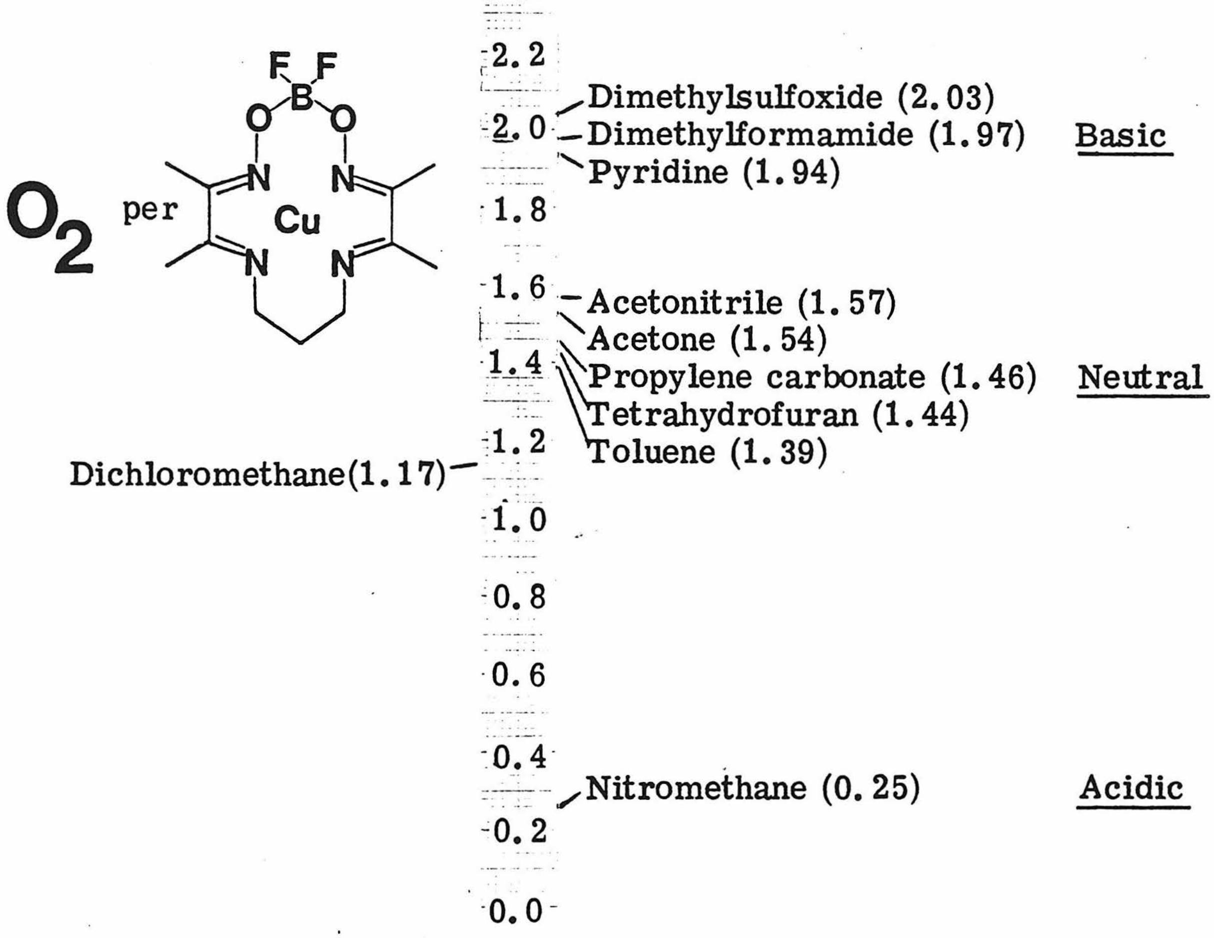


Fig. III-7. Dioxygen per copper stoichiometry of CuLBF$_2$, 1, in various solvents at room temperature.

metry in nitromethane to 0.5 dioxygen per copper atom.

The different stoichiometries are not due to the increased basicity of the solution since addition of sodium hydroxide has no effect on the stoichiometry. Trialkylamines are known to react with hydrogen peroxide to form trialkylamine oxides which react with hydrogen peroxide to form hydrogen peroxide adducts.[6] In either case, both triethylamine and triethylenediamine (also known as 1,4-diazabicyclo(2.2.2)octane) remove hydrogen peroxide and only two electrons rather than four are available from each dioxygen for copper oxidation. This results in a doubled oxygen uptake. Hydrogen peroxide must be present as an intermediate in the oxygenation of $CuLBF_2$ in nitromethane.

Excluding nitromethane, the stoichiometry values are all greater than 1.0 dioxygen per copper atom. Stoichiometries higher than 1.0 dioxygen per copper require that oxidation of the ligand or solvent is occurring. The more basic the solvent, the more such oxidation occurs.

Evidence that the copper atom is involved in the oxygenation reaction, and that oxygen is activated toward substrate oxidation, is seen in studies of the dioxygen reaction with $CuLBF_2$ in the presence of triphenylphosphine. Triphenylphosphine forms a 1:1 complex with $CuLBF_2$ as determined by Job plots and by isolation of the solid adduct. Note that under the conditions of the experiment (room temperature dichloromethane solutions), triphenylphosphine alone does not react with dioxygen. With a 10:1 excess of triphenylphosphine to $CuLBF_2$, the oxygen reaction is almost stopped (uptake 0.08 ± 0.05 dioxygen per copper atom after 48 hours); with small relative amounts the uptake is normal; but in the region of one or two triphenylphosphine per $CuLBF_2$

the uptake is enhanced (Fig. III-8). These observations can be explained at high triphenylphosphine to $CuLBF_2$ ratios by blocking of the reaction at copper(I) by triphenylphosphine since the equilibrium is shifted such that there are almost never any four coordinate copper atoms to react with dioxygen. At the ratios around one to two, triphenylphosphine is acting as a substrate for some "$Cu-O_2$" species. Indeed, triphenylphosphine oxide has been identified in the infrared spectrum of the products. At low ratios $CuLBF_2$ reacts as it does in the absence of triphenylphosphine. The longer the reaction is allowed to run and the small equilibrium concentration of uncomplexed $CuLBF_2$ reacts, the more to the right and the higher the stoichiometry curve in Fig. III-8.

Except for the product in nitromethane, oxygenation of $CuLBF_2$ seems to give polymeric products as once they are removed from solution they are insoluble in acetone, ethanol, dichloromethane, dioxane, acetonitrile, and tetrahydrofuran. The product is soluble in dimethylsulfoxide and dimethylformamide but a satisfactory method of recrystallization has not been found. Attempts to remove the copper(II) atom or reduce it back to the copper(I) oxidation state to permit a useful nuclear magnetic resonance spectrum of the oxygenated product have not been successful.

Slow Dioxygen Reactions of Copper(I) Complexes 3 and 5

Two copper(I) macrocyclic complexes, 3 and 5, were synthesized by D. M. Ingle[8] and found to react quite differently with dioxygen. The macrocyclic complex derived from 1,4-diaminobutane, 3 (Fig. III-1), and that derived by addition of two boron difluoride

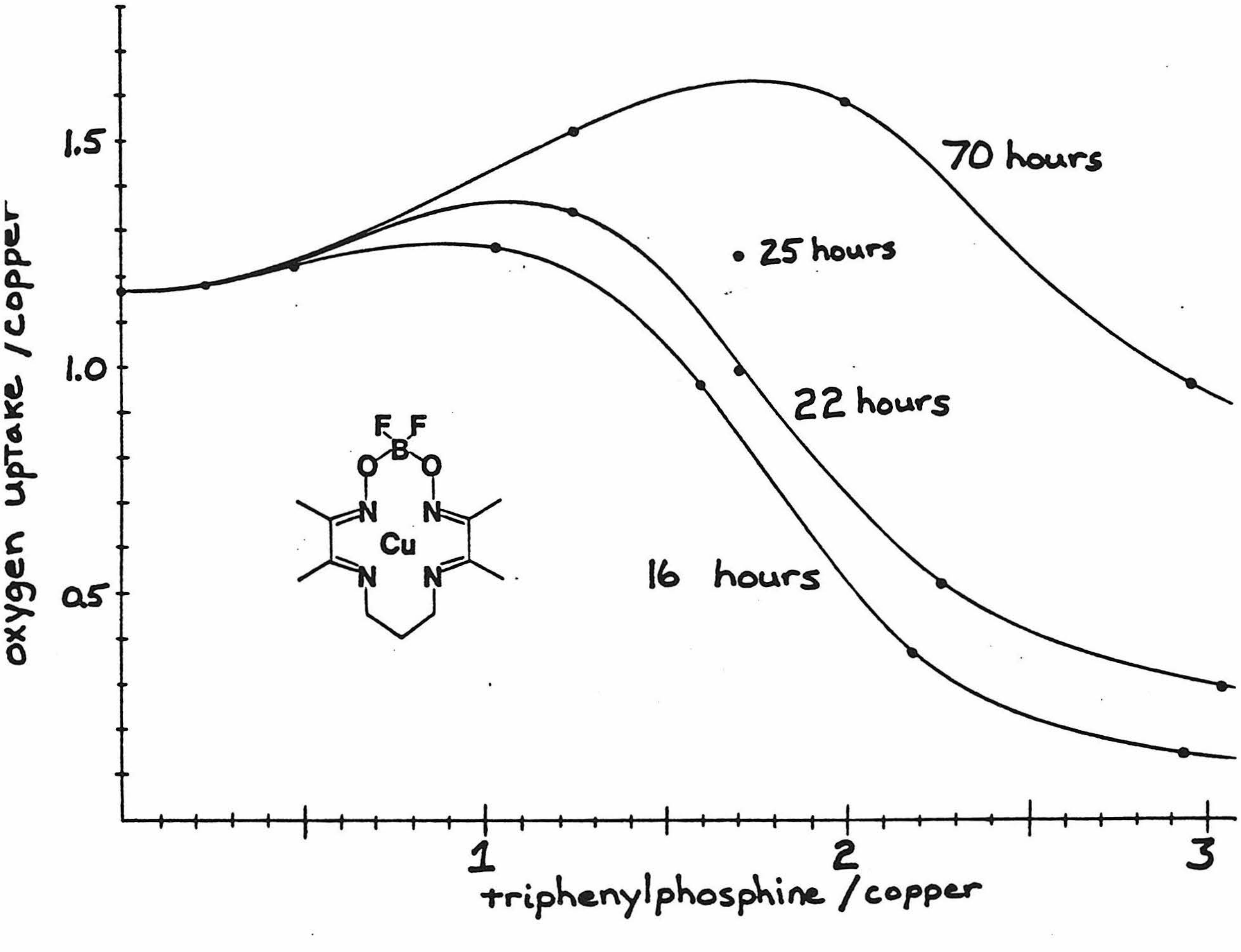
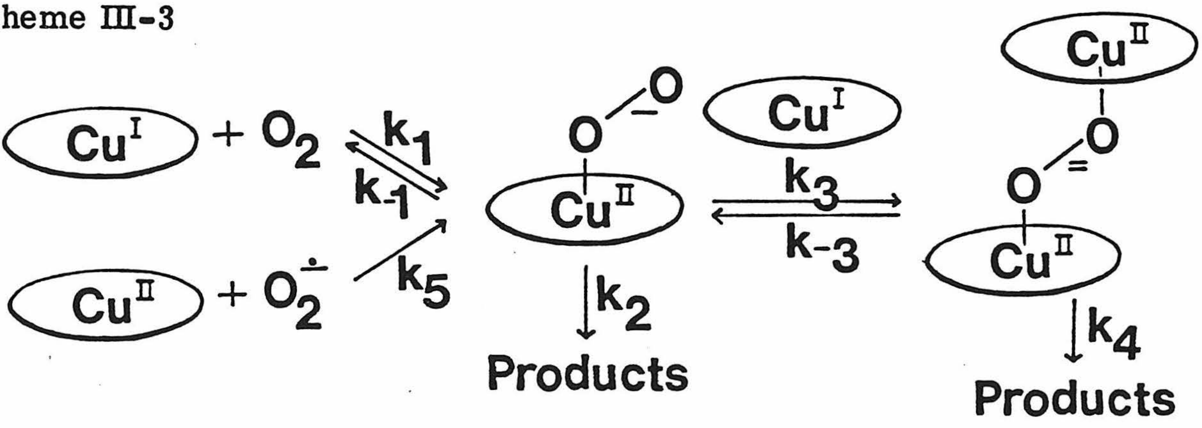


Fig. III-8. Dioxygen per copper stoichiometry of $CuLBF_2$, 1, versus triphenylphosphine per copper present. The different curves are for the same concentrations but different reaction durations.

bridges to the bis-dimethylglyoxime complex, 5 (Fig. III-1), react much slower than $CuLBF_2$, 1, with dioxygen. Dichloromethane solutions of these complexes stay the deep-blue color of the copper(I) complex for over an hour in the presence of dioxygen and are blue well past the first equivalent of dioxygen consumed. The blue color is gone from $CuLBF_2$, 1, solutions within seconds after the addition of dioxygen. Although the oxygen uptake is slower, the amount of oxygen taken up is greater for 3 and 5 than for $CuLBF_2$, 1 (for example, see Fig. III-9).

Alternatively, the copper(II) macrocycles may be reacted with potassium superoxide. The dimethylglyoxime and diaminobutane derivatives give the intense blue color of the copper(I) oxidation state on treatment with potassium superoxide, but $Cu(II)LBF_2ClO_4$ gives the brown color of the oxygenation product. These observations require expanding Scheme III-2 to Scheme III-3. For the dimethylglyoxime and

Scheme III-3



diaminobutane derivatives k_{-1} must be at least competitive with k_2 for

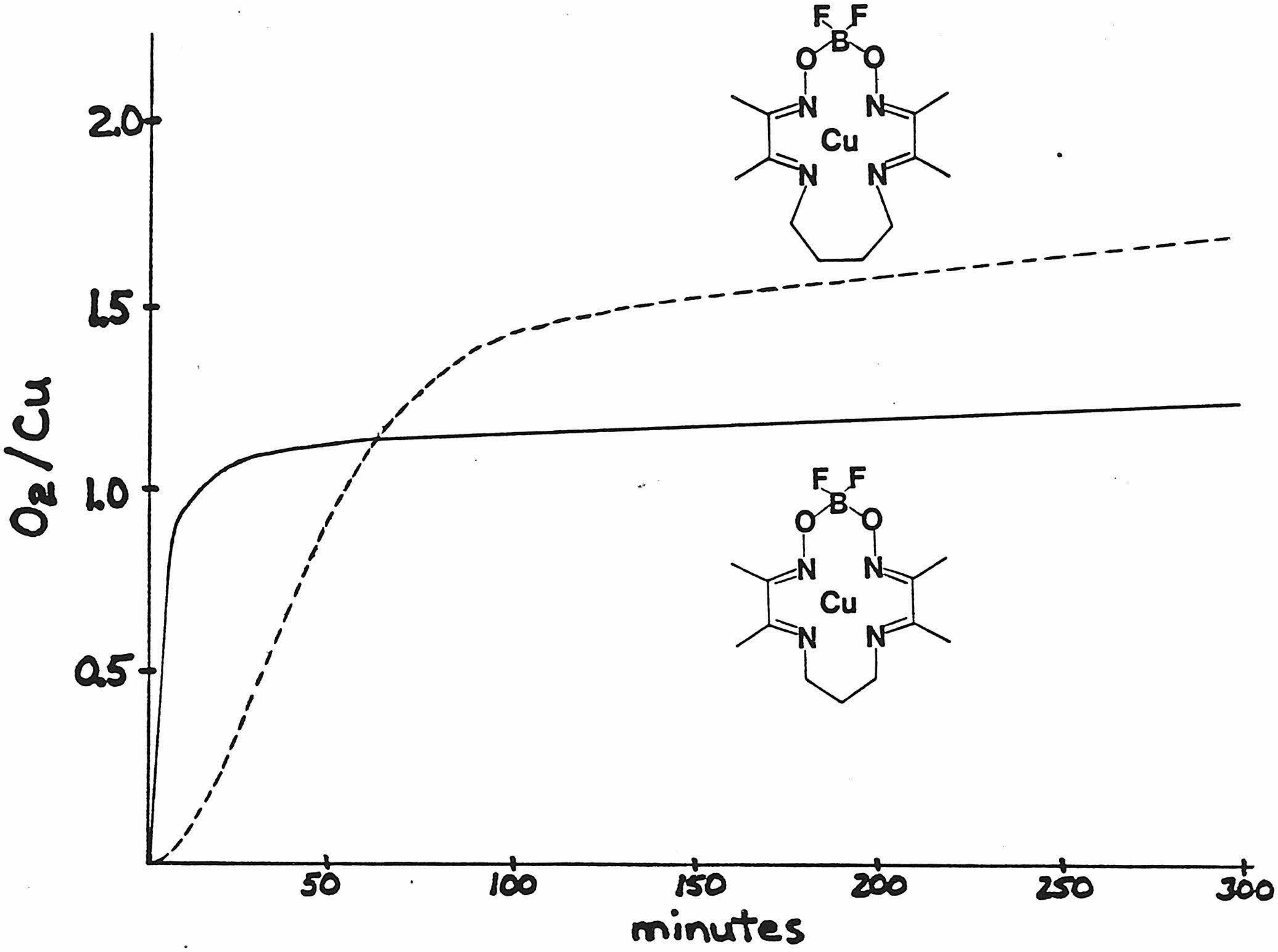


Fig. III-9. Dioxygen uptakes in dichloromethane solution at constant pressure (atmospheric) as a function of time. The solid curve is that found for $CuLBF_2$, 1, and the dashed curve is that found for the diaminobutane derivative, 3. Note that the reaction of 3 with dioxygen is much slower.

the copper(I) complex to be observed.

CuLBF$_2$, 1, Ligand Modification

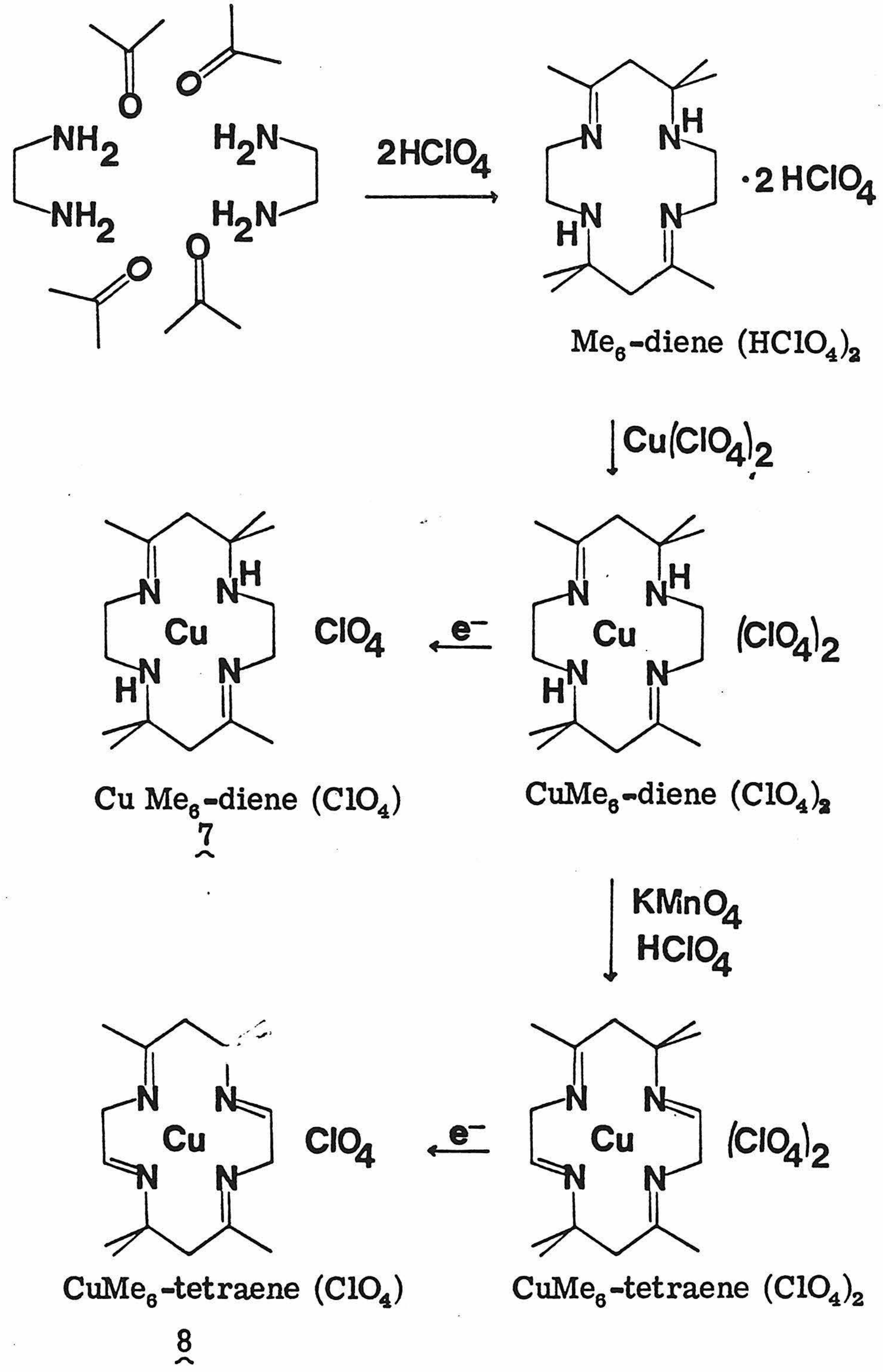
On the basis of other macrocycle oxidations (see Chapter One), ketonation was suspected as one of the macrocycle decomposition products. CuLBF$_2$ macrocycle decomposition upon oxygenation involving the center carbon can be ruled out by the similar dioxygen reactions of the macrocycle synthesized from 2,2-dimethyl-1,3-diaminopropane, 2 (Fig. III-1). The comparison between the diaminopropane, 1, and diaminobutane, 3, derived macrocycles is somewhat questionable due to the differing reaction rates. Nevertheless, the lack of a dioxygen reaction for the macrocycle derived from 1,1,4,4-tetramethyl-1,4-diaminobutane, 4 (Fig. III-1), implicates the saturated carbon atoms next to the nitrogen atoms as the culprits. It has proved impossible to synthesize the 1,1,3,3-tetramethyl-1,3-diaminopropane necessary to verify this hypothesis.[8]

Cu(I)Me$_6$-tetraene(ClO$_4$), 8

Different macrocyclic systems were considered for study since the CuLBF$_2$ ligand substitution possibilities were exhausted. The macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene (shown as the copper(I) complex, 8, in Fig. III-1), has two desirable traits for an oxygenation study. The macrocycle has undergone all the oxidative dehydrogenation possible (see Chapter One) and further substituted macrocyles can be envisioned (vide infra). One drawback was that neither the copper(I) nor the copper(II) complex had been synthesized previously.

Condensation of four acetone and two ethylenediamine in the presence of two equivalents of perchloric acid yields the Me_6diene macrocycle as the dihydroperchlorate (Scheme III-4), and has the advantage of giving only the trans diene isomer.[9-11] (Template reactions of acetone with ethylenediamine complexes of nickel(II) and copper(II) give several isomeric macrocyclic products).[9,12-17] Reaction of the ligand dihydroperchlorate with copper(II) yields the Cu(II)Me_6-diene$(ClO_4)_2$ complex (Scheme III-4). As shown in Scheme III-4, a chemical oxidation procedure to convert Cu(II)Me_6-diene$(ClO_4)_2$ to Cu(II)Me_6-tetraene$(ClO_4)_2$ has now been found. Treatment of Cu(II)Me_6-diene$(ClO_4)_2$ with excess permanganate in a perchloric acid solution oxidatively dehydrogenates the ligand and yields the salmon-colored copper diperchlorate complex. Cu(II)Me_6-tetraene$(ClO_4)_2$ does not have N—H stretching bands in the infrared spectrum at 3220 cm^{-1} as does the Cu(II)Me_6-diene$(ClO_4)_2$, and the new imine groups result in a band at 1656 cm^{-1} in addition to that found in Cu(II)Me_6-diene$(ClO_4)_2$ at 1672 cm^{-1} (Fig. III-10). The reduction of copper(II) to copper(I) is again done electrochemically in acetone, but the soluble Cu(I)Me_6-tetraene(ClO_4) requires careful addition of toluene to induce precipitation of the dark-red solid. The Me_6-tetraene identity of the ligand is conclusively demonstrated by the proton magnetic resonance spectrum. Similar spectra have been observed for [Ni(II)Me_6-tetraene]$(ClO_4)_2$,[18] [Fe(II)Me_6-tetraene-$(CH_3CN)_2$]$(ClO_4)_2$,[19] and [Co(III)Me_6-tetraeneBr_2](ClO_4).[19] The

Scheme III-4



NH$_2$
H$_2$N
O
2HClO$_4$
·2 HClO$_4$
Me$_6$-diene (HClO$_4$)$_2$
Cu(ClO$_4$)$_2$
e$^-$
Cu
ClO$_4$
(ClO$_4$)$_2$
Cu Me$_6$-diene (ClO$_4$)
7
CuMe$_6$-diene (ClO$_4$)$_2$
KMnO$_4$
HClO$_4$
CuMe$_6$-tetraene (ClO$_4$)
8
CuMe$_6$-tetraene (ClO$_4$)$_2$

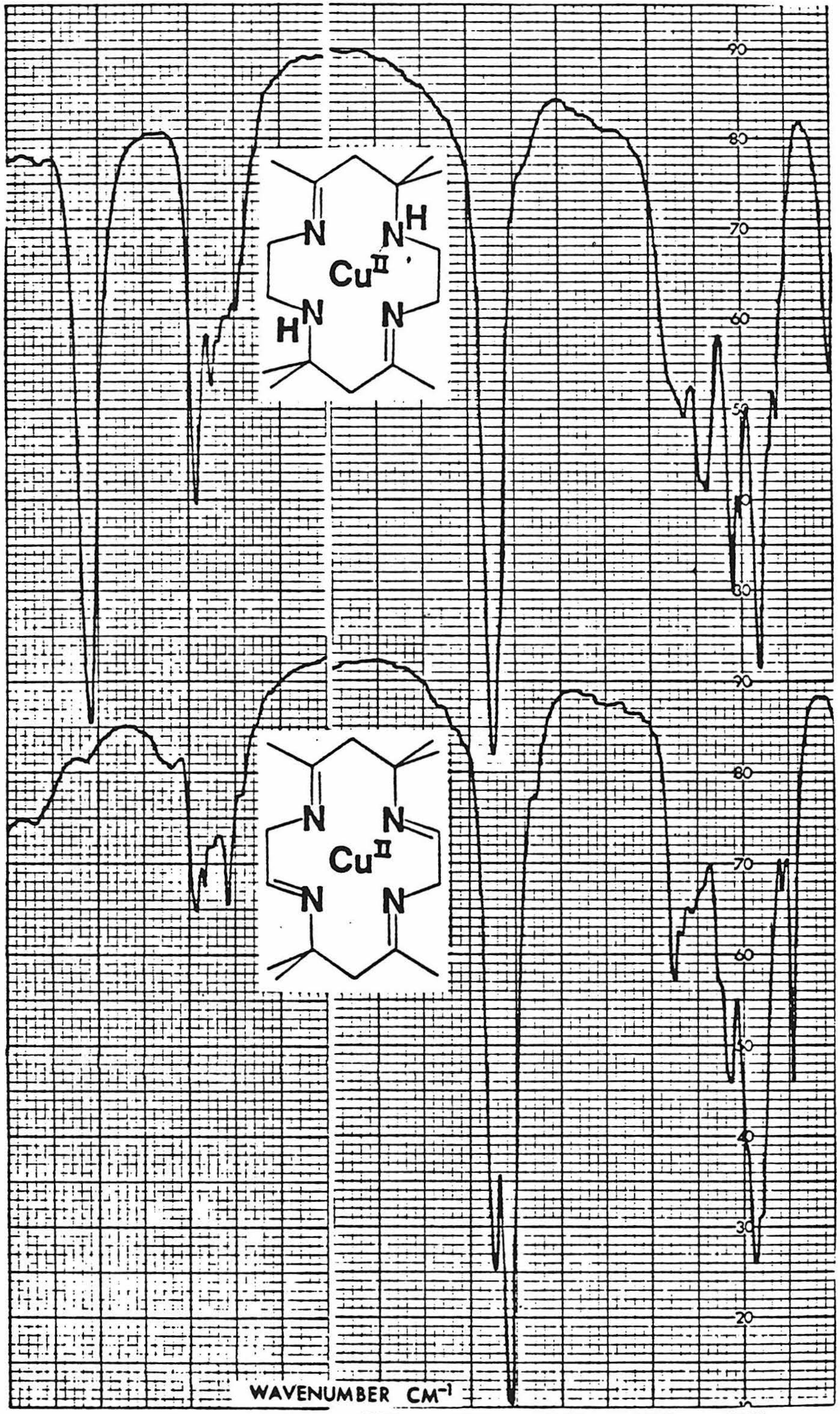


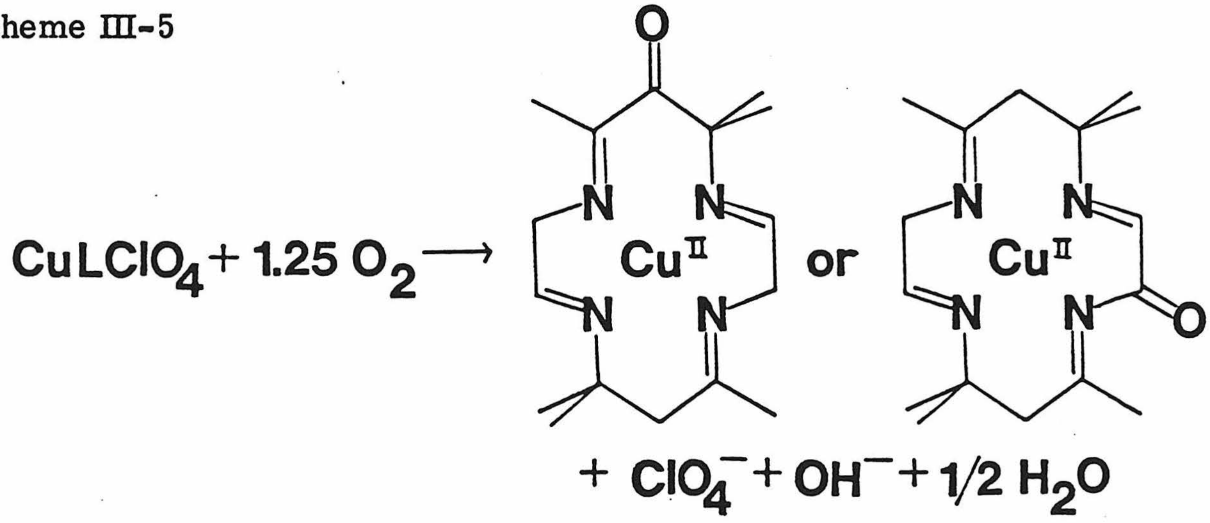
Fig. III-10. Infrared spectra in the regions 1300 to 1850 cm^{-1} and 2700 to 3600 cm^{-1} of Cu(II)Me_6-diene $(ClO_4)_2$ (top) and Cu(II)Me_6-tetraene $(ClO_4)_2$ (bottom).

copper(I) and nickel(II) proton magnetic resonance spectra are shown in Fig. III-11. The spectra are simpler than for the diene complexes;[20] oxidation of Me_6-diene to Me_6-tetraene removes the asymmetric atoms, and the chelate rings appear to undergo rapid flexing giving equivalent gem methyl groups.

Dioxygen Reactions of Cu(I)Me_6-tetraene(ClO_4), 8

Upon addition of dioxygen to dichloromethane solutions of Cu(I)Me_6-tetraene(ClO_4), the orange-red solution turned green and a brown product precipitated in greater than 80% yield by weight. Magnetic susceptibility measurements (25°, Faraday method), indicate copper(II) was formed, as $\mu = 1.6\text{-}1.7$ β.M.. The oxygenated product produced in a fairly clean reaction is the result of ketonation of the macrocycle (Scheme III-5), based on the following observations. 1) The electron

Scheme III-5



paramagnetic resonance spectrum of Cu(II)Me_6-tetraene$(ClO_4)_2$ in frozen propylene carbonate solution shows good resolution and superhyperfine detail (Fig. III-12). The same spectrum is also obtained

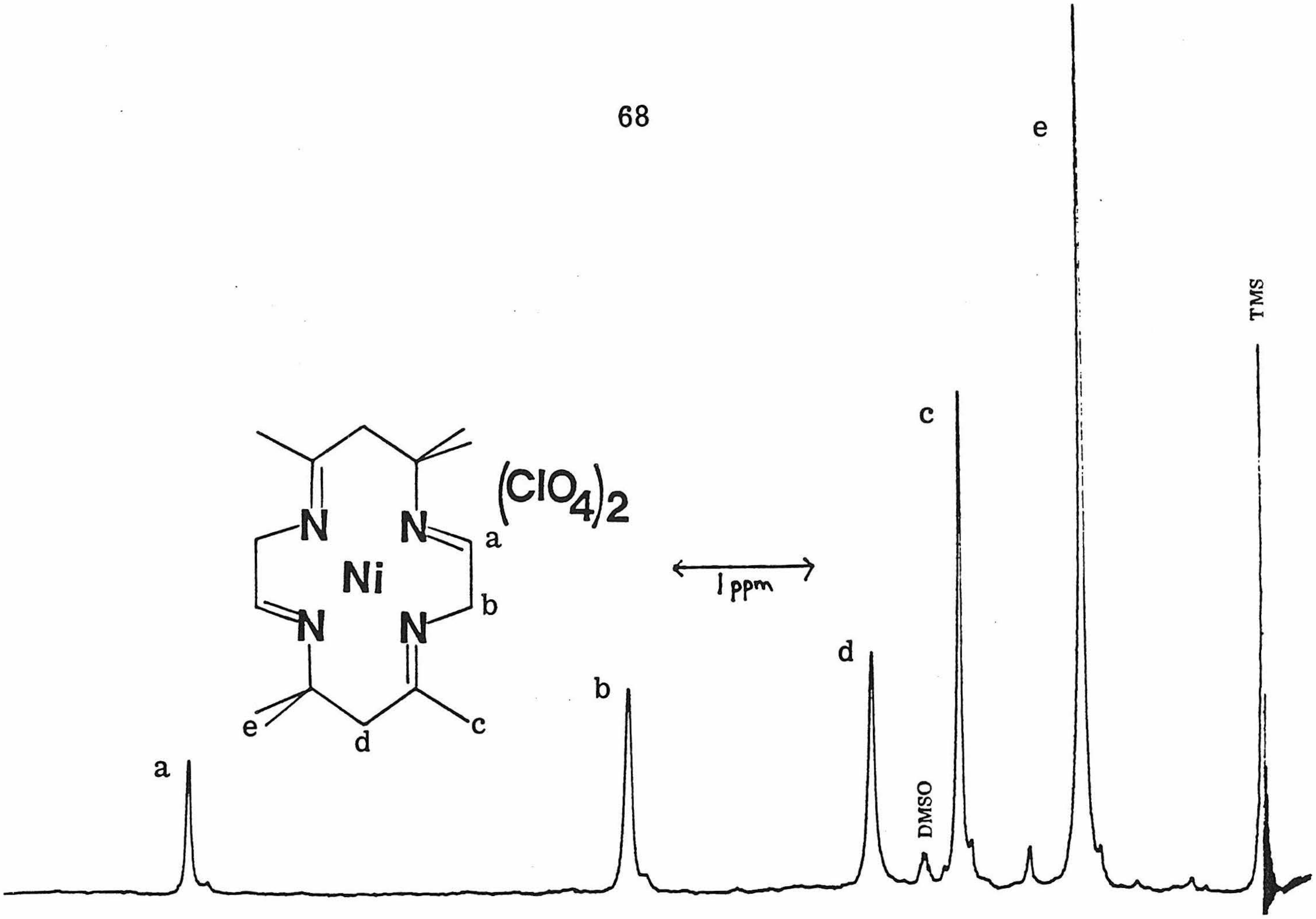
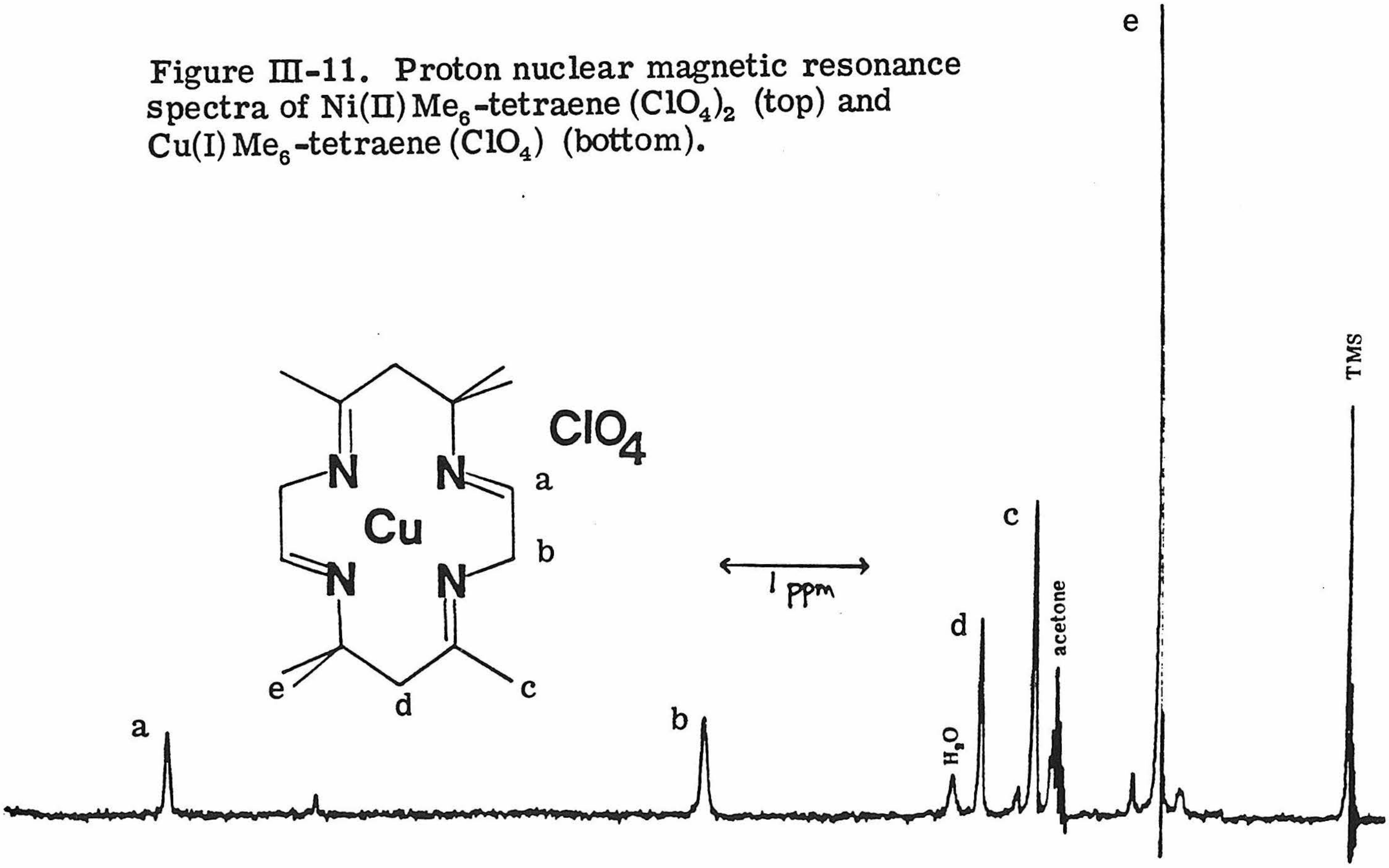


Figure III-11. Proton nuclear magnetic resonance spectra of Ni(II) Me$_6$-tetraene (ClO$_4$)$_2$ (top) and Cu(I) Me$_6$-tetraene (ClO$_4$) (bottom).



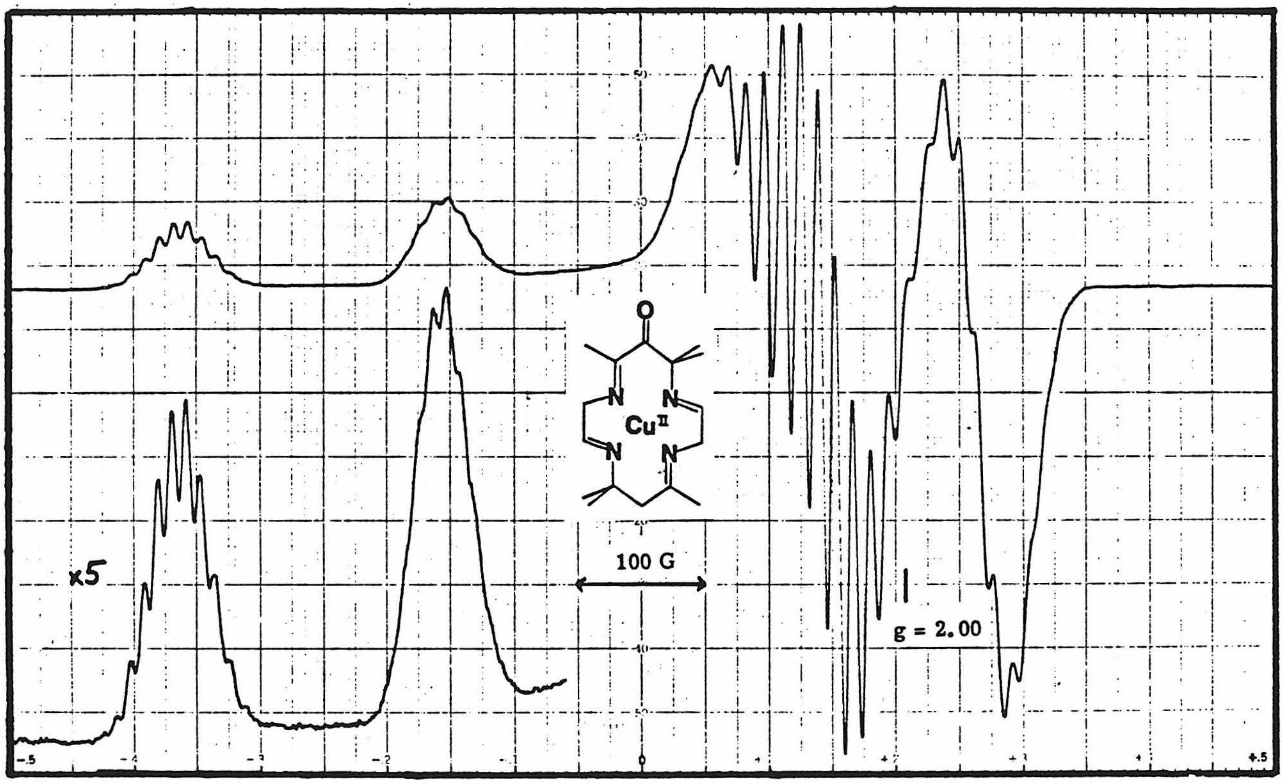


Fig. III-12. Electron paramagnetic resonance spectrum obtained in frozen propylene carbonate solution of Cu(II) Me_6-tetraene $(ClO_4)_2$ or Cu(I) Me_6-tetraene (ClO_4) reacted with dioxygen under a variety of conditions (see text).

in frozen $^{16}O_2$ and $^{17}O_2$ treated propylene carbonate solutions of Cu(I)Me_6-tetraene(ClO_4), **8**, as well as frozen propylene carbonate solutions of the product of the reaction of dioxygen with solid **8** and the precipitate from the reaction of dioxygen with **8** in dichloromethane solution at -79°. Thus the coordination around the copper atom has not changed and the product under a variety of conditions is uniform. 2) The infrared spectrum of the oxygenated solid Cu(I)Me_6-tetraene(ClO_4), **8**, or the precipitate upon oxygenation in dichloromethane at -79°, has new bands at 1580 and 1620 cm^{-1} in comparison with Cu(II)Me_6-tetraene$(ClO_4)_2$. The Me_6 ligand, even after having been previously treated with permanganate and perchloric acid, has been further oxidized! Both of these bands shift 5-10 cm^{-1} when $^{18}O_2$ is used instead of normal abundance dioxygen (Fig. III-13). (The observed frequencies as well as the shift upon isotopic substitution are low for a pure carbonyl vibration. The carbonyl vibration must be part of a larger vibration both decreasing the frequency and lessening the shift upon isotopic substitution).

3) Cu(I)Me_6-tetraene(ClO_4) irreversibly takes up 1.25 ± 0.05 dioxygen per copper atom in dichloromethane solution at -79°. The same irreversible stoichiometry is obtained for the solid at room temperature. Elemental analyses of the oxygenated solids confirm both oxygen incorporation and the 1.25 dioxygen per copper atom stoichiometry. (Calcd for CuMe_6-tetraene(ClO_4) + 1.25 O_2 : C, 40.09; H, 5.89; N, 11.69. Found: C, 39.95; H, 5.50; N, 11.55). 4) Conductivity measurements show the product is a 2:1 electrolyte for a molecular

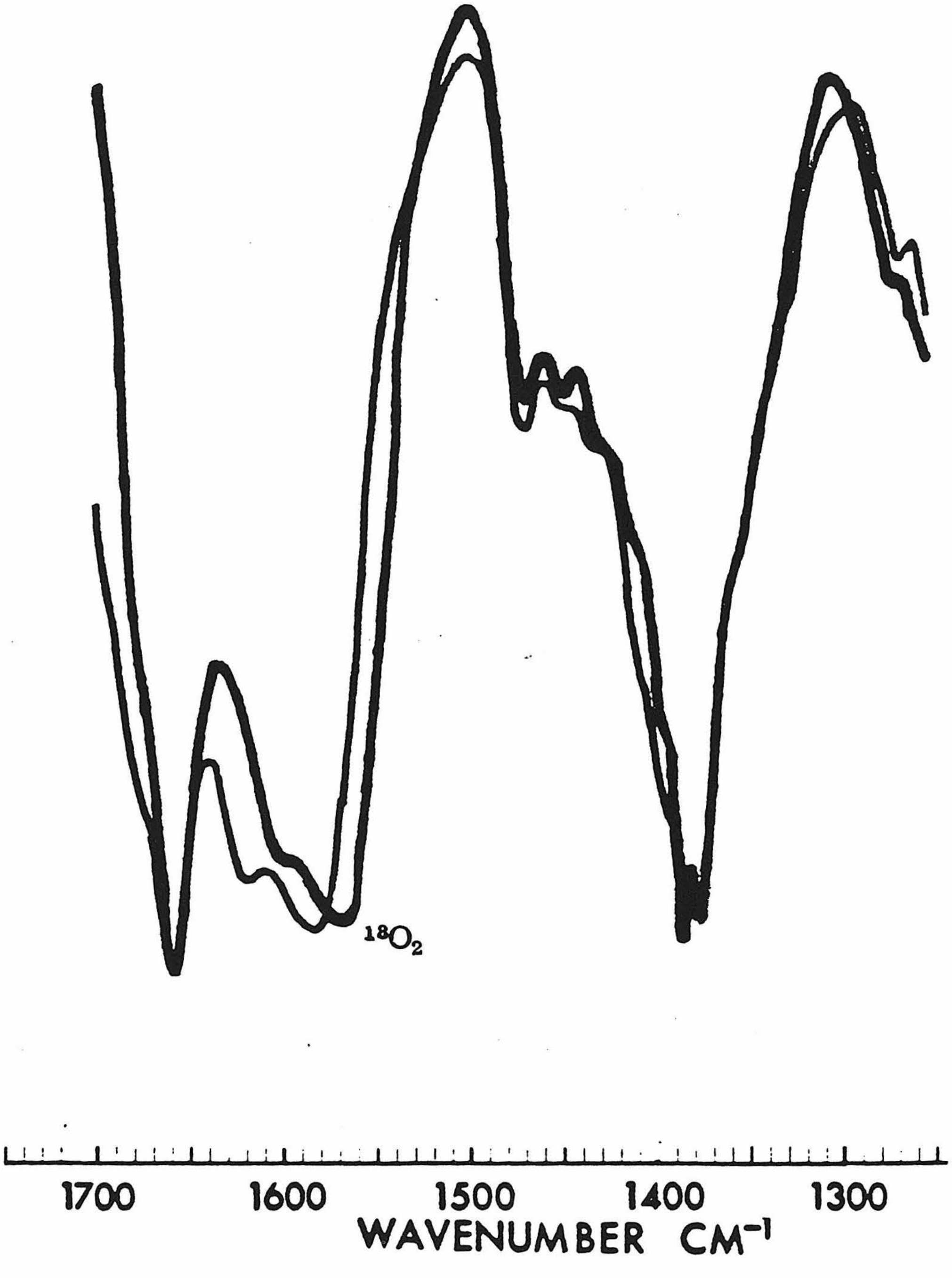


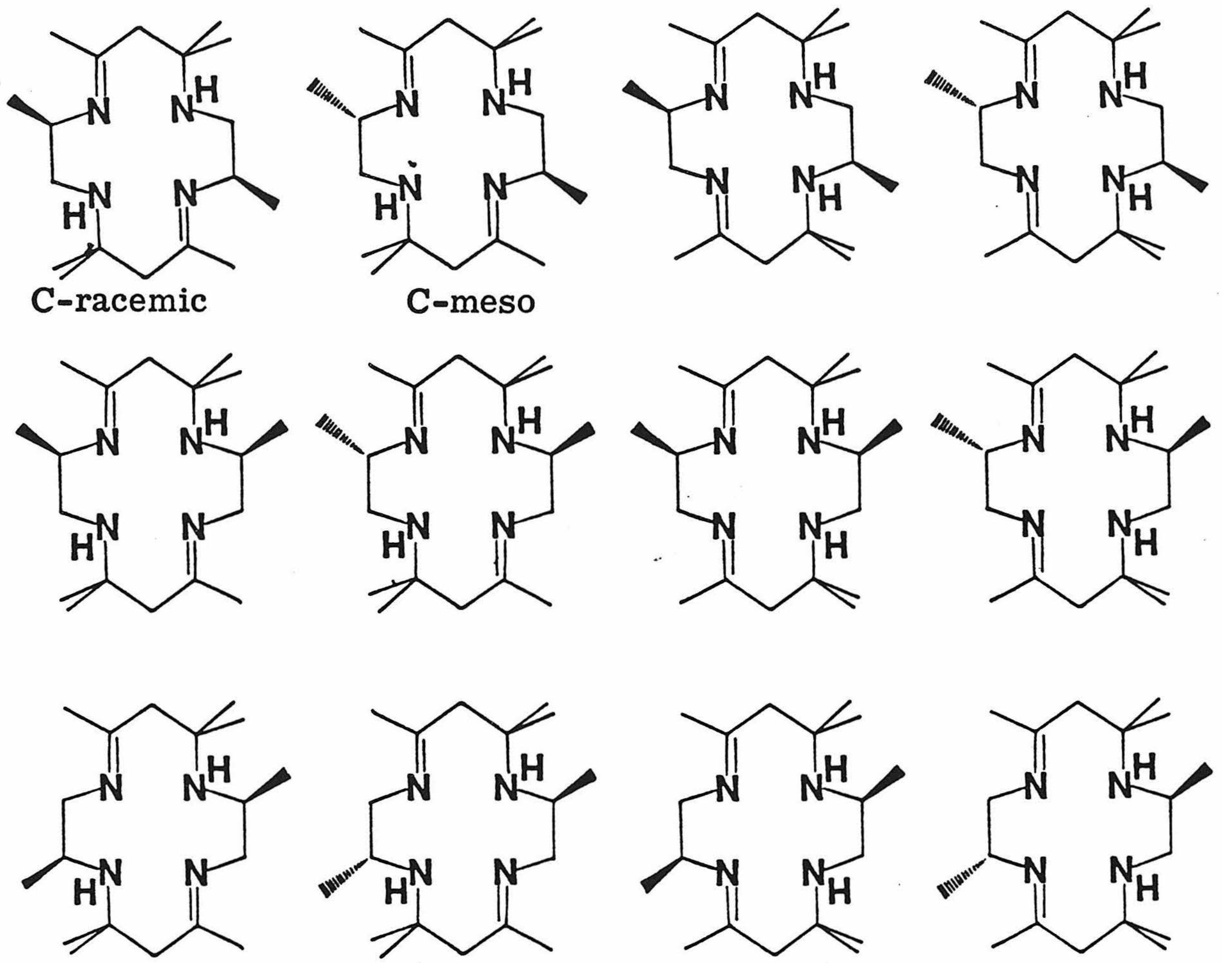
Fig. III-13. Superimposed infrared spectra of the $^{16}O_2$ and $^{18}O_2$ product with Cu(I)Me$_6$-tetraene(ClO$_4$).

weight of about 490 mass units, determined by a plot of the equivalent conductance versus the square root of the equivalent concentration giving a slope of -608 in methanol and -425 in nitromethane.[21] The products are not bridging oxo or hydroxide species. The solubility in other polar organic solvents also supports non-polymeric products.

Ligand Modification of CuMe$_6$-tetraene(ClO$_4$), 8

For Me$_6$-tetraene there are two possible positions for the ketone (Scheme III-5). The ketonation could be blocked by methyl substitution at those positions. Use of 2,3-diaminobutane in place of ethylenediamine in an attempted macrocycle dihydroperchlorate synthesis gave no reaction. Similar template syntheses have previously been reported to be unsuccessful.[13,22]

Template reactions of acetone with 1,2-diaminopropane complexes of nickel(II) and copper(II) give isomeric macrocyclic products.[13,22-24] These isomers could include the cis and trans diene isomers observed for Me$_6$-diene, and cis and trans isomers of the two additional methyl groups, not to mention the C-racemic and C-meso isomers associated with the two asymmetric carbon centers of the diaminopropane residues and the isomers associated with the amine nitrogen atoms (Fig. III-14). Fortunately, only the C-meso C-trans trans-diene (C_i) and C-racemic C-trans trans-diene (perpendicular C_2) isomers have been observed (Fig. III-14, upper left). The C-trans and trans-diene configuration is confirmed by a study of the proton magnetic resonance spectra of the nickel(II) complexes.[25] The crystallographic space group requires the C-meso isomer to be centrosymmetric. A complete



C-racemic

C-meso

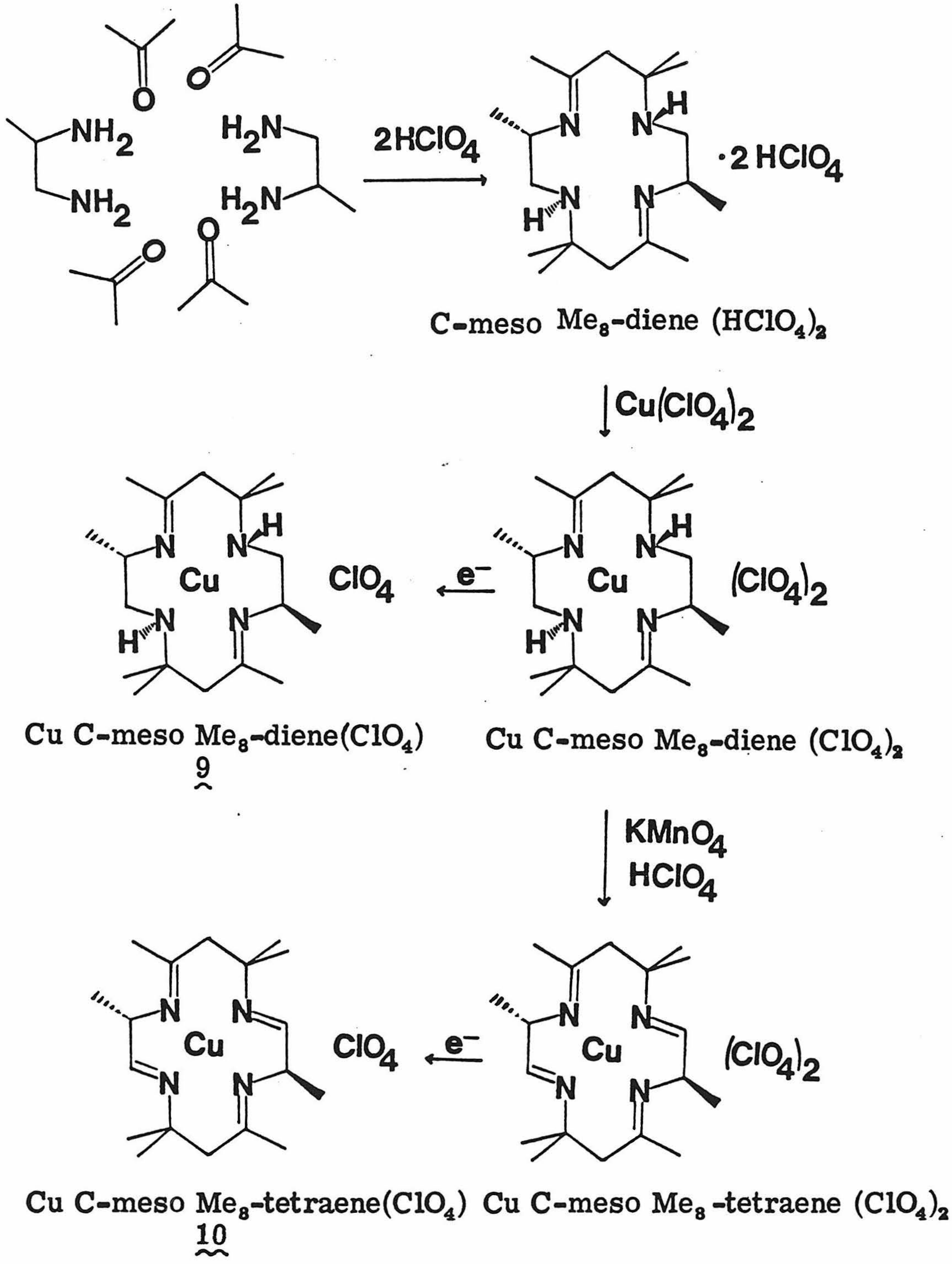
Fig. III-14. Possible isomers from the 1, 2-diaminopropane acetone condensation (N-H isomers ignored).

crystallographic structure has been determined for the C-racemic isomer.[23,26]

Condensation of four acetone and two 1,2-diaminopropane in the presence of two equivalents of perchloric acid slowly yields the Me_8-diene dihydroperchlorate and has the advantage of giving the 3,10-methyl substituted C-meso isomer exclusively (Scheme III-6),[9,23,24] as confirmed by comparison of the published proton magnetic resonance spectra of the orange nickel(II) complexes.[25] The C-meso dihydroperchlorate macrocycle will also yield C-meso copper complexes. Treatment of the purple $Cu(II)Me_8$-diene$(ClO_4)_2$ complex with excess permanganate and perchloric acid gave salmon colored $Cu(II)Me_8$-tetraene$(ClO_4)_2$. Reduction of the copper(II) compound to copper(I) was achieved electrochemically in acetone and the dark-red product isolated by careful addition of toluene. For Me_8-tetraene, the gem methyl groups are no longer equivalent as can be seen in the proton magnetic resonance spectra of the copper(I) and nickel(II) perchlorate complexes (Fig. III-15).

Reaction of $Cu(I)Me_8$-tetraene(ClO_4), 10, as a solid or at -78° in dichloromethane solution with dioxygen, gave stoichiometries of 1.25 dioxygen per copper atom and brown products, just as found for $Cu(I)Me_6$-tetraene(ClO_4), 8. The electron paramagnetic resonance spectra of oxygenated $Cu(I)Me_8$-tetraene(ClO_4), 10, produced under various conditions are also identical with those for oxygenated $Cu(I)Me_6$-tetraene(ClO_4), 8. The infrared spectrum of the oxygenated $Cu(I)Me_8$-tetraene(ClO_4), 10, contains only the band at 1580 cm^{-1} and not the band at 1620 cm^{-1}. The 1580 cm^{-1} band shifts when $^{18}O_2$ is used

Scheme III-6



C-meso Me$_8$-diene (HClO$_4$)$_2$

Cu C-meso Me$_8$-diene(ClO$_4$)
9

Cu C-meso Me$_8$-diene (ClO$_4$)$_2$

Cu C-meso Me$_8$-tetraene(ClO$_4$)
10

Cu C-meso Me$_8$ -tetraene (ClO$_4$)$_2$

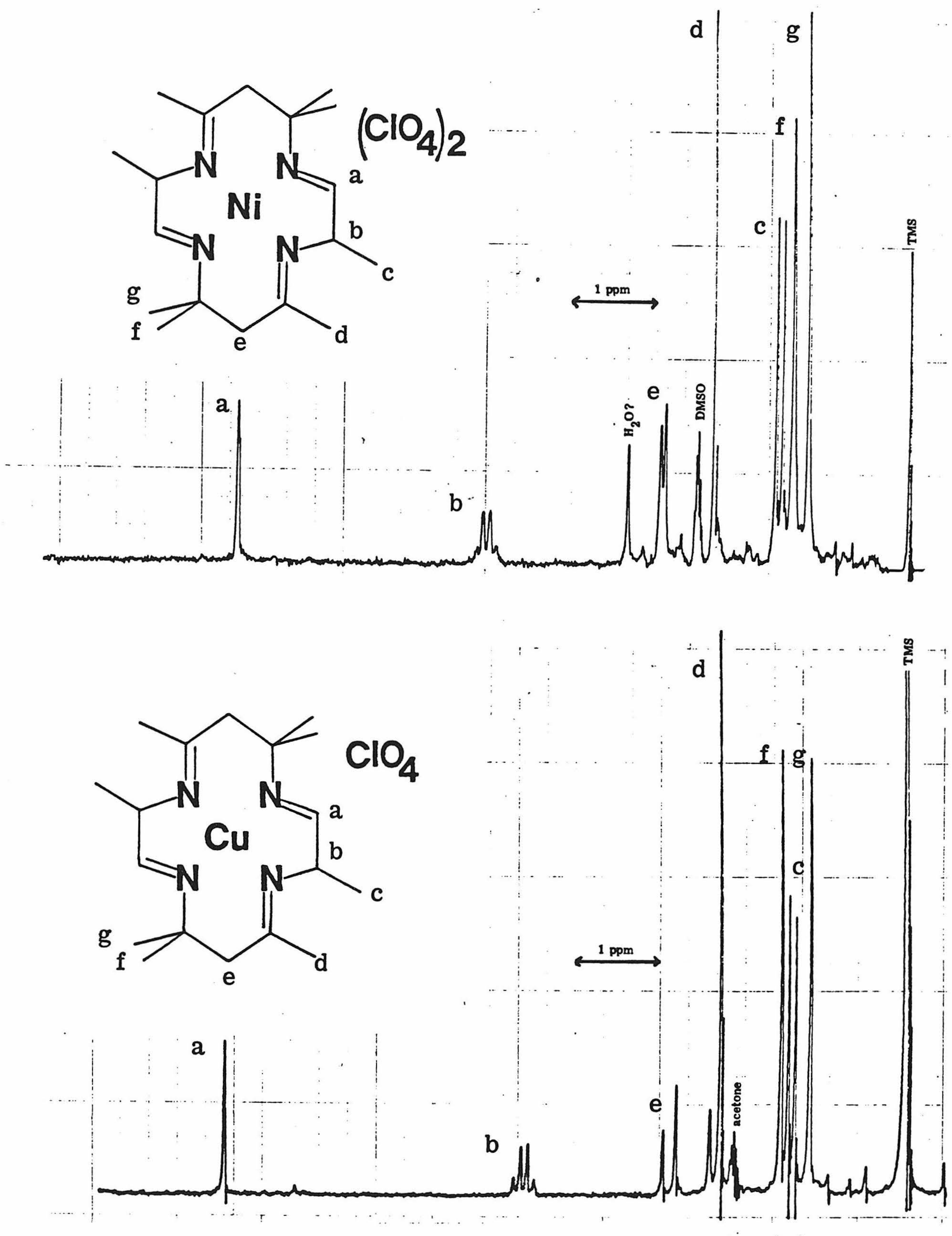


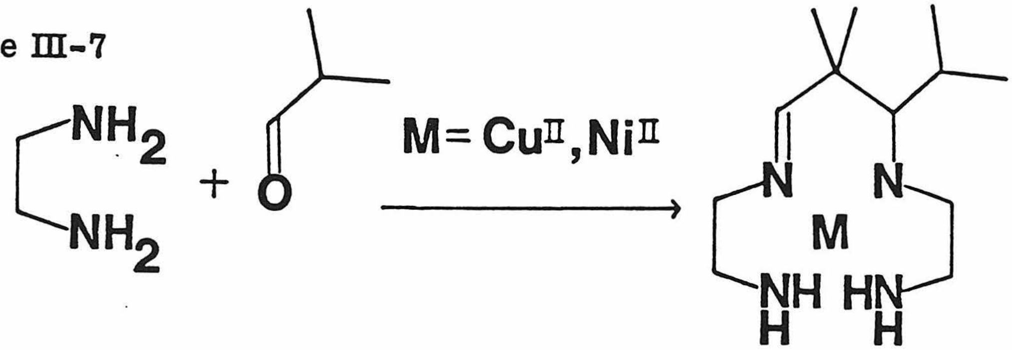
Fig. III-15. Proton nuclear magnetic resonance spectra of Ni(II) Me_8-tetraene $(ClO_4)_2$ (top) and Cu(I) Me_8-tetraene (ClO_4) (bottom).

(Fig. III-16). As predicted there is only one possible site for ketonation in Me$_8$-tetraene since only one band appears in the 1600 cm^{-1} region. That band shifts with $^{18}O_2$ substitution.

For the macrocyclic ligands the mechanism in dichloromethane must include copper(I) being oxidized to copper(II), such that any given macrocycle is only oxidized once. This is necessary in order to be consistent with the stoichiometry. The presence of added copper(II) macrocycle as a substrate in no case increased the stoichiometry value. The two new bands observed in the infrared spectrum of oxygenated Cu(I)Me$_6$-tetraene(ClO$_4$) have a somewhat variable relative intensity. This agrees with only one ketone per macrocycle and a random choice between the two positions. The new band upon oxygenation of Cu(I)Me$_8$-tetraene(ClO$_4$), **10**, does not exhibit variable intensity.

Ligand modification at the last remaining position of attack is difficult. A template synthesis using isobutyraldehyde is known to give the half condensed ligand but not the macrocycle (Scheme III-7).[27]

Scheme III-7



A synthesis using isobutyraldehyde, ethylenediamine, and perchloric acid was attempted. After reacting together for several weeks a small amount of product was obtained which proved to be Me$_6$-diene(HClO$_4$)$_2$! It does not seem likely that the last position can be blocked on the

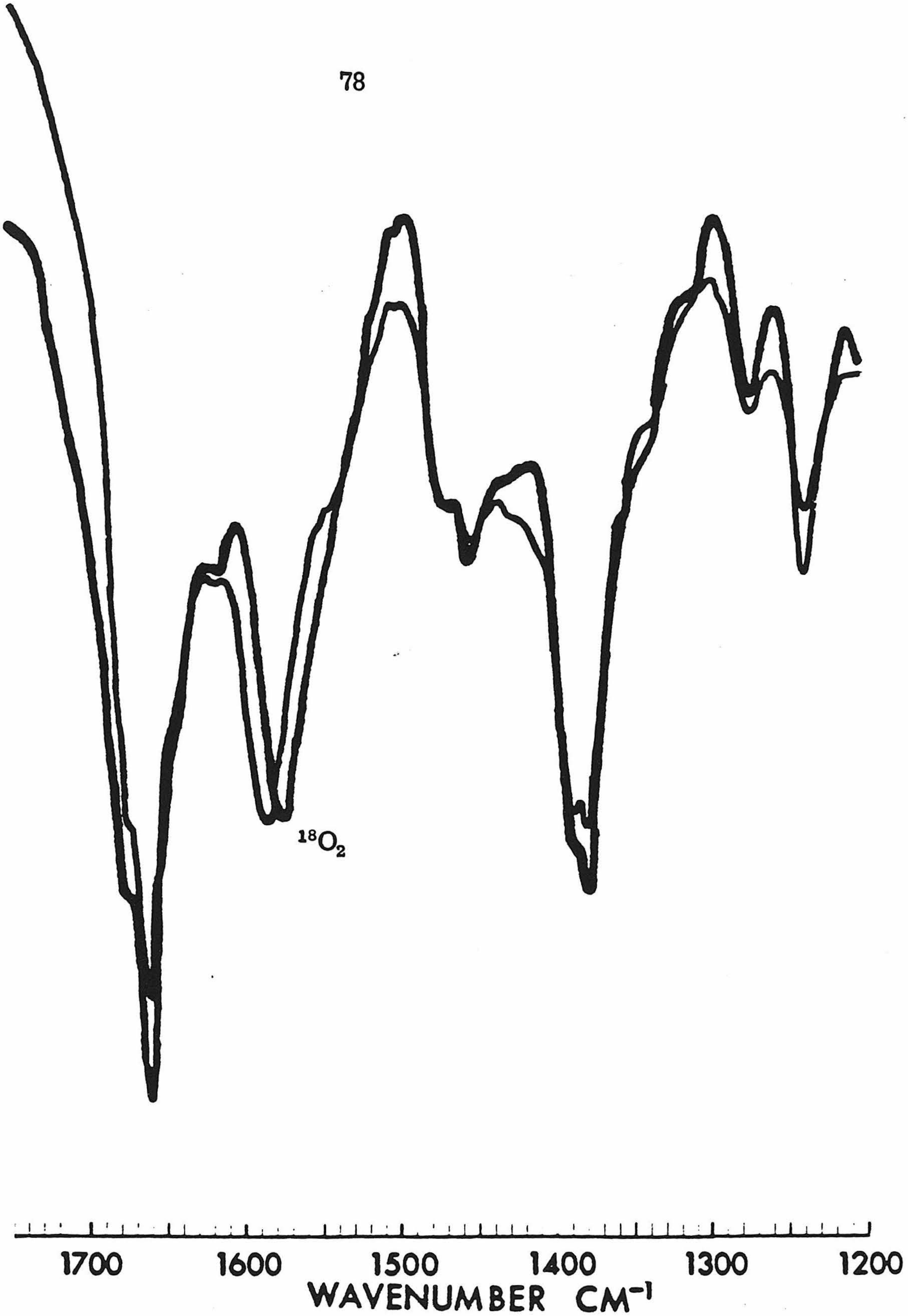


Fig. III-16. Superimposed infrared spectra of the $^{16}O_2$ and $^{18}O_2$ product with Cu(I)Me$_8$-tetraene(ClO$_4$).

macrocycle by this route.

Dioxygen Reactions of Cu(I)Me_6-diene(ClO_4), 7, and Cu(I)Me_8-diene(ClO_4), 9

Both copper(I) complexes 7 and 9 (Fig. III-1) can be prepared by electrochemical reduction in acetone of the corresponding copper(II) complexes and the mono-acetone solvate recovered by filtration. At room temperature both solids absorb dioxygen while slowly changing from yellow to green to purple. Magnetic susceptibility measurements (25°, Faraday method) identify a copper(II) product with $\mu = 1.80$ β.M. for 7 and $\mu = 1.76$ β.M. for 8. A significant change in the macrocycle can be seen by comparing the infrared spectra of the copper(II) complexes with the oxygenated copper(I) complexes. The N-H stretching bands have decreased in intensity in both. Two new bands have appeared near 1600 cm^{-1} for Cu(I)Me_6-diene(ClO_4), 7, but only one band is present for Cu(I)Me_8-diene(ClO_4), 8. The infrared evidence suggests that the diene ligands undergo both partial oxidative dehydrogenation and ketonation.

Preliminary Examination of Dioxygen Reaction with Ni(I)Me_8-tetraene(ClO_4)

Ni(I)Me_8-tetraene(ClO_4) was synthesized by the nitric acid oxidation of Ni(II)Me_8-diene$(ClO_4)_2$ to the tetraene, followed by electrochemical reduction in acetonitrile. The black Ni(I)Me_8-tetraene(ClO_4) obtained on slow addition of toluene is extremely oxygen sensitive and reacts in acetonitrile-toluene solution with dioxygen at less than 5 ppm in our helium atmosphere glove boxes. The successful synthesis involved electrochemical reduction in the glove box and transfer of the solution to a high vacuum line for precipitation of the solid. The nickel(I) complex reacts rapidly with dioxygen in the solid state, becoming brown within seconds after air exposure. The oxygenated products have a new band at 1580 cm^{-1} in the infrared spectrum in comparison with Ni(II)Me_8-tetraene$(ClO_4)_2$. This band shifts upon $^{18}O_2$ substitution just as found for the copper(I) complex (Fig. III-17). Examination of the nickel complexes was designed to give further proof of ketonation by the distinctive ^{13}C nuclear magnetic resonance chemical shift of a ketone carbon. Unfortunately, a substantial amount of paramagnetic material is present in the oxygenated complex and no nuclear magnetic resonance spectra could be obtained.

Discovery of a Copper(I) Complex, 6, Which Does Not React With Dioxygen

A tetradentate ligand derived from the bis(pyridine-2-aldoxime) complex by addition of a boron difluoride bridge is closely related to the tetradentate macrocyclic complexes. The copper(I) complex, 6, (Fig. III-1), was isolated by filtration after the one-electron reduction of the copper(II) complex in acetonitrile. Successful copper(I) synthesis is confirmed by the proton nuclear magnetic resonance spectrum (Fig. III-18). This copper(I) complex, 6, gave a most surprising reaction with dioxygen. It didn't. No uptake was observed by difference on the Toepler pump after 48 hours in dichloromethane. The visible spectrum of methanol, acetonitrile, and acetone solutions are not changed upon addition of dioxygen. Cyclic voltammograms of the copper(I) complex, 6, are unaffected by the presence of dioxygen.

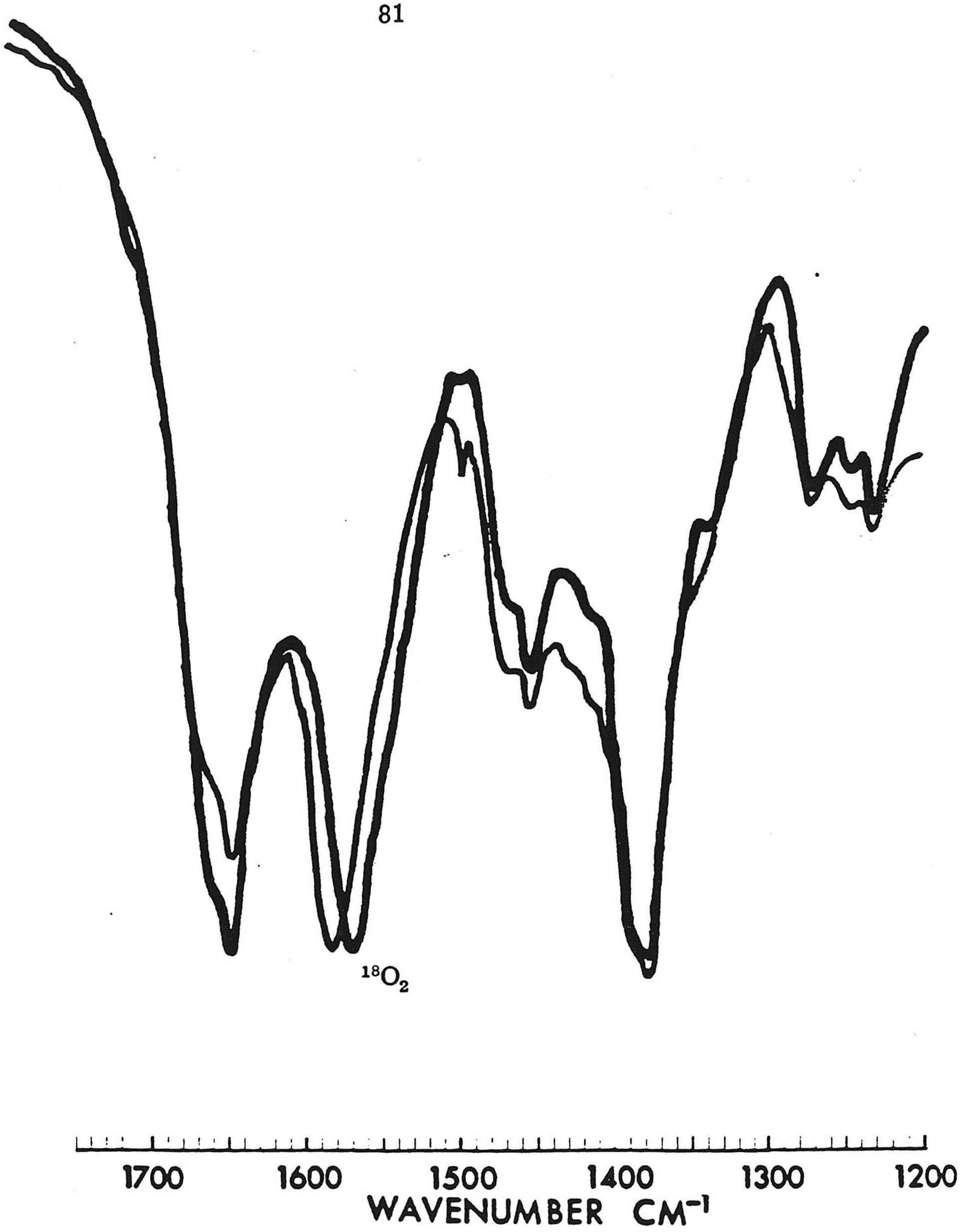


Fig. III-17. Superimposed infrared spectra of the $^{16}O_2$ and $^{18}O_2$ product with Ni(I)Me$_8$-tetraene(ClO$_4$).

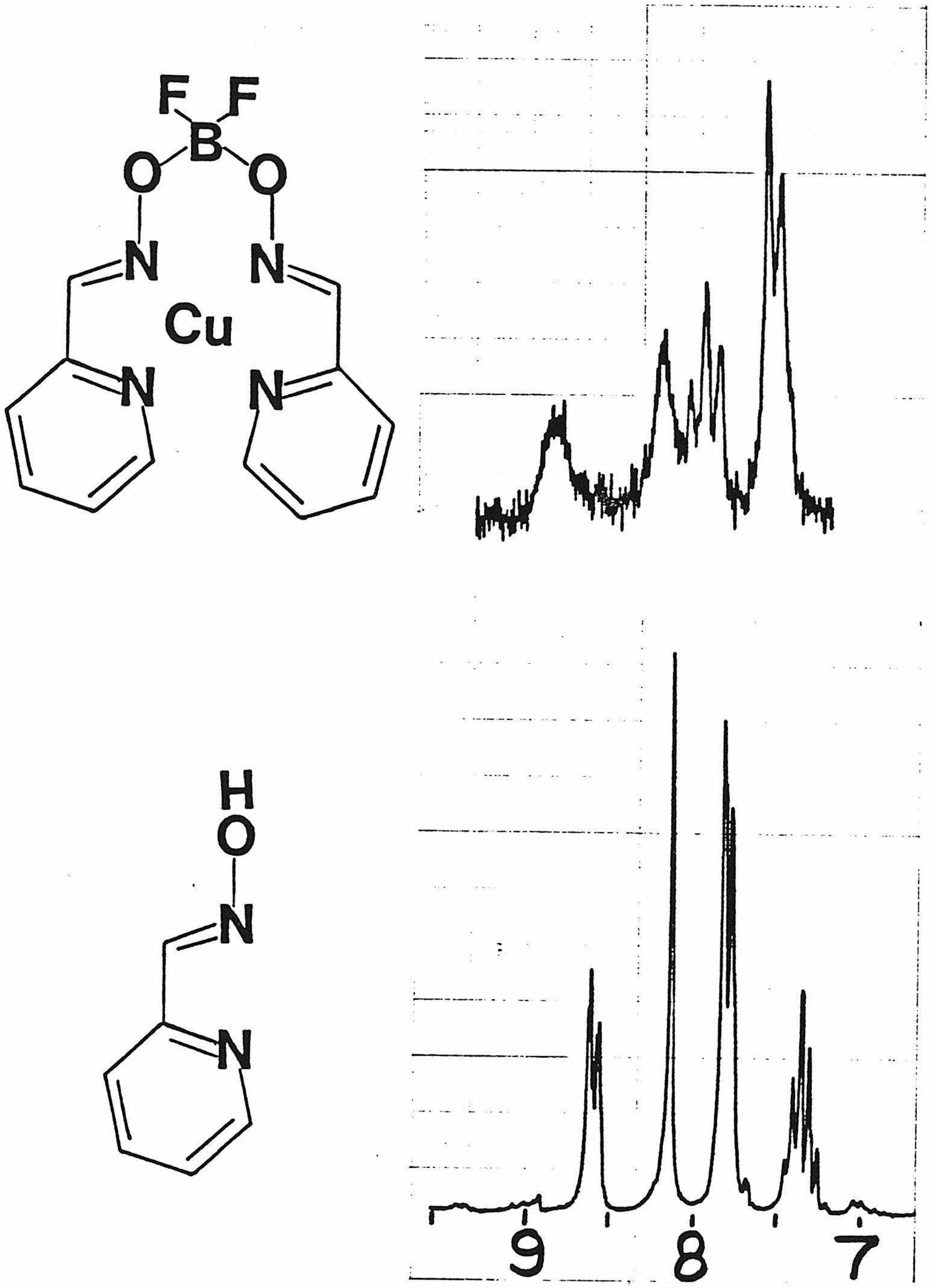


Fig. III-18. Proton nuclear magnetic resonsnce spectra in dimethylsulfoxide-d_6 of pyridine (2-aldoxime) (oxime H not shown), (bottom), and the copper (I) complex 6, (top). The chemical shifts are downfield from TMS. All peaks integrate equally except for the largest "doublet" which integrates in both as twice the area of the others.

One possible reason no oxygenation was observed is that the ligand could not "trap" the oxygen once it interacted with the copper atom. Triphenyl phosphine (1.5 equivalents) was added as a substrate but no oxygen uptake was detected.

Other reasons why no dioxygen reaction was observed stem from the presumably more tetrahedral coordination geometry. Perhaps the copper(I) atom is no longer coordinatively unsaturated. Electrochemical measurements show a 50 mV shift under carbon monoxide. Using a solubility of carbon monoxide in acetonitrile[28] of 8.7×10^{-3} M yields a binding constant of 6.9×10^{2} (for the method of calculation see Ref. 29). Five coordinate complexes are formed with this ligand, although not as strongly as with $CuLBF_2$ or $CuMe_6$-tetraene(ClO_4). A second reason is the potential itself. The copper(I) state may be so favored (E = +0.04 V in acetonitrile vs. SHE) that no "redox" reaction with dioxygen occurs to give an adduct. The reduction potential for this complex is much more positive than that of the macrocycles examined here (see Appendix 2, Table 2).

Summary

In summary, studies of the $CuLBF_2$ and Cu tetraene(ClO_4) systems provide complementary information. A dioxygen containing binuclear intermediate can be frozen out for $CuLBF_2$, even if the reaction is not reversible and decomposition occurs on warming. Cu tetraene(ClO_4) also has a low temperature intermediate which is only observed as a fleeting blue color. In return, the oxidation of the macrocycle is more amenable to study. When one of the two available ketonation positions is blocked by the methyl derivative, only one of the original $^{18}O_2$ shifting infrared bands is observed. Indications are that ketonation is also involved for $CuLBF_2$, 1, as well as in $Cu(I)Me_6$-diene(ClO_4), 7, and $Cu(I)Me_8$-diene(ClO_4), 9. The latter also appear to undergo some oxidative dehydrogenation. Preliminary indications are that the nickel(I) complexes will react similarly. In addition a more tetrahedral tetradentate ligand copper(I) complex has been found to not react with dioxygen.

Experimental

Proton magnetic resonance spectra were obtained on a 90 MHz Varian EM-390 spectrometer. Carbon-13 magnetic resonance spectra were obtained overnight in 12 mm sample tubes for $CuLBF_2$ and its adducts using a Varian XL-100 spectrometer, and after several hours in 5 mm tubes for the diene and tetraene complexes using a Jeol FX-90Q spectrometer. Tetramethylsilane was present as an internal standard in all magnetic resonance samples. Electron paramagnetic resonance spectra were obtained on a modified Varian E-line spectrometer equipped with a Heli-trans low temperature dewar. Spectra were obtained at liquid nitrogen temperatures. Room temperature magnetic measurements were determined on a Cahn Faraday magnetic susceptibility balance. Solution conductivity was measured using a Yellow Springs Instruments Model 31 conductivity bridge. Electrochemical measurements utilized a Princeton Applied Research 174A Polarographic Analyzer. Electrochemical syntheses were accomplished with a Princeton Applied Research model 173 potentiostat equipped with a model 179 digital coulometer. Infrared spectra were obtained via KBr pellets on Beckman Instruments IR-12 and 4240 spectrometers. Visible absorption spectroscopy measurements were recorded on a Cary-14 spectrometer. Operations requiring an inert atmosphere were performed in a Vacuum Atmospheres glove box filled with helium, or on a high vacuum line.

Stoichiometry by difference. An accurately weighed 10^{-4} mole sample and a magnetic stir bar were placed in a 5 ml round-bottom flask attached to an 8 ml calibrated volume. After evacuation of the system 4 ml of freshly degassed solvent was vacuum transferred onto the sample. The sample chamber was closed off, the calibrated volume filled with a known pressure of dry gas (500 to 700 Torr) and the temperature recorded. For low temperature stoichiometry determinations a dry ice acetone slush was placed around the sample chamber at this point. The calibrated volume was then opened to the sample chamber and the oxygenation reaction begun. The dioxygen pressure was about 250 to 350 Torr and the sample was magnetically stirred overnight during the reaction. After the reaction the sample chamber was opened to a degassed Toepler pump, with the solvent being caught in an intervening liquid nitrogen trap. The remaining gas was collected in a 14 ml calibrated volume and the temperature recorded. The amount consumed is the initial amount minus the final amount recovered. A propagation of error analysis suggests that for the parameters used, an error of ±0.03 to 0.07 O_2 per Cu is expected.

A disadvantage of this method is that any dioxygen reversibly bound will be removed and collected as not having reacted. The amount of time for the reaction to go to completion is not known, so duplicate runs of varying duration were always performed. Any leaks in the system will result in too much gas being collected, or equivalently, too little gas being consumed. The most likely errors thus lead to low stoichiometry values of dioxygen consumed per copper atom.

The solvents used for stoichiometry determinations were dried as indicated before vacuum transfer to the reaction vessel: CH_2Cl_2 (CaH_2), CH_3NO_2 ($CaCl_2$), acetone (4A mol sieves, $CaSO_4$), tetrahydrofuran (Na, CaH_2), pyridine (KOH), CH_3CN (4A mol sieves, CaH_2), dimethylsulfoxide (NaOH, vacuum distillation), toluene (H_2SO_4, CaH_2, distillation), propylene carbonate (as obtained), dimethylformamide (4A mol sieves, vacuum distillation).

<u>Stoichiometry at constant pressure</u> was recorded using the apparatus shown in Fig. III-19. Water from a constant temperature bath at 25° was circulated around a gas burette, a pressure reference manometer, and the reaction vessel. The solvent and a stir bar were placed in the reaction vessel. While stirring vigorously, dioxygen was forced through the line and out the spoon joint in order to saturate

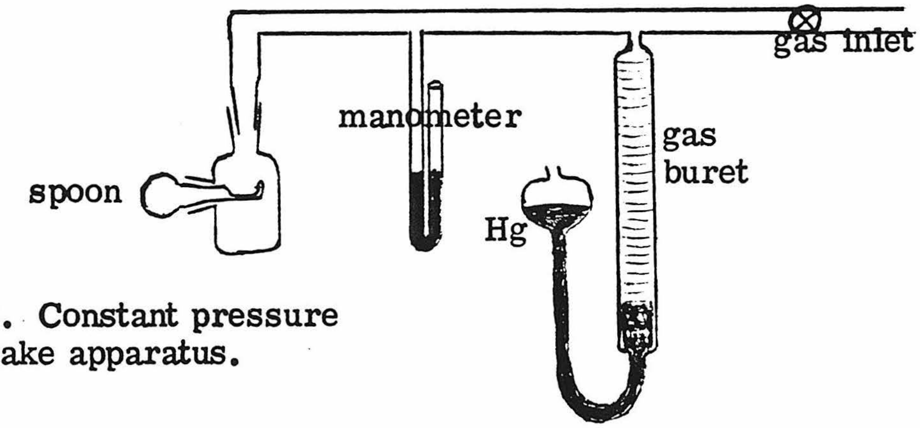


Fig. III-19. Constant pressure oxygen uptake apparatus.

the solvent with dioxygen. A known amount of sample was placed in the spoon, the dioxygen flow stopped, and the spoon placed in the apparatus. When the system was at atmospheric pressure and equilibrium, as judged by the even levels in the silicone oil-filled manometer, the initial volume on the gas burette was recorded and the spoon rotated so the sample fell into the solution. The Hg bulb was manually raised and the uptake measured by the change in volume necessary to maintain the constant pressure. Atmospheric pressure was recorded by a separate measurement.

This method, while useful for measuring reversible oxygen uptake, requires compounds which do not react in the solid state. Solvents with low vapor pressure like propylene carbonate are to be preferred.

Preparation of Compounds

General electrochemical reduction methods. Platinum gauze working and auxiliary electrodes were placed in the 25 ml end compartments of a three compartment H-cell having medium porosity sintered glass frits between compartments. The pseudo-reference electrode,

Ag, supporting electrolyte, solvent //,

where the junction is again a glass frit, was located in the working compartment such that it was not between the working and auxiliary electrodes. Supporting electrolyte (0.05 M tetrabutylammonium perchlorate, dried exhaustively in vacuo before use) was used only in the auxiliary compartments. If the reduced compound could be isolated by filtration, 0.1 M supporting electrolyte was used in all compartments. In practice the compound to be reduced was added, a cyclic voltammogram on a platinum button electrode obtained to verify solvent purity and correct functioning of the reference electrode, and the electrolysis begun. The working compartment was vigorously stirred magnetically. The electrolysis was stopped when the current fell to less than 1 mA, the resting potential of the cell was past the wave, and the desired number of coulombs had been passed. Coulometry was performed for all reductions since occasionally the current would fall off due to coating of the electrode. A cyclic voltammogram of the reduced material was obtained to check for chemical stability during the course of the several hour electrolysis. All reductions were performed in an oxygen-free helium atmosphere glove box.

4, 8-Diaza-3, 9-dimethylundeca-3, 8-diene-2, 10-dione Dioxime. To a warm solution of 100 g 2, 3-butanedione monoxime in 250 ml of ethanol was added 50 ml of 1, 3-propanediamine. The volume of the solution was reduced on a rotary evaporator at 60° until a precipiate began to form (at about 200 ml total volume). After cooling to room temperature, the solid yellow mass was broken up, thoroughly washed with ether until white, and air dried. Yield: 86 g. A proton nuclear magnetic resonance spectrum of the product shows virtually no oxime starting material. Preparation of the product by the published method[3] consistently results in at least a 2:1 mixture of starting oxime to desired product as determined by integration of the proton nuclear magnetic resonance methyl group signals.

4,8-Diaza-3,9-dimethylundeca-3,8-diene-2,10-dione oxime oximato Copper(II) Perchlorate Monohydrate. A warm solution of 25.0 g $Cu(ClO_4)_2\cdot 6H_2O$ in 100 ml acetone was added to a warm solution of 24.0 g of the previous compound in 200 ml acetone. (The $Cu(ClO_4)_2\cdot 6H_2O$ was exhaustively dried in vacuo prior to use.) The solution was stirred and heated for a few minutes and then set aside to let cool. The product was isolated by suction filtration and washed with ether. Yield: 23.5 g.

Bis[1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxo-cyclotetradeca-3,5,10,12-tetraenato copper(II) perchlorate] Monodioxane, $(CuLBF_2)_2(ClO_4)_2\cdot C_4HO_2$. 30 g of the previous compound and 600 ml dioxane were heated to 70° C with stirring in a one-liter Erlenmeyer flask. 24 ml of freshly distilled boron trifluoride etherate was added *slowly.* The solution was left at 100° C for one hour with stirring, and then allowed to cool. The next morning the product was filtered off and washed twice with dioxane, twice with ether, and air dried. Yield 37.5 g. Recrystallization was accomplished by dissolving in a minimum of boiling acetone, filtering hot, and adding a small amount of dioxane to the solution. Upon cooling, the product was recovered by suction filtration and washed with dioxane and ether. Because of the intense color, and the difficulty in determining the minimum amount of solvent necessary, several smaller batches are to be preferred to one large batch. Yield was about 65%.

[1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxo-cyclotetradeca-3,5,10,12-tetraenato] Copper(I), $CuLBF_2$, 1. 0.8 g $CuLBF_2(ClO_4)_2 \cdot C_4H_8O_2$ reduced by constant potential electrolysis in acetone at out to -1.0 V vs. Ag (or about -0.7 V vs. SHE), such that the maximum current allowed was 30 mA. After the electrolysis was complete ($n = 1.0$), the precipitate was filtered from solution, washed 2 × 5 ml with oxygen-free ethanol, and vacuum dried. Yield: 0.37 g.

(1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxo-cyclotetradeca-3,5,10,12-tetraenato) Copper(I)-Triphenylphosphine, $CuLBF_2PPh_3$. 0.0853 g $CuLBF_2$ and 0.1145 g Ph_3P were dissolved in a small amount of O_2-free acetone. (The Ph_3P had been recrystallized from 95% ethanol). Upon slow addition of ether, yellow-green needles precipitated in 60% yield. *Anal.* Calcd. for $CuC_{11}N_4H_{18}BO_2F_2 \cdot C_{18}H_{15}P$: C, 56.83; N, 9.14; H, 5.43; Cu, 10.4. Found: C, 56.90; N, 8.95; H, 5.55; Cu, 11.6. The product is diamagnetic by magnetic susceptibility (25°, Faraday method).

4,8-Diaza-3,6,6,9-tetramethylundeca-3,8-diene-2,10-dione Oxime Oximato Copper(II) Perchlorate.[8] To 2 g acetic acid in 30 ml ethanol was added 3.0 g (30 mmol) 1,3-diaminopropane-2,2-dimethylpropane.[30] To the hot solution was then added 6.0 g 2,3-butanedione-monoxime (60 mmol). After 15 minutes 5.0 g $Cu(ClO_4)_2 \cdot 6H_2O$ (15 mmol) dissolved in minimal hot ethanol was added. After heating an additional 30 minutes, the product was filtered from the cooled solution and recrystallized from hot acetone (150 ml) and dioxane (40 ml). Yield: 1.5 g.

1,1-Difluoro-4,5,8,8,11,12-hexamethyl-1-bora-3,6,10,13-tetraaza-2,4-dioxo-cyclotetradeca-3,5,10,12-tetraenato Copper(II) Perchlorate.[8] Boron trifluoride etherate (0.5 ml) was added to the previous compound (0.9 g) in hot dioxane (20 ml), and the solution heated for one hour. Upon cooling a purple oil separated, which slowly crystallized on standing for several days.

1,1-Difluoro-4,5,8,8,11,12-hexamethyl-1-bora-3,6,10,13-tetraaza-2,4-dioxo-cyclotetradeca-3,5,10,12-tetraenato Copper(I)[8], 2. 0.60 g of the corresponding copper(II) complex was reduced in acetone at out to -1.0 V vs. Ag. After the electrolysis was complete, the solvent was removed under vacuum, the residue dissolved in a minimum of hot acetone (8 ml), and diethyl ether (5 ml) added. The product was isolated by filtration of the cooled solution and washed with ethanol. Yield: 0.25 g.

Complexes 3, 4, and 5. The corresponding copper(II) complexes were synthesized as previously reported.[29] Reduction to copper(I) and isolation of the product[8] was similar to that of **1**.

Monohydrogen Bis-(pyridine-2-aldoxime)-copper(II) nitrate was prepared according to the procedure of Liu and Liu.[31] 2.44 g of pyridine-2-aldoxime dissolved in a minimum amount of ethanol was added slowly to a solution of 2.42 g of copper dinitrate trihydrate in 30 ml of water. Dark-green crystals formed and after a few hours were filtered from solution, washed with a small amount of water and vacuum dried. Calcd for $C_{12}H_{11}N_4O_2CuNO_3$: C, 38.87; N, 18.99; H, 3.07. Found: C, 39.10; N, 18.70; H, 3.25.

Difluoro-bis-(pyridine-2-aldoxime)borate copper (II) nitrate

1.0 g of the previous compound was stirred in 100 ml of warm dioxane. 2 ml of BF_3Et_2O were carefully added and the solution left to reflux for $1\frac{1}{2}$ hours. The pale-blue product is insoluble in dioxane and was filtered off, washed twice with dioxane and twice with ether.

Difluoro-bis-(Pyridine-2-aldoxime)borate copper(I), 6

was prepared by constant potential electrolysis at -0.5 V vs. Ag of the corresponding Cu(II) compound in acetonitrile containing 0.1 M tetraethylammonium perchlorate. The orange product precipitated during the electrolysis was collected by filtration, and washed once with ethanol. Calcd for $C_{12}H_{10}N_4O_2BF_2Cu$: C, 40.65; N, 15.80; H, 2.84. Found: C, 40.60; N, 16.30; H, 3.15.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Dihydroperchlorate, Me_6-diene$(HClO_4)_2$ was prepared in a manner similar to the published procedure.[11] To 1 L of acetone in a 2 L beaker was added 44 ml of ethylenediamine. The solution was stirred while 72 ml of 60% perchloric acid was added dropwise over a half-hour period. (Caution: Use of a safety shield is recommended for this and all perchlorate salt syntheses). After being stirred at room temperature overnight, the product was filtered from the dark-brown solution, washed with acetone until white (3×), and air dried after a diethyl ether wash. Yield: 106 g (73%). If the solution was left stirring for two days, 114 g was obtained. Anal. Calcd for $C_{16}H_{32}N_4 \cdot 2HClO_4$: C, 39.92; H, 7.12; N, 11.64. Found: C, 40.35; H, 7.00; N, 11.40.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetrazacyclotetradeca-4,11-diene Copper(II) Diperchlorate, Cu(II)Me$_6$-diene(ClO$_4$)$_2$. A slurry of 50.0 g copper diacetate tetrahydrate, 110.0 g Me$_6$-diene(HClO$_4$)$_2$, and 1 L of methanol in a 2 L Erlenmeyer flask were stirred at reflux for one hour, and then the solution was left to cool slowly to room temperature. Small red crystals were filtered from the purple solution, washed once with methanol, once with diethyl ether, and air dried. Yield: 114 g (92%). Anal. Calcd for $C_{16}H_{32}N_4Cu(ClO_4)_2$: C, 35.40; H, 5.94; N, 10.32. Found: C, 35.55; H, 5.75; N, 10.30.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Copper(I) Perchlorate Acetone, Cu(I)Me$_6$-diene(ClO$_4$)$\cdot$C$_3$H$_6$O, **7**. 1.0 g Cu(II)Me$_6$-diene(ClO$_4$)$_2$ was reduced by constant potential electrolysis in acetone at out to -0.8 V vs. Ag, such that the maximum current allowed was 20 mA. After the electrolysis was complete ($n = 0.98$), a yellow precipitate was filtered from solution and vacuum dried. Yield: 0.5 g (60%). Anal. Calcd for $C_{16}H_{32}N_4ClO_4 \cdot C_3H_6O$: C, 45.50; H, 7.64; N, 11.17. Found: C, 45.05; H, 7.85; N, 11.45. Acetone solvate $\nu_{C=O}$ is present in the infrared spectrum at 1707 cm^{-1}.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene Copper(II) Diperchlorate, Cu(II)Me$_6$-tetraene(ClO$_4$)$_2$. 40.0 g of Cu(II)Me$_6$-diene(ClO$_4$)$_2$ and 25.0 g sodium permanganate (Research Organic/Inorganic Chemicals) in 400 ml H$_2$O were heated and stirred in a 4 L beaker. 150 ml HClO$_4$ (60%) was added dropwise over a half-hour period. The MnO$_2$ formed, as evidenced by the brown frothy mess obtained, was reduced to aqueous Mn(II) by further heating.

Then the minimum amount of H_2O necessary to dissolve any product present as precipitate at reflux was added and the boiling solution suction filtered hot. As the solution cooled, crystalline product was obtained. After being cooled in an ice bath, purple crystals were isolated by filtration and washed with 100% ethanol. If the product is relatively pure tetraene complex, the purple crystals will dry to a salmon-colored powder during the ethanol wash.

The product should be checked for the presence of $CuMe_6$-diene-$(ClO_4)_2$, as indicated by the N-H stretching frequency at 3220 cm^{-1} in the infrared spectrum. If any N-H band is seen, the material should be retreated as above, scaling the reaction to assume all product is $CuMe_6$-diene$(ClO_4)_2$. Note that the tetraene complex is more soluble in hot H_2O than the diene complex, so less additional H_2O will have to be added before filtering. Often two treatments (but never three) were found to be necessary. Treatment with greater quantities of sodium permanganate and perchloric acid did not seem to affect the tetraene/diene ratio obtained but did result in the contamination of the product with sodium perchlorate. (Use of potassium permanganate rather than the sodium salt always resulted in product contaminated with white crystalline potassium perchlorate which gave poor elemental analyses even after multiple recrystallizations.) All permutations of $CuMe_6$-diene$(ClO_4)_2$, $NaMnO_4$, and $HClO_4$ additions were tried with the yield of this procedure being superior. Yield: 50% from each treatment. Anal. Calcd. for $C_{16}H_{28}N_4Cu(ClO_4)_2$: C, 35.66; H, 5.24; N, 10.40. Found: C, 35.25; H, 5.05; N, 10.20.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene Copper(I) Perchlorate, Cu(I)Me$_6$-tetraene(ClO$_4$), 8 was prepared by constant potential reduction of 1.4 g of the copper(II) complex in acetone at out to -0.8 V vs. Ag, such that the maximum current allowed was 20 mA. After electrolysis was complete (n = 1.08), the contents of the working compartment were filtered, and the 20 ml solution diluted to 50 ml with deoxygenated toluene. The flask was then scratched to induce crystallization. When the Cu(II)Me$_6$-tetraene-(ClO$_4$)$_2$ was contaminated with small amounts of Cu(II)Me$_6$-diene(ClO$_4$)$_2$, only oils were obtained. After a half hour, the solution was slowly diluted to 200 ml with toluene, and the dark red product filtered from solution and dried in vacuo. Yield: 0.68 g (60%). Proton nuclear magnetic resonance indicates no supporting electrolyte is present. Anal. Calcd for $C_{16}H_{28}N_4Cu(ClO_4)$: C, 43.73; H, 6.42; N, 12.75. Found: C, 43.70; H, 6.30; N, 12.40.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetra-4,11-diene Dihydroperchlorate, Me$_8$-diene(HClO$_4$)$_2$. To 1.5 L of acetone in a 2 L Erlenmeyer flask was added 85 ml of 1,2-diaminopropane (Aldrich). The solution was stirred while 109 ml of 60% perchloric acid was added dropwise over a half-hour period. After stirring at room temperature for one *week*, the product was suction filtered from the dark-brown solution and washed consecutively with acetone (3×), diethyl ether (1×), acetone (1×), and diethyl ether (1×). The white product was air dried. Yield: 69 g (27%). Anal. Calcd for $C_{18}H_{36}N_4 \cdot 2HClO_4$: C, 42.44; H, 7.52; N, 11.00. Found: C, 42.60; H, 7.15; N, 10.80.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Copper(II) Diperchlorate, Cu(II)Me$_8$-diene(ClO$_4$)$_2$. 25.8 g copper diacetate monohydrate was dissolved in 1 L hot methanol. Upon addition of 60.0 g Me$_8$-diene(HClO$_4$)$_2$ the solution almost solidified with purple precipitate. The heating was continued for half an hour and the product cooled to room temperature, filtered, and washed with methanol and diethyl ether. Yield: 65.7 g (98%). Anal. Calcd for $C_{18}H_{36}N_4Cu(ClO_4)_2$: C, 37.87; H, 6.36; N, 9.81. Found: C, 38.20; H, 6.30; N, 9.70.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Copper(I) Perchlorate Acetone, Cu(I)Me$_8$-diene(ClO$_4$), **9**. 0.90 g Cu(II)Me$_8$-diene(ClO$_4$)$_2$ was reduced by constant potential electrolysis in acetone at out to -0.8 V vs. Ag, such that the maximum current allowed was 20 mA. After the electrolysis was complete (n = 0.97), a yellow precipitate was filtered from solution and vacuum dried. Yield: 0.40 g (48%). Anal. Calcd for $C_{18}H_{36}N_4CuClO_4 \cdot C_3H_6O$: C, 47.63; H, 7.99; N, 10.58. Found: C, 47.45; H, 7.85; N, 10.40. Acetone solvate $\nu_{C=O}$ is present in the infrared spectrum at 1712 cm^{-1}.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene Copper(II) Diperchlorate, Cu(I)Me$_8$-tetraene-(ClO$_4$)$_2$. 40.0 g of Cu(II)Me$_8$-diene(ClO$_4$)$_2$ and 28.0 g sodium permanganate in 500 ml H_2O were heated and stirred in a 4 L beaker. 200 ml $HClO_4$ (60%) was added dropwise over a half-hour period. The MnO_2 formed, as evidenced by the brown frothy mess obtained, was reduced to aqueous Mn(II) with further heating (1 hour). The solution was then cooled in an ice bath and the crude product filtered from solution. The product was recrystallized by dissolving in a refluxing solution of 2.5 L methanol and 250 ml H_2O and filtering hot. As the purple solution cooled, salmon-colored needles precipitated. The product was filtered from solution, washed with methanol, and dried with diethyl ether. Yield: 11.3 g (28%). The infrared spectrum has no peaks between 3200 and 3300 cm^{-1}. Anal. Calcd for $C_{18}H_{32}N_4Cu(ClO_4)_2$: C, 38.14; H, 5.69; N, 9.88. Found: C, 38.30; H, 5.75; N, 9.70.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene Copper(I) Perchlorate, Cu(I)Me_8-tetraene-(ClO_4), 10, was prepared by a constant potential reduction at -0.9 V vs. Ag in acetone of 1.31 g Cu(II)Me_8-tetraene$(ClO_4)_2$. Due to the very low solubility of the copper(II) complex, an initial cyclic voltammogram could not be obtained and currents during the electrolysis were small. The electrolysis cell was shaken periodically to aid dissolution. Due to the long time involved (about 9 hours), the auxiliary compartments were emptied and refilled with fresh solution after half the theoretical number of coulombs had been passed. After the electrolysis was complete (n = 1.04), and no copper(II) complex was visibly present as a solid, a dark-red solid was isolated from the filtered solution by a procedure identical to that for Cu(I)Me_6-tetraene(ClO_4), **8**. Yield: 0.64 g (59%). Proton nuclear magnetic resonance spectra indicate no supporting electrolyte is present. Anal. Calcd for $C_{18}H_{32}N_4CuClO_4$: C, 46.25; H, 6.90; N, 11.99. Found: C, 46.15; H, 6.70; N, 11.60.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Nickel(II) Diperchlorate, Ni(II)Me_6-diene$(ClO_4)_2$. 51.5 g nickel diacetate tetrahydrate was dissolved in 750 ml methanol, 90.0 g Me_6-diene$(HClO_2)_2$ added, and the solution refluxed for one hour.[11] After cooling to room temperature, the yellow product was isolated by suction filtration, washed with methanol and dried with diethyl ether. Yield: 100.0 g (99%). Anal. Calcd. for $C_{16}H_{32}N_4Ni(ClO_4)_2$: C, 35.72; H, 5.99; N, 10.41. Found: C, 36.30; H, 5.90; N, 10.20.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Nickel(I) Perchlorate, Ni(I)Me_6-diene(ClO_4) was prepared by a scaled-up literature preparation [32] in a Schlenck apparatus under argon. 5.0 g Ni(II)Me_6-diene$(ClO_4)_2$ in 250 ml deaerated CH_3CN was added to 1.25 g Na metal in 150 g Hg. After stirring for one hour, the solution was filtered and evaporated to dryness. The black crystalline product from the filtrate was washed with 250 ml deaerated H_2O, vacuum dried, and transferred to the glove box. Yield: 3.55 g (87%). Anal. Calcd for $C_{16}H_{32}N_4NiClO_4$: C, 43.81; H, 7.35; N, 12.77. Found: C, 43.70; H, 7.15; N, 12.95.

5,7,7,12,14,14,-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene Nickel(II) Diperchlorate, Ni(II)Me_6-tetraene$(ClO_4)_2$. 50 ml of conc HNO_3 (70%) was diluted to 400 ml with H_2O, 100.0 g Ni(II)Me_6-diene$(ClO_4)_2$ added, and the mixture refluxed for about half an hour until no more brown oxides of nitrogen were given off. Upon cooling in an ice bath, yellow crystals were filtered from solution and washed with acetone and diethyl ether. Yield: 71.0 g (72%). The infrared spectrum has no peak at 3180 cm^{-1}. Anal. Calcd for $C_{16}H_{28}N_4Ni(ClO_4)_2$: C, 35.99; H, 5.28; N, 10.49. Found: C, 35.85; H, 4.80; N, 10.35.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Nickel(II) Diperchlorate, Ni(II)Me_8-diene$(ClO_4)_2$. 25.0 g nickel diacetate tetrahydrate was dissolved in 400 ml methanol, 35.0 g Me_8-diene$(HClO_4)_2$ added, and the solution refluxed for $1\frac{1}{2}$ hours. After cooling to room temperature, the orange product was isolated by suction filtration, washed with methanol, and dried with diethyl ether. Yield: 32.2 g (83%). Anal. Calcd for $C_{18}H_{36}N_4Ni(ClO_4)_2$: C, 38.19; H, 6.41; N, 9.90. Found: C, 38.50; H, 6.15; N, 9.70.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene Nickel(II) Diperchlorate, Ni(II)Me_8-tetraene-$(ClO_4)_2$. 30 ml conc HNO_3 (70%) was diluted to 150 ml with H_2O, 20.0 g Ni(II)Me_8-diene$(ClO_4)_2$ added, and the mixture refluxed for 20 minutes until no more brown oxides of nitrogen were given off. Upon cooling, large, bright-yellow crystals were filtered from solution and washed with acetone and diethyl ether. Yield: 17.8 g (89%). The infrared spectrum has no peak at 3180 cm^{-1}. Anal. Calcd for $C_{18}H_{32}N_4Ni(ClO_4)_2$: C, 38.46; H, 5.74; N, 9.97. Found: C, 38.50; H, 5.80; N, 9.90.

3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene Nickel(I) Perchlorate, Ni(I)Me_8-tetraene-(ClO_4) was prepared by electrochemical reduction of 1.34 g Ni(II)Me_8-tetraene$(ClO_4)_2$ in CH_3CN. Due to the high solubility of the Ni(II) complex, the first 80% of the electrolysis was performed under constant current conditions of 20 mA. The remainder was constant potential electrolysis out to -1.15 V vs. Ag. After the electrolysis was complete (n = 1.06), the working solution was filtered and transferred in the glove box to a Schlenck filtering apparatus. The sealed apparatus was attached to a high vacuum line, the volume of the solution reduced to 10 ml, and 125 ml of dry degassed toluene (CaH_2 treated) added by vacuum transfer. After warming to room temperature, a black precipitate was filtered off and the filtrate evaporated overnight. The sealed apparatus was then returned to the glove box and the filtered precipitate retained. Yield: 0.57 g (52%). Addition of toluene in the glove box resulted in precipitation of a tan nickel(II) complex.

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Chapter Four. Mechanism Consideration and Summary

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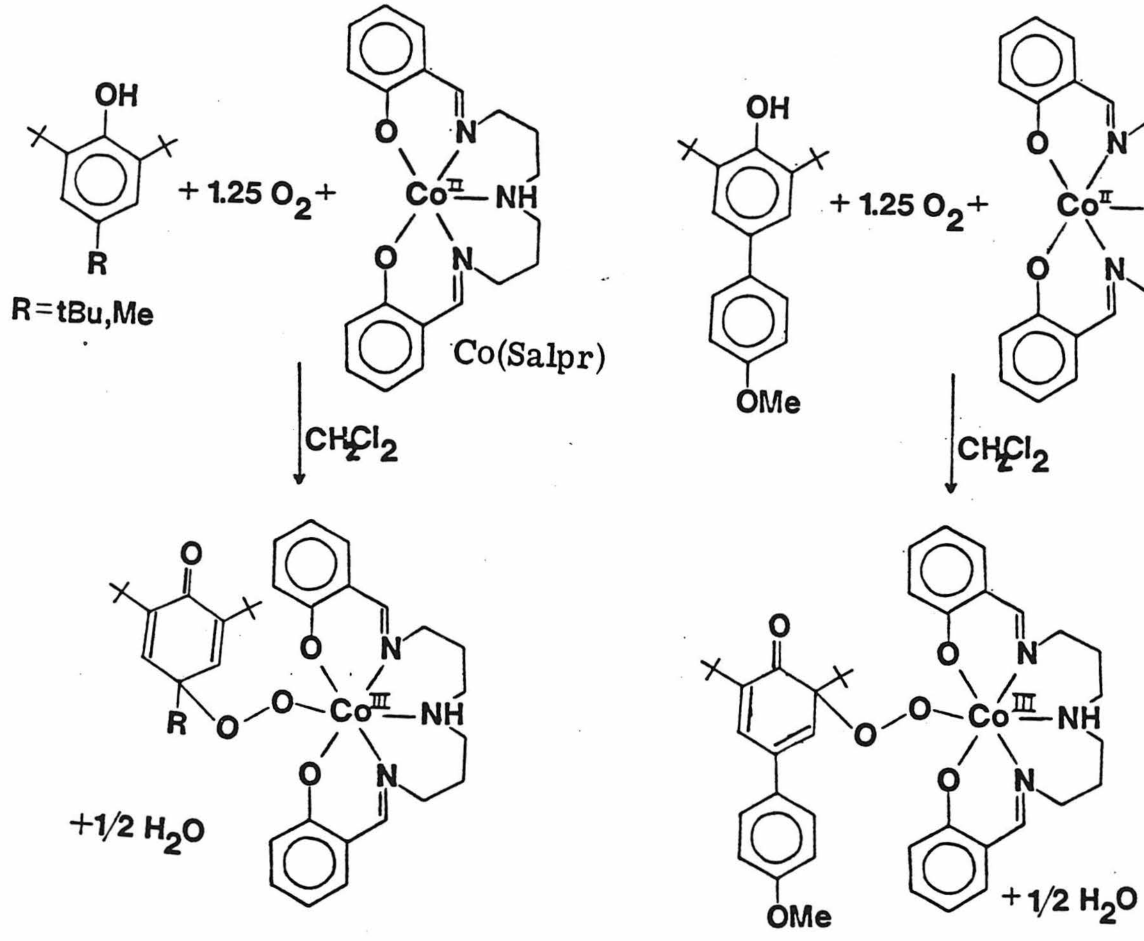
Consideration of Mechanism

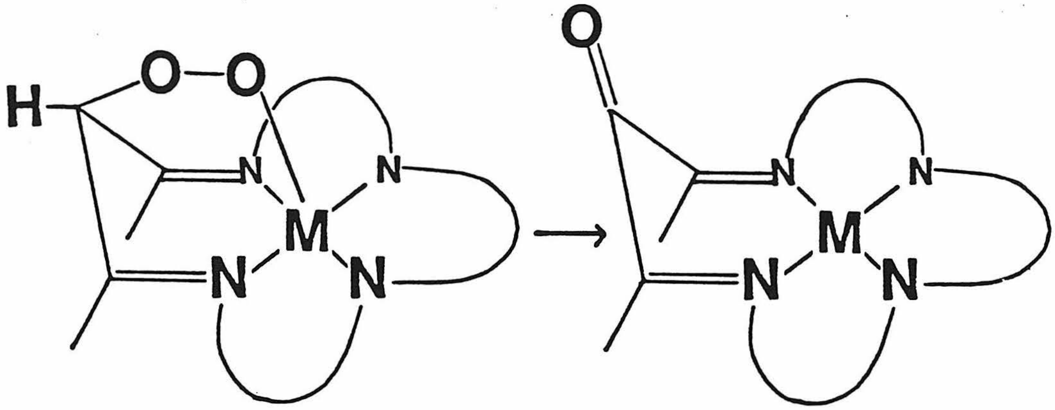
The actual mechanism of the ketonation reactions cannot be determined from the data obtained. Nevertheless it is appropriate to examine oxygen activation mechanisms proposed for other metals in light of the current reactions. Two such catalytic mechanisms will be examined here. The first concerns oxygenation of hindered phenols by (bis-(3-salicylideneaminopropyl)amine)cobalt(II) and dioxygen. The second is that of the P-450 oxygenase cytochromes.

Recently Nishinaga and coworkers[1-5] have examined the role of Co(Salpr) dioxygen complexes in the oxidation of hindered phenols (Scheme IV-1). Of particular interest is the reaction stoichiometry of 1.25 O_2/Co and isolation of crystalline organo-peroxy Co(III) complexes in some solvents. (In methanol the reaction is catalytic with the corresponding hydroperoxide obtained at -10°, and the p-quinol obtained on warming).[3-5] The same stoichiometry of 1.25 O_2 per metal atom was observed for the dioxygen reactions of $CuMe_6$-tetraene-(ClO_4) and $CuMe_8$-tetraene(ClO_4). A peroxy intermediate has been proposed for the ketonation of cobalt macrocycles (Scheme IV-2) and is a likely intermediate for the copper macrocycle ketonations. Thus Co(Salpr) consumption of 1.25 O_2/Co to give a peroxy compound could have the same mechanisms as the first part of the Cu(I) macrocycle oxygenation reactions.

Scheme IV-1


OH
R
R=tBu,Me
+ 1.25 O2+
O
N
CoII
NH
Co(Salpr)
OH
OMe
+ 1.25 O2+
CH2Cl2
CH2Cl2
O
R
CoIII
+1/2 H2O
OMe
+1/2 H2O

Scheme IV-2



Nishinaga and coworkers have proposed Scheme IV-3 as the mechanism.[2,3] In this mechanism dioxygen incorporation is initiated

Scheme IV-3

$$\mathrm{Co(II)} + \mathrm{O_2} \rightleftharpoons \mathrm{Co(III)O_2^-}$$

$$\mathrm{Co(III)O_2^-} + \mathrm{PhOH} \xrightarrow{\text{slow}} \mathrm{Co(III)OOH} + \mathrm{PhO\cdot}$$

$$\mathrm{Co(III)OOH} \rightarrow \mathrm{Co(III)OH} + \tfrac{1}{2}\mathrm{O_2} \qquad \mathrm{PhO\cdot} + \mathrm{Co(II)} \xrightarrow{\text{fast}} \mathrm{PhO^-Co(III)}$$

$$\mathrm{Co(III)OH} + \mathrm{PhOH} \xrightarrow{\text{fast}} \mathrm{PhO^-Co(III)} + \mathrm{H_2O}$$

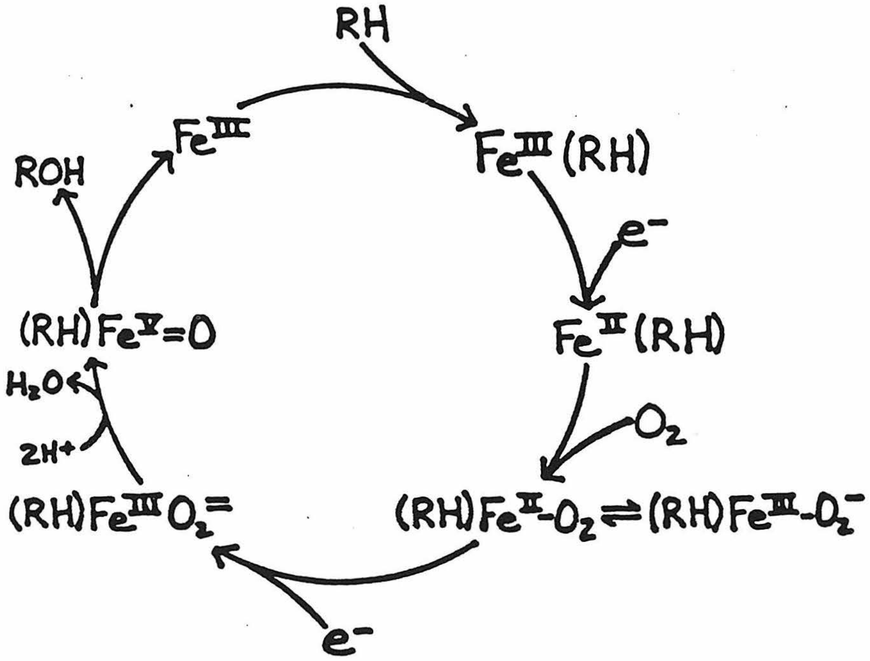
$$\mathrm{PhO^-Co(III)} + \mathrm{O_2} \rightarrow \mathrm{Ph(OH)OOCo(III)}$$

through hydrogen abstraction by $\mathrm{Co(III)O_2^-}$ from the phenol. The phenoxy radical was detected by electron paramagnetic resonance. The mechanism is also supported by the Co(III)OOH obtained as well as half the normal amount of Ph(OH)OOCo(III) and a stoichiometry of 1.0 O_2/Co when Co(N-Me Salpr) derivatives are used instead of

Co(Salpr). Co(III)(N-Me Salpr)OOH is apparently stable and the left-hand part of Scheme IV-3 does not then apply.[2,3] While a mechanism like Scheme IV-3 seems to fit the oxygenation of hindered phenols, it is difficult to apply it to the copper(I) macrocycle oxygenation regardless of the similar stoichiometry and products. The basic problem is that the macrocycle is attached to the copper and intramolecular reactions would occur faster than intermolecular reactions. It is also not clear how the cobalt(III) phenolate is oxygenated in the published mechanism to give the peroxy compounds, nor if this applies in any way to the ketonation of copper macrocycles.

The observed ketonation appears to be the product of electrophilic attack on the macrocycle CH_2 groups. Electrophilic attack derived from dioxygen has been best studied in the P-450 oxygenase cytochromes, and the mechanism is shown in Scheme IV-4.[6,7]

Scheme IV-4



Fe(III)(RH) is meant to indicate binding of the substrate to the enzyme in the vicinity of the Fe(III), as shown in Fig. IV-1.

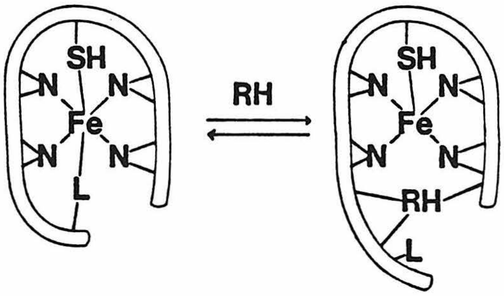


Fig. IV-1. Substrate binding of cytochrome P-450.

The most controversial step, postulation of an "oxene" as the active species, is justified as follows.[8-11] 1) The reaction pattern is similar to the reactions of carbenes giving insertion into C-H bonds with retention of configuration, and addition to alkenes to produce a three-membered ring. 2) For a large number of enzymatic hydroxylations of aromatic compounds the substituent at the position which is eventually hydroxylated frequently shifts to an adjacent carbon ("NIH shift"), indicating an arene oxide intermediate and migration as the keto tautomer. 3) Treatment of iron(III) and chromium(III) porphyrins with iodosylbenzene gives iodobenzene and a $\mathrm{M(V)=O^{2-}} \leftarrow \mathrm{M(IV)\text{-}O^{\overset{-}{\cdot}}} \longleftarrow \mathrm{M(III)\ O}$ species. This reactive intermediate was found to epoxidize cis-olefins and hydroxylate alkanes.[10-13] Application of a cytochrome P-450-like mechanism to the oxygenation of copper(I) macrocycles again is fraught with difficulty. Perhaps an intermediate like $\mathrm{Cu(I) + O_2 \rightarrow Cu(II)\text{-}O_2^{-} \leftrightarrow Cu(III)\text{-}O_2^{=}}$ or $\mathrm{2Cu(I) + O_2 \rightarrow Cu(II)\text{-}O_2^{=}\text{-}Cu(II) \rightarrow 2Cu(II)\text{-}O^{-} \leftrightarrow 2Cu(III){=}O}$ applies and the ligand itself is the proton source.

The most obvious lesson in examining these mechanisms is that the focus should be shifted from the metal dioxygen species itself to the reduced reactive oxygen species. Determination of the true structural identity of the oxygen derivative that attacks the macrocycle, the mechanism by which the active form of dioxygen is generated, and the mode by which the oxygen is incorporated into the macrocycle are questions that have not yet been examined.

Summary

The original object of this study was to synthesize stable copper(I) macrocyles, react them with dioxygen, and identify the products. These objectives have been attained. A binuclear copper dioxygen species has been identified in solution at low temperature. Ketonation of several copper(I) macrocycles has been observed, as well as blockage of ketonation by macrocycle substitution. A hydroxylated ligand copper(I) autoxidation has been identified crystallographically.

Prior to the work of R. R. Gagné, J. L. Allison, myself, and D. M. Ingle, only one copper(I) N_4-macrocycle had been isolated. Our collective work has greatly increased this number. The synthetic hurdle of preparing fairly large quantities of pure copper(I) materials required for the studies reported here has been overcome. Along the way, several new geometries have been observed crystallographically, including square-planar, square pyramidal, and whatever geometry the binuclear complex described in Chapter Two turns out to have.

As expected, the lability of copper complexes is a problem. Dioxygen reactions of copper(I) multidentate complexes with additional dissociable ligands are complicated by ligand dissociation. Macrocyclic ligands stay coordinated, but in return, the metal cannot be removed to obtain nuclear magnetic resonance spectra of the products. There must be coordinatively unsaturated copper(I) to react with dioxygen, as shown by the triphenylphosphine inhibition and enhancement of dioxygen per copper atom taken up.

Several pitfalls in studying dioxygen reactions should be recalled. The measured dioxygen per copper stoichiometry does not necessarily agree with the amount found in the isolated solids, as observed for the mononuclear complexes in Chapter Two. Reversible color changes do not necessarily mean reversible oxygenation, as found for $CuLBF_2$ in Chapter Three.

It has been shown that Scheme III-5 is applicable to copper(I) dioxygen reactions, where the "decomposition" reaction includes oxygen incorporation into substrates. The oxidation of CO to $CO_3^=$, ligand hydroxylation, metal involved oxidation of triphenyl phosphine to triphenyl phosphine oxide, and ketonation of a macrocyclic ligand have all been identified.

Reduction of dioxygen to water, hydroxide, or oxo species has been observed in conjunction with oxidation of copper(I) to copper(II). The tetrameric hydroxide bridged species produced upon dioxygen reaction of the mononuclear ligand in Chapter Two is the best verified, but stoichiometries of 0.25 dioxygen per copper atom can mean little else. Available protons, as in nitromethane solution, favor this simple redox reaction. There is a large aprotic solvent dependence of the stoichiometry on basicity. Ligand or solvent oxidation appears quite common for copper(I) systems under aprotic conditions.

Further work on this problem could go in several directions. More mechanistic information, including identification of the observed intermediate for the ketonation of the Cu(I) tetraene complexes, could be obtained. Low temperature solution infrared experiments should be very useful in following the reactions, if precipitation of the product in the infrared cell is not a problem. Investigation of oxidation of added substrates could be carried out. Further ligand modification to prevent any ketonation may finally yield a solid room temperature stable copper dioxygen complex. In conclusion, it should be stated once more that copper(I) dioxygen products are very reactive species indeed.

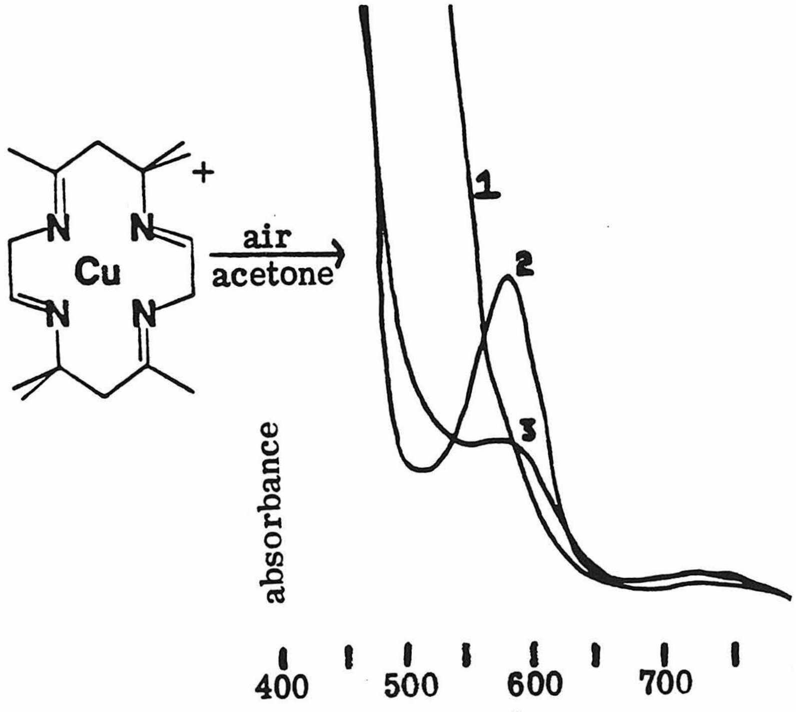


Fig. IV-2. Spectroscopically observed intermediate in the reaction of dioxygen with Cu(I)Me$_6$-tetraene(ClO$_4$) in acetone solution.

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Appendices

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Reaction of Molecular Oxygen with Copper(I). Structural Characterization of Dimeric μ-Carbonato and Tetrameric μ-Hydroxo Complexes Resulting from the Autoxidation of a Copper(I) Carbonyl Complex

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Received May 12, 1978

Condensation of 1,2-dicyanobenzene with 2-amino-4-methylpyridine yields the tridentate ligand 1,3-bis(2-(4-methylpyridyl)imino)isoindoline, HL, **1**. Reaction of HL with $Cu(OAc)_2$ gives Cu(L)OAc, **2**, while HL plus CuCl in the presence of triethylamine and carbon monoxide gives diamagnetic, presumably four-coordinate Cu(I)-containing Cu(L)CO, **3** (ν_{CO} 2068 cm^{-1}). This carbonyl complex, Cu(L)CO, reacts with dioxygen in dry benzene or toluene to give a variety of products, two of which were characterized by crystal structure determinations. A carbonate-bridged dimeric complex $(CuL)_2(\mu\text{-}CO_3)$, **4**, in which the carbonate group presumably results from metal-promoted oxidation of CO via O_2, crystallizes in the space group $P\bar{1}$ with $a = 11.420$ (1) Å, $b = 16.479$ (1) Å, $c = 10.954$ (1) Å, $\alpha = 90.98$ (1)°, $\beta = 113.83$ (1)°, $\gamma = 101.71$ (1)°, and $Z = 2$. The structure was solved using 4578 reflections and gave $R(F) = 0.058$. Each Cu(II) is approximately square planar, being coordinated to three nitrogen atoms of the tridentate ligand and to one oxygen atom of the bridging carbonate group. A hydroxyl-bridged tetrameric complex $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, **5**, crystallizes with 2.5 benzene molecules and one water molecule per tetramer in the space group $P\bar{1}$ with $a = 14.586$ (1) Å, $b = 14.925$ (1) Å, $c = 20.781$ (2) Å, $\alpha = 105.48$ (1)°, $\beta = 105.48$ (1)°, $\gamma = 80.24$ (1)°, and $Z = 2$. An $R(F)$ of 0.065 was obtained using 9334 reflections. The molecule contains two square-planar and two trigonal-bipyramidal Cu(II) atoms, each being coordinated to three nitrogen atoms of the tridentate ligand and linked in a linear array by three bridging hydroxyl groups. In addition a single oxygen atom, located on a pyridyl α carbon of the tridentate ligand, is distributed nonstatistically over the four tridentate ligands. This oxidation of the ligand presumably results from copper activation of dioxygen.

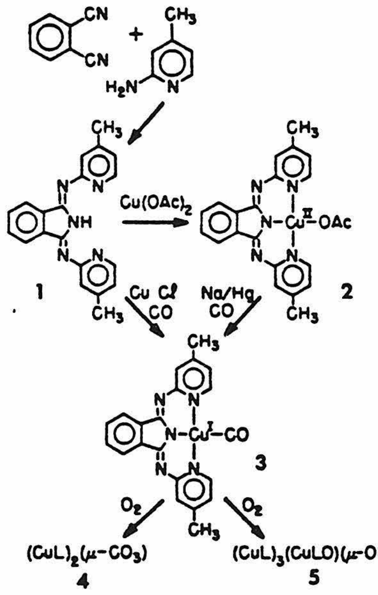
Introduction

Several copper-containing proteins ultilize molecular oxygen in rather varied physiological processes.[1-4] Thus, hemocyanin,[5-7] tyrosinase,[8] cytochrome oxidase,[9] and laccase[10-12] all react with O_2, possibly forming intermediate copper–dioxygen complexes. Little is known about the nature of the active sites of these proteins or about the formal oxidation states, relative locations, or ligand environments of the copper atoms; indeed, it is not even known whether these proteins share common structural features. The principal information concerning the nature of the copper–dioxygen interaction derives from the resonance Raman spectrum of oxyhemocyanin;[13-16] a band at 742 cm^{-1} has been attributed to peroxide-like, presumably coordinated, dioxygen. However, there is no indication whether O_2 is bound to one or both of the copper atoms comprising this active site. The other ligands bound to copper are, most probably, imidazole nitrogens of histidyl residues.

Our present understanding of the reactions of O_2 with relatively simple copper complexes does little to help clarify protein behavior. Most Cu(II) complexes do not react with O_2. No well-characterized dioxygen complexes derived from Cu(I) are known,[17] although claims of O_2 adduct formation have appeared.[18-26] Treatment of Cu(I) complexes with O_2 usually results in irreversible oxidation to Cu(II), but oxidation products have not been fully characterized nor have kinetic studies yielded much mechanistic information.[27]

In an effort to better understand the nature of the copper–dioxygen interactions in proteins, we are studying relatively simple mononuclear[28-30] and binuclear[31] Cu(I) complexes. As we have discussed elsewhere,[29] the use of polydentate ligands can minimize associations and dissociation in solution, making it more likely that solid-state crystal structures correspond to solution structures and sometimes permitting more facile determination of solution mechanisms. Indeed, a good model for "blue" copper proteins which takes advantage of this feature of polydentate ligands has recently been reported.[32] We have examined copper complexes of the tridentate ligand 1,3-bis(2-(4-methylpyridyl)imino)isoindoline, **1**, which has a nitrogen ligand environment for Cu(I) similar to that suggested for hemocyanin.[13-16,33,34] Herein we report the synthesis of an apparently four-coordinate Cu(I) carbonyl complex of **1**, as well as structural characterization of two oxygenation products.

Scheme I



Results

Preparation of the Cu(I) Carbonyl Complex, 3 (Scheme I). The tridentate ligand **1** is synthesized by the condensation of 2-amino-4-methylpyridine with 1,2-dicyanobenzene. Reaction of **1** with cupric acetate gives a mononuclear Cu(II) acetate complex CuL(OAc), **2**.[35-37] Reaction of **1** with cuprous chloride in the presence of triethylamine and carbon monoxide gives a Cu(I) carbonyl complex Cu(L)CO, **3** (ν_{CO} 2068 cm^{-1}), as a light yellow powder. The carbonyl complex **3** is also

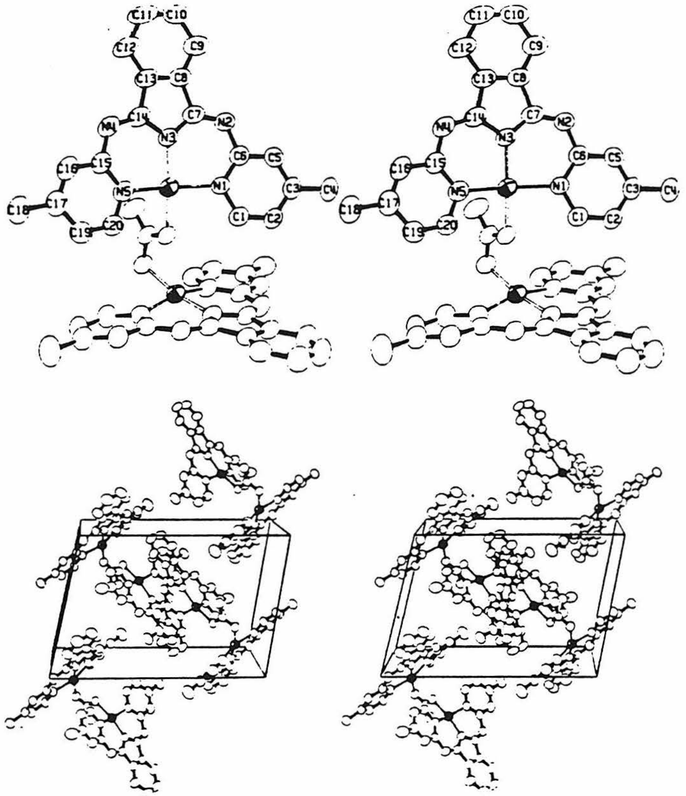


Figure 1. The carbonate-bridged dimer $(CuL)_2(\mu\text{-}CO_3)$, **4**: top, stereoview of a single molecule, showing the numbering scheme used for the ligand; bottom, stereoview of the crystal structure. The thermal ellipsoids are drawn at the 50% probability level.[58]

obtained by reduction of the acetate complex **2** with sodium amalgam and subsequent treatment with CO.

The carbonyl complex **3** can be recrystallized from toluene in a CO atmosphere. Recrystallization under nitrogen, however, results in disproportionation to Cu(II) and Cu(0), implying that the coordinated CO is labile and that the three-coordinate complex is quite unstable. Attempts to produce the three-coordinate Cu(I) complex without a fourth ligand (e.g., via CuCl and **1**) result in a dark insoluble product. Attempts to incorporate other ligands besides carbon monoxide, namely acetonitrile, tetrahydrofuran, or pyridine, similarly gave dark insoluble products whose infrared spectra showed no indication of the desired coordination.[38] These dark products may be polymeric.

The carbonyl complex **3** is only slightly soluble in common organic solvents. In order to increase its solubility, the methyl substituents on the pyridine rings were replaced by *tert*-butyl groups. However, this modified Cu(I) carbonyl complex (ν_{CO} 2067 cm^{-1}) showed only a slightly increased solubility.

Reaction of the Cu(I) Carbonyl Complex 3 with Oxygen. Upon exposure to dry O_2, light yellow suspensions of the carbonyl complex **3** in dry solvents such as benzene gradually turn brown. Reddish brown solids could be isolated from these suspensions, but low solubility and an unchanged infrared spectrum[38] made characterization difficult. In an attempt to define the nature of the oxygenation reaction, we obtained crystals directly from the reaction solution as follows.

A small amount of the carbonyl complex **3** was dissolved in a large amount of benzene open to the atmosphere. The solution was allowed to evaporate slowly, and dark red crystals formed. An X-ray diffraction analysis of these crystals showed a dimeric μ-carbonate complex $(CuL)_2(\mu\text{-}CO_3)$, **4** (Scheme I). A reaction involving atmospheric carbon dioxide seems to be precluded, since crystals of **4** were also obtained under CO_2-free conditions.

From the same CO_2-free benzene solution a second product of the reaction of Cu(L)CO, **3**, with O_2 was also obtained in crystalline form. A crystal-structure determination showed this compound to be a tetrameric complex $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, **5** (Scheme I), which crystallizes with 2.5 molecules of benzene and one molecule of water per tetramer.

Description of the Carbonate-Bridged Dimer, 4. Stereoscopic views of the carbonate-bridged dimer **4** and of the arrangement of the molecules in the crystal are shown in Figure 1; details of the bridging system are given in Figure 2. The coordination about the copper atoms is approximately square planar, each copper being coordinated to three nitrogen atoms of the tridentate ligand and to one oxygen atom of the bridging carbonate group. The Cu–N distances to the pyridine nitrogen atoms N1 and N5, which are equal within experimental error at 2.020 (3) Å, are appreciably longer than those to the pyrrole nitrogen atoms N3, at 1.885 (4) Å. The cis bond angles at the copper atoms range from 89 to 94° and the trans angles from 159 to 167° (Table I).

The square-planar coordination is tetrahedrally distorted with the dihedral angles between the N3–Cu–N5 and N1–Cu–O planes, or between the N3–Cu–N1 and N5–Cu–O planes, being 22° for ligand A and 24° for ligand B. (These

Table I. Coordination Angles (deg)[a]

		$(CuL)_2(\mu\text{-}CO_3)$, 4			
O1–Cu1–N1A	90.7	O2–Cu2–N5B	92.8	N3A–Cu1–O1	167.3
N5A–Cu1–N3A	90.0	N1B–Cu2–N3B	90.5	N1A–Cu1–N5A	159.1
N3A–Cu1–N1A	90.1	N3B–Cu2–N5B	89.3	N3B–Cu2–O2	166.9
O1–Cu1–N5A	93.9	O2–Cu2–N1B	91.3	N5B–Cu2–N1B	162.4
		$(CuL)_3(CuLO)(\mu\text{-}OH)_3$, 5			
N3A–Cu1–N1A	90.7	N3D–Cu4–N1D	89.2	O1–Cu1–N3A	151.1
N5A–Cu1–O1	93.0	N5D–Cu4–O3	93.5	N1A–Cu1–N5A	156.6
O1–Cu1–N1A	98.5	O3–Cu4–N1D	98.9	O3–Cu4–N3D	155.2
N3A–Cu1–N5A	88.8	N3D–Cu4–N5D	89.9	N1D–Cu4–N5D	152.3
N3B–Cu2–O2	128.9	N1B–Cu2–O2	92.1	N1C–Cu3–O2	93.3
O2–Cu2–O1	106.5	N1B–Cu2–N3B	89.9	N1C–Cu3–N3C	88.6
N3B–Cu2–O1	124.6	N1B–Cu2–O1	90.6	N1C–Cu3–O3	85.9
		N5B–Cu2–O2	88.5	N5C–Cu3–O2	91.0
N3C–Cu3–O2	150.0	N5B–Cu2–O1	89.7	N5C–Cu3–N3C	88.9
O2–Cu3–O3	96.2	N5B–Cu2–N3B	89.3	N5C–Cu3–O3	91.0
N3C–Cu3–O3	113.8	N5B–Cu2–N1B	179.2	N1C–Cu3–N5C	174.9

[a] Esd's are 0.1–0.2°.

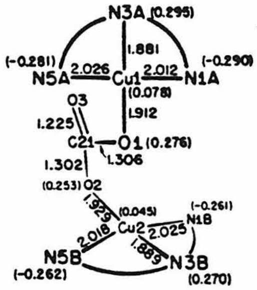


Figure 2. Bond distances and atom numbering scheme of the coordinated atoms for the carbonate-bridged dimer 4. Esd's are about 0.004 Å for the Cu–O and Cu–N distances and about 0.006 Å for C–O distances. Numbers in parentheses are deviations, in Å, from the best planes through the four coordinating atoms.

angles would be 0° for a planar geometry and 90° for a tetrahedral geometry.) Alternatively, the distortion can be described by the deviations from the best planes through the four coordinating atoms, as in Figure 2. This tetrahedral distortion is achieved not by bending of the tridentate ligand but rather by raising the copper atom and the coordinated oxygen atom out of the plane of the tridentate ligand. Atom Cu1 is 0.360, O1 is 1.126, Cu2 is 0.305, and O2 is 1.039 Å above the respective planes of the three coordinated nitrogen atoms. Whatever the description, the distortion serves to relieve the steric interference between the coordinated oxygen atom and the hydrogen atoms on C1 and C20; these O---H distances range from 2.26 to 2.46 Å.

The carbonate group has been shown by crystallographic analyses to coordinate to transition metals as a monodentate,[39] bidentate,[40] bridging bidentate,[41,42] binuclear bridging tridentate,[43] and trinuclear bridging tridentate[44] ligand. In the present structure 4, the carbonate group is bridging bidentate. Two steric effects govern the relative orientations of the CuL moieties and the bridging bidentate carbonate group: first, the sp^2 hydridization of the oxygen atoms suggests that the copper atoms will lie in the plane of the carbonate group with C21–O–Cu angles of about 120°; second, when the plane of the carbonate group is approximately perpendicular to the planes of the tridentate ligands, ligand–ligand repulsion will be minimized. With these constraints, three conformations are possible: a symmetric arrangement with the noncoordinating oxygen atom directed away from the metal atoms; a second symmetric arrangement with the noncoordinating oxygen atom directed inward between the metal atoms; and a nonsymmetric pinwheel arrangement.

The first symmetric arrangement is known[41] but is clearly ruled out in the present case because of the required close contacts between the tridentate ligands. The second symmetric arrangement has yet to be observed crystallographically for any transition metal. The nonsymmetric arrangement is also known[42] and is the observed configuration for 4. In the nonsymmetric carbonate coordination, the relatively short Cu2---O1 (2.407 Å) and Cu1---O3 (2.637 Å) distances are not due to a fifth coordination but are simply a consequence of the geometry of the carbonate group.

The carbonate group is nearly planar as expected. Within the carbonate group, the C21–O3 distance of 1.255 (4) Å is much shorter than the other C–O distances of 1.304 (3) Å, indicating that the double bond is not equally shared. The O2–C21–O1 angle opposite the shortest bond, 114.7°, is the smallest; the O3–C21–O2 angle is 123.8° and the O1–C21–O3 angle is 121.5°. The C21–O–Cu angle is 107.5° for Cu1 and 103.2° for Cu2.

The intermolecular packing (Figure 1, bottom) features the intimate pairing of planar ligand groups that is typical of large aromatic systems. The spacing between adjacent parallel ligands is about 3.5 Å.

Description of the Hydroxyl-Bridged Tetramer, 5. The triclinic unit cell contains two tetrameric molecules, five benzene molecules, and two molecules of water. A single tetramer is shown in Figure 3, top, and the arrangement of molecules is shown in Figure 3, bottom. Hydroxyl bridges join the copper atoms together so as to form an interleaving arrangement of CuL moieties, with successive parallel ligands rotated by approximately 90° with respect to one another in an alternating sequence that suggests a variable capacitor. This 90° rotation permits a systematic sandwiching of the pyridine ring of one ligand with the pyrrole rings of the neighboring layers. The stacking distance between adjacent ligands is fairly uniform at about 3.5–4.0 Å.

The tetrameric molecule contains two five-coordinate and two four-coordinate Cu(II) atoms; some details of the geometry about the copper atoms are shown in Figure 4. For a given tridentate ligand the distances from the copper atoms to the pyrrole nitrogen atoms are shorter than those to the pyridine nitrogen atoms, as was found for 4. The Cu–N distances involving the five-coordinate copper atoms in 5 are longer than those involving the four-coordinate copper atoms in 4 and 5, by an average of 0.033 Å.

The outermost copper atoms, Cu1 and Cu4, are each bonded to three nitrogen atoms of the tridentate ligand and to one

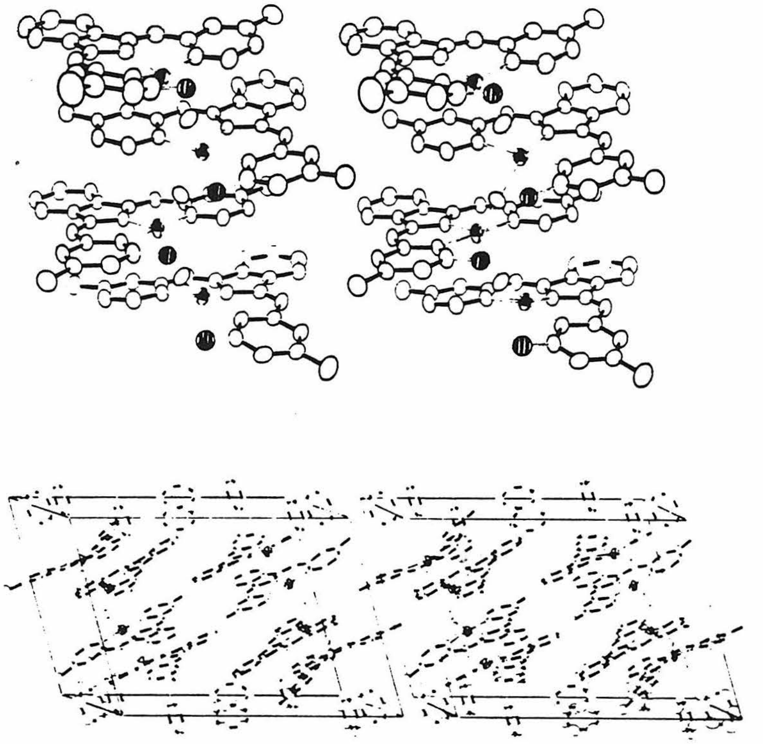


Figure 3. The hydroxyl-bridged tetramer $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, 5: top, stereoview of a single molecule (the disordered oxygen atoms O4 (see text) are shaded); bottom, stereoview of the crystal structure (the disordered oxygen atoms are not shown).

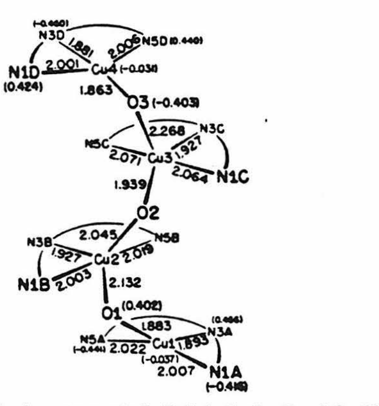


Figure 4. Coordination geometry in 5. Esd's in the Cu–O and Cu–N distances are about 0.005 Å. Numbers in parentheses are deviations, in Å, from the best planes through the coordinating atoms of the two terminal, four-coordinate copper atoms. The two central copper atoms have approximate trigonal-bipyramidal coordination, with N1 and N5 in the axial positions.

bridging hydroxyl oxygen atom in a distorted square-planar geometry similar to that found in the bridging carbonate dimer, 4, but the tetrahedral distortion is larger for the four-coordinate copper coordination in 5 than in 4. The tetrahedral distortion in 5 is illustrated by: (1) the displacements from the best plane through the four coordinating atoms (Figure 4); (2) the displacements from the plane through the three coordinating nitrogen atoms of 0.401 Å for Cu1, 1.631 Å for O1, −0.468 Å for Cu4, and −1.643 Å for O3; and (3) the dihedral angles between the N3–Cu–N5 and N1–Cu–O planes or between the N3–Cu–N1 and N5–Cu–O planes of 36°. Besides relieving the nonbonded interactions between the oxygen atoms and the ligands, this increased distortion serves to increase the distance between successive ligands. The cis bond angles at Cu are all between 89 and 99° and the trans angles are between 151 and 157° (Table I).

The two five-coordinate copper atoms, in contrast to the four-coordinate copper atoms, are approximately in the planes of the coordinating nitrogen atoms (the deviations are 0.003 Å for Cu2 and 0.082 Å for Cu3) and the ligands themselves are more nearly planar. The geometry about these copper atoms is best described as distorted trigonal bipyramidal, the equatorial planes containing two oxygen atoms and a nitrogen atom N3. The equatorial angles are 106.5, 124.5, and 128.9° for Cu2 and 96.2, 113.8, and 150.0° for Cu3. In both cases the cis angles to the axial atoms N1 and N5 are between 88 and 93°; the trans angle is 179.2° for Cu2 and 174.9° for Cu3.

The water molecules of crystallization, O5, apparently form weak hydrogen bonds to the nitrogen atoms N2 of two ligands C and D in different molecules; the N–O distances are 3.067 and 3.029 Å, and the N–O–N angle is 134°. the five benzene molecules in each cell occupy voids in the structure (Figure 3, bottom) one of them lying on a crystallographic center of symmetry and the other four being in general positions.

With only three hydroxyl groups bridging the four CuL^+ groups, the molecule would be expected to be a monocation; in fact, it is a neutral species. The additional negative charge is contributed by an oxygen atom, O4, which is distributed at the C1 position among the four ligands in each tetramer and is always found on the end of the molecule where overlap of the ligands does not occur (see Figure 3, top). Our least-squares refinement led to occupancy factors of 0.677 (10), 0.134 (5), 0.106 (5), and 0.070 (5) for this oxygen atom on the four ligands, for a total of 0.987 (13) per tetramer and within experimental error of the value 1.0 that corresponds to a neutral molecule. While we choose to designate the molecule as $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, in any given tetramer molecule the oxygenated ligand LO can occupy any one of the four positions with varying probabilities.

The partial oxygen atoms O4 are especially interesting. The C1–O4 bond lengths in the four ligands are as follows: A, 1.264 (5); B, 1.31 (2); C, 1.35 (3); D, 1.27 (4) Å (the increasing values of the esd's reflect the decreasing values of the occupancy coefficients); the weighted average is 1.269 (5) Å. This value is considerably shorter than found in normal C–O single bonds, typical distances being 1.43 Å for paraffinic systems[45] and 1.36 Å for phenols.[46] However, it seems a reasonable value for a phenolate group, which we presume it to be. (We have found no example of a C–O distance in a phenolate ion.) The negative charge on this phenolate group is apparently stabilized partly by weak bonds to the Cu atoms (the Cu–O4 distances range from 2.93 to 3.11 Å) and partly by hydrogen bonds from the bridging OH groups, as each of the partial O4 atoms has at least one OH neighbor within 2.8 Å. The hydrogen atoms of the bridging OH groups, which were located with the help of difference maps, point in the general directions of the O4 atoms but the details of the hydrogen bonding are not clear.

The peculiarly uneven distribution of the phenolate group among the four ligands is not entirely senseless. One would expect a phenolated ligand to prefer one of the terminal, four-coordinate copper atoms over an inner, five-coordinate one, and the observed ratio of terminal-to-inner occupancy is 3:1. In addition, the C1 position of ligand D is in close contact with one of the benzene molecules of crystallization. The distances from the site of O4D to the sites of the carbon atoms C33 and C35 are impossibly short, at 2.49 and 2.51 Å; accordingly, the presence of a phenolate group on ligand D must cause a displacement of the benzene molecule and, hence, a disruption in the crystal lattice. (Our least-squares refinement strongly suggests some disorder associated with this benzene molecule; see Experimental Section.) There is no such steric problem associated with ligand A, which shows the highest occupancy factor for the phenolate group.

The preference for atom C1 as the site of phenolation rather than C20, on the opposite side of the molecule, appears to be total. It is clearly dictated by the positions of the bridging OH groups, which in all cases are oriented so as to be able to interact with the O4 sites on C1 but not on C20.

The bridging Cu–O distances (Figure 4) are, at first glance, bewilderingly irregular. At second glance, they make a good deal of sense. As expected, the Cu–O bonds to the terminal, four-coordinate atoms Cu1 and Cu4 are the shortest. Then, because of conjugation effects, the two central bonds Cu2–O2 and Cu3–O2 are shorter than the penultimate bonds Cu2–O1 and Cu3–O3. Finally, asymmetry between the two halves of the tetramer is caused by the unequal distribution of the phenolate oxygen atom O4 among the four ligands. Since this atom is found on ligand A most of the time, Cu1 is less electron deficient than Cu4 and the Cu1–O1 bond is longer than the Cu4–O3 bond; by conjugation, Cu2–O2 is longer than Cu3–O2, and Cu3–O3 is longer than Cu2–O1. The bridging Cu–O–Cu angles range from 120.1 to 124.8°.

The structure determinations of 4 and 5 have resulted in six independent determinations of the geometry of the tridentate ligand, and, assuming C_{2v} (mm) symmetry for the ligand, in 12 independent measurements of most of the bond lengths and angles. Averaged values are shown in Figure 5, and the individual values are available as supplementary material.

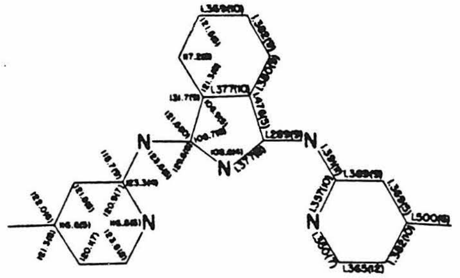


Figure 5. Average values for the bond distances and angles for the tridentate ligand in 3 and 4. Most values are averages of 12 independent measurements, based on a presumed $mm2$ (C_{2v}) symmetry of the ligand. The esd in a single such measurement, as obtained from our least-squares refinement, is about 0.008 Å or 0.6°; values in parentheses are the observed standard deviations about the average value. The esd in an *average* distance is about $0.008(12^{1/2})$, or 0.002 Å, and in an angle is about 0.2°.

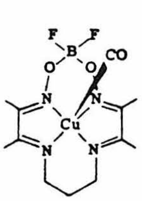
Reaction Stoichiometry. A suspension of Cu(L)CO, 3, in benzene was oxygenated on a vacuum line over a 12-h period, and the amounts of O_2 consumed and of CO evolved were measured. Reproducible results were obtained. They indicated that 0.5 ± 0.1 mol of O_2 were consumed and 0.91 ± 0.05 mol of CO were evolved/mol of complex 3. This stoichiometry is consistent with the formation of a dioxygen–bridged dimer:

$$2Cu(L)CO + O_2 \rightarrow (CuL)_2O_2 + CO$$

However, the oxygenation reaction appears to be irreversible, and neither infrared nor mass spectroscopy of the product suggested the presence of a dioxygen-bridged dimer.

Discussion

The copper(I) carbonyl complex Cu(L)CO, 3, prepared in this study joins a number of stable copper(I) carbonyl species that have been synthesized recently. These include [hydrotris(pyrazolyl)borato]copper(I) carbonyl, 6, and its dimethyl analogue [hydrotris(3,5-dimethyl-1-pyrazolyl)borato]copper(I) carbonyl, 7.[47,48] The expected tetrahedral geometry for these complexes has been confirmed by a crystal structure determination of the former.[49] More recently, we have reported the synthesis, properties, and structure of a five-coordinate copper(I) carbonyl complex, 8, in which the Cu(I) has a square-pyramidal environment.[28,29] The mixed-valence Cu^ICu^{II} complex 9 probably also contains a five-coordinate Cu(I) carbonyl group.[31] Thus far, the insolubility of the present compound, 3, has precluded a crystal structure study, but a distorted square-planar geometry seems likely. The C–O stretching frequencies for these carbonyl complexes are 2068 cm^{-1} for 3, 2067 cm^{-1} for the *tert*-butyl analogue of 3, 2083 cm^{-1} for 6, 2066 cm^{-1} for 7, 2068 cm^{-1} for 8, and 2065 cm^{-1} for 9; for hemocyanin (1:2 CO/Cu), the observed value is in



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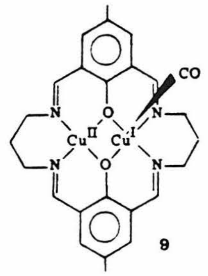

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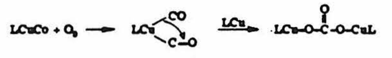
Scheme II



the range 2040–2060 cm^{-1}.[50,51] Thus, analogy with simple Cu(I) carbonyl complexes suggests any of a variety of possible metal stereochemistries for hemocyanin.

Our present work is one example of a reaction between Cu(I) and O_2 whose stoichiometry suggests the formation of a dioxygen complex but which, upon detailed examination, must be far more complicated. The oxygenation reaction is irreversible, and we have not been able to isolate a dioxygen species. Instead, we obtained from the reaction mixture crystals of a carbonate-bridged dimer, **4**, and of a hydroxy-bridged tetramer, **5**, in which one-quarter of the ligand molecules have been oxidized to a phenolate, as well as large amounts of noncrystalline material which we have not been able to identify. We have no reason to doubt that the crystalline products are representative of the products formed during oxygenation, although they were obtained under slightly different conditions than were used for the measurements of the reaction stoichiometry.

Although we have not been able to isolate any dioxygen compounds, it is likely that they are involved as intermediates in the various oxidation reactions. For example, a plausible mechanism for the formation of the μ-carbonato complex **4** involves intramolecular insertion of coordinated CO into coordinated dioxygen (Scheme II). In somewhat analogous reactions, carbonyl complexes of Ir(I) and Rh(I) coordinated to tridentate phosphine ligands are presumed to form mononuclear, five-coordinate carbonato complexes through dioxygen intermediates.[52,53] The overall stoichiometry of the reaction in Scheme II (eq 1) does not by itself account for the

$$2Cu(L)CO + O_2 \rightarrow (CuL)_2CO_3 + CO \qquad (1)$$

amount of CO liberated. As one of several processes going on it could help explain the stoichiometry of less than 1.0 CO/Cu liberated.

Formation of the tetrameric species $(CuL)_3(CuLO)(\mu\text{-}OH)_3$ may also involve a dioxygen intermediate, with copper-promoted activation of coordinated O_2 leading to ligand hydroxylation (Scheme III). Hydrocarbon hydroxylations mediated by the cytochromes P_{450} (Fe) and by tyrosinase (Cu) are thought to proceed via coordinated O_2, and macrocyclic ligand oxidations via O_2 to give ketones, apparently promoted by cobalt, have been reported.[54,55] Examples of hydrocarbon hydroxylations in which the oxidizing agent has been clearly demonstrated to be dioxygen coordinated to a simple metal complex are apparently unknown. Equation 2 agrees with the

$$2Cu(L)CO + O_2 \rightarrow CuLO + CuL^+ + OH^- + 2CO \qquad (2)$$

overall stoichiometry we observed for the oxygenation reaction; however, it would lead to the formation of equal amounts of the normal complex CuL^+ and of the phenolated complex Cu(LO), whereas the tetramer contains them in a 3:1 ratio. It is quite possible, though, that charge balance, ligand–ligand overlap, and crystal forces could account for the selective crystallization of the tetrameric species; we emphasize again that crystalline material represented only a small portion of the reaction products. It is also conceivable that the small amount of phenolated ligand necessary to produce the crystals resulted from an impurity in the starting material and that the bridging hydroxyl groups were formed by any of a number of mechanisms including simple protonation of a μ-oxo species.

Conclusions

The carbonyl complex Cu(L)CO, **3**, reacts with oxygen with a seductively simple stoichiometry. Characterizable oxidation products, however, indicate that the reaction is in fact very complex. Our results once again indicate that caution must be exercised in drawing conclusions concerning the formation and nature of metal–oxygen complexes on the basis of a few observations and in the absence of firm structural evidence. The preparation of a stable copper–dioxygen complex continues to present a challenge to the synthetic chemist. Our own efforts are continuing in this area.

Scheme III

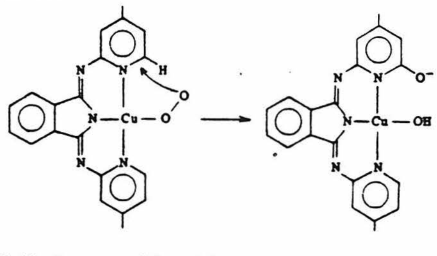


Table II. Summary of Crystal Data

	$Cu_2C_{40}H_{32}$-$N_{10}CO_3$	$Cu_4C_{80}H_{66}N_{20}O_4\cdot(C_6H_6)_{2\cdot5}H_2O$
formula wt	839.85	1839.01
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.420 (1)	14.586 (1)
b, Å	16.479 (1)	14.925 (1)
c, Å	10.954 (1)	20.781 (2)
α, deg	90.98 (1)	105.48 (1)
β, deg	113.83 (1)	105.48 (1)
γ, deg	101.71 (1)	80.24 (1)
V, Å^3	1835	4178
Z	2	2
d, g/cm^3	1.520 (calcd) 1.50 (3) (obsd)	1.462 (calcd) 1.43 (2) (obsd)
μ, cm^{-1}	19.20	17.18
unique data used	4578	9334
R(*F*)	0.058	0.065

Experimental Section

Preparation of the Free Ligand L and of Cu(L)OAc. The free ligand, **1**, and the Cu(II) acetate complex Cu(L)OAc, **2**, were prepared by the procedure of Siegl.[35]

(Carbonyl){1,3-bis(2-(4-methylpyridyl)imino)isoindoline}copper(I), Cu(L)CO, 3. A solution of triethylamine (0.75 mL, 5.4 mmol) in ethanol (35 mL) was purged with CO and then added all at once to a mixture of the free ligand **1** (0.5 g, 1.5 mmol) and CuCl (0.15 g, 0.76 mmol) in a Schlenk apparatus. The red reaction mixture was stirred under CO. A finely divided yellow solid began to precipitate after 5 min and was collected by filtration under CO after 6 h. The solid was washed with CO-saturated ethanol (2 × 5 mL) and dried in a slow stream of CO. The yield was 0.55 g (88%); ν_{CO} 2068 cm^{-1}. Anal. Calcd for $C_{21}H_{16}N_5OCu$: C, 60.35; H, 3.85; N, 16.75; Cu, 15.2. Found: C, 60.05; H, 4.1; N, 16.9; Cu, 15.2.

The carbonyl complex **3** was also prepared by reduction of the Cu(II) acetate complex **2** under nitrogen as follows. The Cu(II) complex Cu(L)OAc, **2** (0.5 g, 1.1 mmol), was warmed in toluene (70 mL, 60 °C). Sodium amalgam (5 g, 1%) was added with stirring to give a red solution and a gray solid. After 1 h the suspension was filtered. Treatment of the red filtrate with CO led to gradual deposition of a finely divided yellow solid which was collected and washed as above. The yield was 0.3 g (65%).

Measurement of O_2 Consumption and CO Evolution for the Reaction of Cu(L)CO, 3, with O_2. The carbonyl complex **3** in dry benzene was allowed to react with a premeasured amount of O_2 at 25 °C. At the end of the reaction a Toepler pump was used to determine the amounts of CO evolved and of O_2 remaining. In a typical experiment, dry benzene (~15 mL) was distilled in a vacuum line onto a sample of the complex **3** (0.144 g, 0.344 mmol) at −196 °C. The frozen mixture was warmed to 25 °C after a measured amount of O_2 (1.01 mmol) had been added (partial pressure of O_2 ~200 torr). The suspension was stirred at 25 °C for 12 h, during which time the mixture turned from yellow to red. At the end of the reaction the total amount of

Table III. Positional and Thermal Parameters[a] for $(CuL)_2(\mu\text{-}CO_3)$, 4

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	57884 (7)	14707 (4)	89121 (7)	450 (4)	456 (4)	523 (4)	92 (3)	146 (4)	52 (3)
Cu2	85542 (7)	37078 (4)	90611 (7)	480 (4)	518 (4)	520 (4)	102 (4)	132 (4)	56 (4)
O1	6955 (3)	2438 (2)	8768 (3)	47 (2)	46 (2)	44 (2)	8 (2)	8 (2)	6 (2)
O2	6990 (3)	3396 (2)	7405 (3)	53 (2)	53 (2)	52 (2)	9 (2)	12 (2)	10 (2)
O3	5183 (4)	2389 (2)	6895 (4)	55 (2)	64 (2)	78 (3)	10 (2)	−1 (2)	8 (2)
N1A	5804 (4)	2038 (2)	10562 (4)	42 (2)	49 (2)	49 (2)	9 (2)	14 (2)	8 (2)
N2A	3705 (4)	1213 (3)	10390 (4)	50 (3)	59 (3)	58 (3)	6 (2)	18 (2)	10 (2)
N3A	4351 (4)	627 (2)	8791 (4)	44 (2)	46 (2)	55 (3)	7 (2)	14 (2)	5 (2)
N4A	4208 (4)	−374 (2)	7072 (4)	53 (3)	46 (3)	67 (3)	11 (2)	11 (2)	0 (2)
N5A	6217 (4)	697 (2)	7776 (4)	55 (3)	47 (2)	61 (3)	16 (2)	18 (2)	4 (2)
C1A	6851 (5)	2671 (3)	11301 (5)	48 (3)	64 (4)	57 (3)	10 (3)	15 (3)	6 (3)
C2A	6962 (5)	3106 (3)	12423 (5)	56 (3)	66 (4)	48 (3)	10 (3)	11 (3)	−2 (3)
C3A	5980 (6)	2925 (4)	12885 (5)	67 (4)	77 (4)	46 (3)	16 (3)	16 (3)	3 (3)
C4A	6065 (6)	3402 (4)	14123 (6)	73 (4)	121 (6)	54 (4)	9 (4)	21 (3)	−14 (4)
C5A	4922 (5)	2289 (4)	12151 (5)	63 (4)	74 (4)	58 (4)	10 (3)	29 (3)	10 (3)
C6A	4830 (5)	1852 (3)	11020 (5)	47 (3)	56 (3)	55 (3)	20 (3)	14 (3)	13 (3)
C7A	3556 (5)	674 (3)	9440 (5)	45 (3)	50 (3)	62 (3)	9 (2)	12 (3)	18 (3)
C8A	2387 (5)	−31 (3)	8872 (5)	50 (3)	57 (3)	63 (4)	7 (3)	13 (3)	19 (3)
C9A	1315 (6)	−264 (4)	9190 (6)	56 (4)	78 (4)	80 (4)	5 (3)	17 (3)	18 (3)
C10A	403 (6)	−990 (4)	−8476 (7)	47 (4)	95 (5)	105 (5)	0 (3)	21 (4)	30 (4)
C11A	542 (6)	−1444 (4)	7516 (7)	60 (4)	66 (4)	109 (5)	−11 (3)	12 (4)	16 (4)
C12A	1607 (6)	−1205 (3)	7179 (6)	63 (4)	51 (4)	93 (5)	2 (3)	8 (4)	10 (3)
C13A	2526 (5)	−485 (3)	7906 (5)	41 (3)	51 (3)	69 (4)	11 (2)	7 (3)	18 (3)
C14A	3792 (5)	−78 (3)	7860 (5)	48 (3)	46 (3)	64 (4)	15 (2)	7 (3)	9 (3)
C15A	5424 (5)	−39 (3)	7065 (5)	59 (3)	48 (3)	51 (3)	18 (3)	14 (3)	7 (2)
C16A	5796 (6)	−509 (3)	6273 (5)	74 (4)	53 (3)	55 (3)	17 (3)	13 (3)	2 (3)
C17A	6980 (6)	−267 (3)	6202 (5)	77 (4)	62 (4)	62 (4)	32 (3)	24 (3)	9 (3)
C18A	7377 (6)	−780 (4)	5363 (6)	79 (4)	78 (4)	72 (4)	35 (4)	24 (4)	−1 (3)
C19A	7780 (6)	480 (4)	6953 (6)	61 (4)	74 (4)	80 (4)	14 (3)	33 (3)	0 (3)
C20A	7384 (6)	933 (3)	7696 (6)	66 (4)	59 (4)	80 (4)	6 (3)	35 (3)	−8 (3)
N1B	7846 (4)	4606 (2)	9633 (4)	52 (3)	45 (2)	61 (3)	11 (2)	15 (2)	3 (2)
N2B	9285 (4)	4758 (3)	12026 (4)	68 (3)	61 (3)	56 (3)	15 (2)	12 (2)	3 (2)
N3B	9891 (4)	3806 (2)	10816 (4)	46 (2)	45 (2)	54 (3)	9 (2)	14 (2)	4 (2)
N4B	11088 (4)	2818 (2)	10526 (4)	49 (2)	54 (3)	54 (3)	10 (2)	18 (2)	3 (2)
N5B	9592 (4)	3120 (3)	8374 (4)	43 (2)	61 (3)	56 (3)	13 (2)	17 (2)	5 (2)
C1B	6853 (5)	4863 (3)	8651 (6)	58 (4)	49 (3)	74 (4)	20 (3)	18 (3)	18 (3)
C2B	6231 (6)	5428 (3)	8936 (6)	58 (4)	60 (4)	76 (4)	20 (3)	14 (3)	22 (3)
C3B	6585 (5)	5755 (3)	10253 (6)	55 (3)	44 (3)	78 (4)	11 (3)	23 (3)	10 (3)
C4B	5897 (6)	6354 (4)	10581 (6)	63 (4)	65 (4)	99 (5)	25 (3)	31 (4)	17 (4)
C5B	7610 (5)	5504 (3)	11226 (5)	59 (3)	47 (3)	67 (4)	13 (3)	23 (3)	2 (3)
C6B	8230 (5)	4943 (3)	10901 (5)	53 (3)	41 (3)	62 (3)	10 (2)	9 (3)	8 (3)
C7B	9975 (5)	4251 (3)	11924 (5)	51 (3)	42 (3)	56 (3)	9 (2)	14 (3)	0 (2)
C8B	11038 (5)	4073 (3)	13135 (5)	46 (3)	57 (3)	55 (3)	6 (3)	12 (3)	3 (3)
C9B	11544 (6)	4368 (4)	14466 (6)	64 (4)	88 (4)	63 (4)	22 (3)	15 (3)	−3 (3)
C10B	12593 (6)	4066 (4)	15358 (6)	85 (5)	115 (6)	49 (4)	25 (4)	12 (3)	7 (4)
C11B	13079 (6)	3471 (4)	14917 (6)	68 (4)	102 (5)	64 (4)	30 (4)	16 (3)	21 (4)
C12B	12563 (5)	3182 (4)	13584 (6)	51 (3)	74 (4)	68 (4)	20 (3)	21 (3)	12 (3)
C13B	11549 (5)	3487 (3)	12703 (5)	41 (3)	53 (3)	53 (3)	7 (2)	13 (2)	9 (2)
C14B	10823 (5)	3322 (3)	11226 (5)	46 (3)	46 (3)	57 (3)	4 (2)	16 (3)	8 (2)
C15B	10545 (5)	2737 (3)	9131 (5)	52 (3)	50 (3)	63 (3)	5 (2)	28 (3)	1 (3)
C16B	11079 (6)	2243 (3)	8552 (5)	65 (4)	60 (4)	61 (4)	15 (3)	23 (3)	4 (3)
C17B	10748 (6)	2192 (4)	7193 (6)	72 (4)	66 (4)	73 (4)	17 (3)	30 (3)	−4 (3)
C18B	11350 (7)	1692 (4)	6548 (7)	115 (6)	107 (6)	86 (5)	46 (5)	48 (5)	−3 (4)
C19B	9835 (6)	2630 (4)	6432 (6)	79 (4)	87 (4)	58 (4)	19 (4)	31 (3)	−1 (3)
C20B	9271 (6)	3057 (4)	7038 (5)	68 (4)	79 (4)	53 (4)	21 (3)	19 (3)	8 (3)
C21	6322 (5)	2726 (3)	7642 (5)	44 (3)	50 (3)	53 (3)	12 (2)	9 (2)	−5 (2)

[a] The fractional coordinates are multiplied by 10^5 for the copper atoms and by 10^4 for other atoms. The form of the temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$. The U_{ij} elements are multiplied by 10^4 for the copper atoms and by 10^3 for other atoms. Numbers in parentheses in this table are estimated standard deviations in units of the last digit.

gas remaining, X, was measured using a Toepler pump. The gas was then circulated over CuO (240 °C) to oxidize CO to CO_2, which was trapped at −196 °C. Measurement of the amount of CO_2 produced gave the amount of CO evolved (0.32 mmol) and, by difference (X −CO), the amount of O_2 remaining (0.85 mmol). The amount of O_2 at the start (1.01 mmol) less the amount of O_2 remaining (0.85 mmol) gave the amount of O_2 consumed. In this case, 95% of the total CO was recovered and the Cu/O_2 stoichiometry was 2.00/0.94.

The infrared spectrum of the product isolated by suction filtration and air-drying was virtually identical with that of Cu(L)CO, 3, except for the absence of ν_{CO} and slight changes near 1100 cm^{-1}. No peaks attributable to $\nu_{C\equiv O}$ or to carbonate were observable. The mass spectrum showed a large peak at 44 mass units (CO_2), which does not appear in the mass spectrum of Cu(L)CO, 3, as well as a significant peak at 456/458 mass units. (This latter peak appears very weakly in the spectrum of Cu(L)CO and has not been assigned.)

Growth of Single Crystals from Cu(L)CO in Benzene. The carbonyl complex Cu(L)CO, 3 (50 mg), was added to dry benzene (30 mL) in air and stirred for 5 min, giving a deep red-brown solution. The solution was filtered and then allowed to slowly evaporate at 25 °C.

Under a microscope, dark parallelepipeds and dark amorphous masses were observed (as well as some yellow crystals of the free ligand, which were separated by hand). The infrared spectrum of the crystalline material showed no obvious $\nu_{C\equiv O}$ or any indication of carbonate, but elemental analysis was consistent with the formula $C_{40}H_{32}N_{10}Cu_2CO_3$. Anal. Calcd: C, 58.65; H, 3.8; N, 16.7; Cu, 15.15. Found: C, 58.75; H, 3.95; N, 16.45; Cu, 14.8. Magnetic susceptibility measurements of the sample gave a μ_{cor} of 1.5 μ_B (25 °C, Faraday method). The mass spectrum of a parallelepiped crystal showed a strong peak at 44 mass units (CO_2), as well as significant

Table IV. Positional and Thermal Parameters[a] for $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, 5

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	18219 (4)	21856 (5)	13605 (3)	333 (4)	702 (5)	419 (4)	−34 (3)	45 (3)	98 (4)
Cu2	2272 (4)	9950 (5)	17345 (3)	301 (4)	673 (5)	375 (4)	67 (3)	38 (3)	21 (3)
Cu3	10238 (4)	−12729 (5)	20060 (3)	342 (4)	633 (5)	394 (4)	53 (3)	56 (3)	142 (3)
Cu4	−6201 (5)	−27299 (5)	21148 (3)	444 (4)	745 (6)	519 (4)	−44 (4)	116 (3)	174 (4)
O1	776 (2)	1469 (2)	1045 (1)	40 (2)	77 (2)	31 (2)	−20 (2)	6 (1)	6 (2)
O2	335 (2)	−432 (2)	1428 (1)	43 (2)	48 (2)	40 (2)	0 (2)	−5 (1)	13 (2)
O3	9 (2)	−2397 (2)	1556 (1)	55 (2)	66 (2)	45 (2)	−18 (2)	18 (2)	5 (2)
O5	5009 (3)	8416 (3)	2057 (2)	84 (3)	125 (4)	115 (4)	9 (3)	28 (3)	40 (3)
N1A	2430 (2)	1687 (3)	558 (2)	34 (2)	63 (3)	31 (2)	−3 (2)	3 (2)	11 (2)
N2A	4051 (2)	1509 (3)	1238 (2)	32 (2)	73 (3)	42 (2)	2 (2)	8 (2)	13 (2)
N3A	3023 (2)	2465 (2)	1953 (2)	29 (2)	55 (3)	40 (2)	−5 (2)	2 (2)	10 (2)
N4A	2579 (2)	3411 (3)	2977 (2)	40 (2)	61 (3)	44 (2)	−9 (2)	3 (2)	5 (2)
N5A	1184 (2)	3161 (2)	2033 (2)	37 (2)	50 (3)	45 (2)	3 (2)	6 (2)	8 (2)
O4A	962 (4)	1790 (3)	−175 (2)	5.21 (0.19)[b]					
C1A	1855 (3)	1568 (3)	−83 (2)	33 (3)	67 (4)	55 (3)	5 (3)	8 (2)	22 (3)
C2A	2212 (3)	1180 (3)	−667 (2)	62 (3)	65 (4)	34 (3)	−12 (3)	8 (2)	13 (3)
C3A	3161 (3)	869 (3)	−611 (2)	56 (3)	54 (4)	46 (3)	−5 (3)	18 (3)	11 (3)
C4A	3544 (4)	409 (4)	−1235 (3)	74 (4)	88 (5)	59 (4)	−9 (3)	28 (3)	−4 (3)
C5A	3740 (3)	1005 (3)	42 (2)	43 (3)	64 (4)	50 (3)	−2 (3)	15 (2)	14 (3)
C6A	3384 (3)	1408 (3)	610 (2)	41 (3)	53 (3)	45 (3)	−4 (2)	12 (2)	15 (3)
C7A	3871 (3)	1984 (3)	1811 (2)	33 (3)	54 (3)	50 (3)	−9 (2)	6 (2)	16 (3)
C8A	4614 (3)	2121 (3)	2459 (2)	36 (3)	55 (3)	46 (3)	−9 (2)	1 (2)	18 (3)
C9A	5575 (3)	1790 (4)	2596 (2)	41 (3)	72 (4)	52 (3)	1 (3)	6 (2)	16 (3)
C10A	6096 (3)	2059 (4)	3255 (3)	37 (3)	87 (4)	68 (4)	−9 (3)	−7 (3)	21 (3)
C11A	5692 (4)	2643 (4)	3756 (2)	56 (3)	99 (5)	52 (3)	−18 (3)	−14 (3)	16 (3)
C12A	4740 (3)	2977 (4)	3628 (2)	50 (3)	81 (4)	48 (3)	−12 (3)	−1 (3)	1 (3)
C13A	4200 (3)	2704 (3)	2962 (2)	39 (3)	59 (4)	49 (3)	−11 (2)	2 (2)	16 (3)
C14A	3181 (3)	2908 (3)	2637 (2)	42 (3)	53 (3)	45 (3)	−12 (2)	4 (2)	6 (3)
C15A	1614 (3)	3585 (3)	2686 (2)	45 (3)	43 (3)	54 (3)	−8 (2)	11 (2)	14 (3)
C16A	1071 (3)	4212 (3)	3104 (2)	53 (3)	50 (3)	62 (3)	−7 (2)	17 (3)	5 (3)
C17A	116 (3)	4448 (3)	2877 (2)	53 (3)	37 (3)	78 (4)	−2 (2)	25 (3)	9 (3)
C18A	−476 (4)	5114 (4)	3330 (3)	66 (4)	67 (4)	103 (5)	1 (3)	33 (3)	14 (3)
C19A	−295 (3)	4030 (3)	2204 (3)	41 (3)	64 (4)	74 (4)	9 (3)	14 (3)	20 (3)
C20A	248 (3)	3400 (4)	1819 (2)	47 (3)	74 (4)	52 (3)	1 (3)	4 (2)	16 (3)
N1B	−1098 (2)	1117 (2)	1143 (2)	31 (2)	47 (2)	38 (2)	4 (2)	6 (2)	9 (2)
N2B	−1885 (2)	2134 (2)	2002 (2)	30 (2)	49 (3)	47 (2)	5 (2)	12 (2)	7 (2)
N3B	−214 (2)	1798 (2)	2511 (2)	28 (2)	44 (2)	34 (2)	1 (2)	7 (2)	5 (2)
N4B	1233 (2)	1806 (2)	3419 (2)	34 (2)	51 (3)	36 (2)	3 (2)	5 (2)	6 (2)
N5B	1558 (2)	888 (2)	2341 (2)	29 (2)	51 (3)	38 (2)	4 (2)	6 (2)	6 (2)
O4B	−473 (15)	−184 (15)	245 (11)	4.00[b]					
C1B	−1211 (3)	645 (3)	481 (2)	39 (3)	58 (3)	40 (3)	6 (2)	6 (2)	4 (2)
C2B	−2059 (3)	655 (3)	3 (2)	55 (3)	56 (3)	34 (3)	−6 (2)	2 (2)	7 (2)
C3B	−2865 (3)	1178 (3)	186 (2)	36 (3)	52 (3)	48 (3)	−4 (2)	−3 (2)	19 (2)
C4B	−3794 (3)	1231 (4)	−336 (2)	51 (3)	76 (4)	61 (3)	−6 (3)	−2 (3)	21 (3)
C5B	−2763 (3)	1648 (3)	863 (2)	30 (2)	54 (3)	50 (3)	5 (2)	4 (2)	15 (2)
C6B	−1891 (3)	1624 (3)	1337 (2)	30 (2)	45 (3)	42 (3)	−1 (2)	5 (2)	11 (2)
C7B	−1131 (3)	2191 (3)	2507 (2)	36 (3)	40 (3)	43 (3)	−2 (2)	11 (2)	12 (2)
C8B	−1181 (3)	2735 (3)	3206 (2)	39 (3)	45 (3)	40 (3)	3 (2)	14 (2)	10 (2)
C9B	−1923 (3)	3264 (3)	3747 (2)	40 (3)	56 (3)	51 (3)	6 (2)	14 (2)	10 (3)
C10B	−1721 (3)	3684 (3)	4166 (2)	55 (3)	65 (4)	53 (3)	12 (3)	27 (3)	7 (3)
C11B	−826 (4)	3573 (4)	4577 (2)	70 (4)	76 (4)	36 (3)	3 (3)	18 (3)	−2 (3)
C12B	−76 (3)	3049 (3)	4311 (2)	46 (3)	67 (4)	41 (3)	5 (3)	7 (2)	6 (3)
C13B	−281 (3)	2631 (3)	3617 (2)	42 (3)	44 (3)	39 (3)	1 (2)	17 (2)	7 (2)
C14B	333 (3)	2033 (3)	3172 (2)	45 (3)	39 (3)	39 (3)	−4 (2)	8 (2)	10 (2)
C15B	1837 (3)	1248 (3)	3025 (2)	34 (3)	43 (3)	40 (3)	−6 (2)	4 (2)	8 (2)
C16B	2780 (3)	1063 (3)	3375 (2)	40 (3)	53 (3)	36 (3)	−3 (2)	−2 (2)	8 (2)
C17B	3449 (3)	522 (3)	3051 (2)	27 (2)	48 (3)	53 (3)	−2 (2)	1 (2)	14 (2)
C18B	4455 (3)	315 (4)	3442 (3)	36 (3)	86 (4)	70 (4)	4 (3)	−1 (3)	19 (3)
C19B	3156 (3)	168 (3)	2351 (2)	32 (3)	51 (3)	57 (3)	6 (2)	13 (2)	15 (3)
C20B	2233 (3)	363 (3)	2025 (2)	37 (3)	56 (3)	38 (3)	1 (2)	9 (2)	6 (2)
N1C	1789 (2)	−2026 (2)	1295 (2)	39 (2)	55 (3)	36 (2)	4 (2)	8 (2)	11 (2)
N2C	3244 (2)	−2426 (2)	2081 (2)	30 (2)	53 (3)	41 (2)	0 (2)	7 (2)	9 (2)
N3C	2092 (2)	−1565 (2)	2722 (2)	27 (2)	47 (3)	34 (2)	1 (2)	4 (2)	13 (2)
N4C	1515 (2)	−803 (2)	3746 (2)	37 (2)	52 (3)	36 (2)	3 (2)	3 (2)	9 (2)
N5C	263 (2)	−626 (2)	2747 (2)	33 (2)	51 (3)	37 (2)	−1 (2)	6 (2)	11 (2)
O4C	421 (20)	−1756 (19)	412 (14)	4.00[b]					
C1C	1313 (3)	−2153 (4)	632 (2)	50 (3)	82 (4)	49 (3)	9 (3)	12 (3)	16 (3)
C2C	1662 (3)	−2744 (4)	99 (2)	62 (3)	76 (4)	43 (3)	−0 (3)	10 (3)	11 (3)
C3C	2532 (3)	−3255 (3)	227 (2)	59 (3)	52 (3)	48 (3)	1 (3)	17 (3)	10 (3)
C4C	2901 (4)	−3916 (4)	−352 (3)	94 (4)	66 (4)	73 (4)	7 (3)	41 (3)	5 (3)
C5C	3030 (3)	−3120 (3)	901 (2)	45 (3)	62 (4)	50 (3)	8 (2)	15 (2)	16 (3)
C6C	2663 (3)	−2508 (3)	1428 (2)	39 (3)	50 (3)	51 (3)	3 (2)	17 (2)	17 (3)
C7C	2971 (3)	−2013 (3)	2634 (2)	30 (3)	39 (3)	43 (3)	−5 (2)	3 (2)	15 (2)
C8C	3628 (3)	−1985 (3)	3314 (2)	36 (3)	45 (3)	42 (3)	0 (2)	6 (2)	14 (2)
C9C	4572 (3)	−2355 (3)	3509 (2)	39 (3)	53 (3)	54 (3)	6 (2)	8 (2)	13 (3)
C10C	4978 (3)	−2229 (3)	4206 (2)	36 (3)	60 (4)	60 (3)	4 (2)	−4 (2)	16 (3)
C11C	4460 (3)	−1775 (3)	4682 (2)	50 (3)	67 (4)	45 (3)	4 (3)	−12 (2)	9 (3)

Table IV (*Continued*)

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C12C	3522 (3)	−1412 (3)	4495 (2)	51 (3)	62 (4)	42 (3)	7 (3)	0 (2)	7 (3)
C13C	3117 (3)	−1533 (3)	3798 (2)	36 (3)	47 (3)	39 (3)	−2 (2)	−1 (2)	14 (2)
C14C	2146 (3)	−1257 (3)	3417 (2)	37 (3)	44 (3)	39 (3)	1 (2)	3 (2)	16 (2)
C15C	590 (3)	−509 (3)	3431 (2)	38 (3)	40 (3)	42 (3)	−4 (2)	5 (2)	11 (2)
C16C	4 (3)	−65 (3)	3883 (2)	48 (3)	51 (3)	37 (3)	−1 (2)	13 (2)	7 (2)
C17C	−916 (3)	286 (3)	3650 (2)	40 (3)	40 (3)	60 (3)	4 (2)	18 (2)	15 (2)
C18C	−1526 (3)	800 (4)	4137 (3)	61 (3)	76 (4)	69 (4)	12 (3)	25 (3)	25 (3)
C19C	−1252 (3)	142 (3)	2946 (2)	30 (3)	65 (4)	53 (3)	5 (2)	8 (2)	17 (3)
C20C	−655 (3)	−287 (3)	2531 (2)	36 (3)	66 (4)	45 (3)	3 (2)	−1 (2)	18 (3)
N1D	−1859 (2)	−2996 (3)	1434 (2)	47 (2)	65 (3)	49 (3)	−8 (2)	12 (2)	8 (2)
N2D	−2890 (2)	−2289 (3)	2207 (2)	38 (2)	68 (3)	52 (3)	−1 (2)	11 (2)	18 (2)
N3D	−1257 (2)	−2507 (3)	2828 (2)	42 (2)	59 (3)	47 (2)	−1 (2)	10 (2)	21 (2)
N4D	95 (3)	−2486 (3)	3801 (2)	54 (3)	59 (3)	50 (3)	−6 (2)	7 (2)	17 (2)
N5D	602 (3)	−3119 (3)	2742 (2)	47 (2)	61 (3)	64 (3)	3 (2)	16 (2)	22 (2)
O4D	−982 (31)	−3826 (30)	689 (21)	4.00[b]					
C1D	−1801 (4)	−3448 (4)	785 (2)	59 (4)	72 (4)	63 (4)	−9 (3)	16 (3)	−1 (3)
C2D	−2576 (4)	−3642 (4)	257 (2)	63 (4)	82 (4)	57 (4)	−10 (3)	10 (3)	−5 (3)
C3D	−3484 (4)	−3367 (4)	375 (2)	59 (3)	69 (4)	61 (4)	−11 (3)	−5 (3)	8 (3)
C4D	−4358 (4)	−3570 (5)	−194 (3)	80 (4)	119 (6)	81 (5)	−10 (4)	−9 (4)	−8 (4)
C5D	−3548 (3)	−2914 (4)	1030 (2)	44 (3)	74 (4)	59 (3)	−8 (3)	3 (2)	18 (3)
C6D	−2741 (3)	−2739 (3)	1562 (2)	48 (3)	61 (4)	54 (3)	−3 (3)	15 (2)	19 (3)
C7D	−2210 (3)	−2198 (3)	2765 (2)	38 (3)	54 (3)	57 (3)	−5 (2)	11 (2)	23 (3)
C8D	−2375 (3)	−1751 (3)	3450 (2)	49 (3)	55 (3)	46 (3)	−8 (3)	11 (2)	14 (3)
C9D	−3179 (3)	−1335 (4)	3675 (3)	44 (3)	68 (4)	68 (4)	−4 (3)	18 (3)	7 (3)
C10D	−3089 (4)	−973 (4)	4371 (3)	66 (4)	73 (4)	71 (4)	−13 (3)	32 (3)	−5 (3)
C11D	−2226 (4)	−1037 (4)	4829 (2)	85 (4)	72 (4)	52 (3)	−21 (3)	24 (3)	−1 (3)
C12D	−1406 (3)	−1462 (3)	4611 (2)	64 (3)	60 (4)	50 (3)	−15 (3)	4 (3)	10 (3)
C13D	−1500 (3)	−1811 (3)	3919 (2)	51 (3)	47 (3)	49 (3)	−7 (2)	14 (2)	15 (3)
C14D	−801 (3)	−2294 (3)	3514 (2)	50 (3)	51 (3)	52 (3)	−10 (3)	2 (2)	24 (3)
C15D	771 (3)	−2961 (3)	3429 (2)	56 (3)	47 (3)	59 (3)	−9 (3)	10 (3)	18 (3)
C16D	1654 (3)	−3276 (4)	3812 (2)	49 (3)	67 (4)	64 (3)	−8 (3)	1 (3)	29 (3)
C17D	2357 (3)	−3776 (4)	3501 (3)	46 (3)	61 (4)	95 (4)	−8 (3)	9 (3)	36 (3)
C18D	3302 (4)	−4124 (4)	3898 (3)	53 (3)	85 (5)	122 (5)	−2 (3)	−2 (3)	50 (4)
C19D	2169 (3)	−3944 (4)	2800 (3)	44 (3)	69 (4)	104 (5)	11 (3)	29 (3)	36 (3)
C20D	1305 (4)	−3602 (4)	2446 (3)	57 (3)	84 (4)	74 (4)	1 (3)	23 (3)	22 (3)
C21	6173 (4)	5389 (4)	3978 (3)	83 (4)	75 (5)	92 (5)	16 (3)	−29 (4)	−10 (4)
C22	6195 (4)	5470 (4)	4643 (3)	46 (3)	94 (5)	144 (6)	−1 (3)	15 (4)	52 (4)
C23	6826 (4)	5963 (4)	5136 (3)	69 (4)	135 (6)	60 (4)	18 (4)	23 (3)	30 (4)
C24	7428 (4)	6396 (4)	4975 (3)	61 (4)	88 (5)	98 (5)	−7 (3)	5 (3)	−2 (4)
C25	7438 (4)	6319 (4)	4323 (3)	104 (5)	88 (5)	123 (6)	14 (4)	63 (4)	43 (4)
C26	6801 (5)	5802 (4)	3814 (3)	137 (6)	109 (5)	48 (4)	53 (4)	33 (4)	24 (4)
C27	6417 (4)	4259 (4)	1951 (3)	115 (5)	87 (5)	57 (4)	36 (4)	33 (4)	27 (3)
C28	6317 (4)	5156 (4)	1892 (3)	114 (5)	84 (5)	70 (4)	−1 (4)	40 (4)	22 (3)
C29	5463 (5)	5701 (4)	1937 (3)	125 (5)	61 (4)	78 (4)	22 (4)	35 (4)	26 (3)
C30	4736 (4)	5350 (4)	2041 (3)	90 (5)	92 (5)	71 (4)	22 (4)	25 (4)	29 (3)
C31	4852 (4)	4444 (4)	2085 (3)	101 (5)	103 (5)	87 (5)	−15 (4)	17 (4)	35 (4)
C32	5698 (5)	3906 (4)	2047 (3)	158 (6)	55 (4)	73 (4)	3 (4)	34 (4)	26 (3)
C33	40 (10)	4134 (7)	202 (7)	227 (11)	133 (9)	149 (10)	−97 (9)	93 (9)	−34 (8)
C34	600 (6)	4776 (1)	579 (4)	138 (7)	132 (9)	115 (7)	−47 (6)	41 (6)	5 (7)
C35	652 (7)	5633 (7)	462 (6)	171 (9)	100 (8)	151 (10)	−58 (6)	79 (8)	−9 (7)

[a] See note *a*, Table III. [b] Isotropic *B*.

peaks at 326 (L), 327 (HL), and 389/391 (CuL) mass units. These do not appear in the spectrum of Cu(L)CO, 3. The mass spectrum of one of the amorphous masses showed a weak peak at 44 mass units, as well as a significant peak at 456/458 mass units. A subsequent crystal structure analysis of one of the parallelepipeds showed a carbonate-bridged structure $(CuL_2)(\mu\text{-}CO_3)$, 4.

Growth of Single Crystals from Benzene in the Absence of Carbon Dioxide. The same crystal-growing process was carried out in a glovebox in which air near atmospheric pressure was continuously passed over Ascarite in order to remove any carbon dioxide. Again dark red parallelepipeds were formed, together with amorphous material. The infrared spectrum of the sample was identical with that of the product isolated in the previous experiment. Several crystals were examined by photographic X-ray diffraction techniques. Some were found to have the cell dimensions of the bridging carbonate dimer structure, 4, while others had a different cell. A structure determination of these latter crystals showed a high molecular weight tetrameric complex $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, 5.

X-ray Data Collection. Preliminary precession and Weissenberg photographs showed triclinic symmetry for the crystals of $(CuL)_2$-$(\mu\text{-}CO_3)$, 4, and $(CuL)_3(CuLO)(\mu\text{-}OH)_3$, 5. Further data were collected on a Datex-automated General Electric quarter-circle diffractometer using Cu Kα radiation (λ 1.5418 Å). Lattice parameters (Table II) were derived from a least-squares fit to the setting angles for 16 manually centered reflections for 4 and 17 for 5. Intensities were measured using θ–2θ scans with a scanning rate of 1°/min, a takeoff angle of 3°, and background counts of 20 s at each extremum; the scan range was 1.8° for 4 and varied from 1.8° (at $2\theta = 3°$) to 3.0° (at $2\theta = 120°$) for 5. For 4, 4578 reflections were measured out to $2\theta = 110°$, of which 4406 had positive net intensities and were used in the structure analysis; for 5, 9334 reflections were measured out to $2\theta = 120°$, of which 8709 were positive. Three check reflections measured periodically for each crystal showed no significant changes. The intensities for 5 were corrected for absorption[56] (the crystal had dimensions 0.10 × 0.10 × 0.37 mm), with the transmission coefficients ranging from 0.79 to 0.86; intensities for 4 (0.08 × 0.15 × 0.38 mm) were not corrected. The observational variances $\sigma^2(F_o^2)$ were based on counting statistics plus an additional term $(0.025S)^2$, where S is the scan count.

Structure Solution and Refinement

The function minimized in the least-squares refinements was $\sum w(F_o^2 - F_c^2)^2$, with weights w equal to $\sigma^{-2}(F_o^2)$.[57] The R index is $\sum||F_o| - |F_c||/\sum|F_o|$. Neutral-atom scattering factors for Cu were taken from Cromer and Waber,[60] those for C, N, and O from ref 42, and those for H from Stewart et al.[61] The real component of anomalous dispersion was included for Cu.[62]

$(CuL)_2(\mu\text{-}CO_3)$, 4. Most of the atoms in the asymmetric unit were found by direct methods.[59] Difference Fourier maps yielded the positions of the remaining nonhydrogen atoms and, eventually, of the methyl hydrogen atoms; the remaining hydrogen atoms were positioned in idealized locations with C–H = 0.96 Å. Final refinement was by blocked least squares, with the coordinates of the 56 heavier atoms in one matrix and their anisotropic temperature parameters, a scale factor, and an extinction parameter in a second. The final *R* index was 0.058 for 4578 observations and 506 parameters. A final difference map showed no features greater than 0.4 e/Å^3. Final atomic parameters for the nonhydrogen atoms are given in Table III; those for the hydrogen atoms are available as supplementary material.

$(CuL)_3(CuLO)(\mu\text{-}OH)_3$, 5. Positions for all copper, bridging oxygen, and nitrogen atoms were obtained by direct methods;[59] difference maps showed the positions of the ligand carbon atoms and of the 2.5 benzene molecules in the asymmetric unit. Isotropic refinement based on data out to 80° in 2θ lowered *R* to 0.086. Hydrogen atoms were assigned idealized coordinates (C–H = 0.96 Å) except for those of the methyl groups and the bridging OH groups, which were located on difference maps.

After initial block-diagonal anisotropic refinement, a difference map showed a number of features. The most prominent were two peaks of magnitude approximately 5 e/Å^3, one being identified as a water molecule, O5, and the second located close to the ring carbon atom C1 of ligand A; three smaller peaks were located close to the C1 atoms of the other three ligands. These latter four peaks were identified as oxygen atoms, O4, in partially occupied sites.

In the final least-squares cycles, the matrices were blocked in the following way. The coordinates of C1A and O4A, the anisotropic temperature parameters for C1A, and an isotropic temperature parameter and a population factor of O4A were refined in one matrix. Similar matrices were set up for C1B and O4B, for C1C and O4C, and for C1B and O4D, except that the isotropic temperature factors for these O4 atoms were not refined. In all four cases a partial hydrogen atom, with a population factor equal to the difference between 1.0 and that of the corresponding O4 atom, was placed in the idealized position (C–H = 0.96 Å); its parameters were not refined. The coordinates and anisotropic temperature parameters of the three carbon atoms C33–C35 of the benzene ring lying on a center of symmetry were also included in a single matrix, since the thermal motion of this molecule was very large and the C–C distances were irregular. (They remained irregular at the conclusion of the refinement, varying from 1.31 to 1.56 Å. It is likely that this molecule is somewhat disordered.) The coordinates and anisotropic temperature parameters of the remaining Cu, O, N, and C atoms were blocked into a 3 × 3 and a 6 × 6 matrix for each atom.

The final *R* index was 0.065 and the goodness of fit $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ was 1.87 for $p = 1125$ parameters and $n = 9334$ reflections. The largest residual peaks on a difference map were 0.78 e/Å^3 near Cu4 and 0.52 e/Å^3 near Cu1. Final atomic parameters for the nonhydrogen atoms are given in Table IV; those for the hydrogen atoms are available as supplementary material.

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Registry No. 2, 62341-98-4; 3, 64811-68-3; 4, 68682-94-0; 5 (isomer A), 68715-72-0; 5 (isomer B), 68738-46-5.

Supplementary Material Available: Positional and thermal parameters used for the hydrogen atoms in the refinement of 4 (Table V) and 5 (Table VI), individual bond distances (Table VII) and angles (Table VIII) for the tridentate ligands, bond distances and angles for the benzene molecules in the unit cell of 5 (Table IX), and listings of the structure factor amplitudes for 4 (Table X) and 5 (Table XI) (58 pages). Ordering information is given on any current masthead page.

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Appendix Two. Oxidation State of Copper in Reduced Copper(II) Macrocycles and Their Adducts

The eighteen-electron $CuLBF_2$ macrocycle was found to react with carbon monoxide and form a twenty-electron system.[1] The crystal structure[2] of $CuLBF_2$ shows no unusual bond distances that would indicate macrocyle reduction rather than copper reduction upon synthesis from $Cu(II)LBF_2(ClO_4)$, and the macrocycle is slightly twisted toward tetrahedrality as expected for copper(I). The crystal structure[3] of $CuLBF_2$ CO shows a very unusual five-coordinate geometry, with the copper atom 0.96 Å above the plane of the four nitrogen atoms and a 120° angle between α-diimine planes. Both of these structures are now listed in Cotton and Wilkinson's fourth edition text[4] as examples of new coordination types shown by copper(I).

The crystal structures seem to indicate that $CuLBF_2CO$ is the unusual state and $CuLBF_2$ is the normal; examination of a series of infrared[2] and carbon-13 nuclear magnetic resonance spectra by this author suggests the opposite. $Cu(II)LBF_2(ClO_4)$ has infrared bands assigned to the α-diimine unit at 1660 and 1590 cm^{-1}. In four coordinate $CuLBF_2$ there are no bands in this region, but two new bands are found at 1470 and 1320 cm^{-1}. Loss of the infrared imine bands upon one-electron reduction sounds suspiciously like ligand reduction. In $CuLBF_2CO$ the α-diimine bands are again found and are located at 1640 and 1560 cm^{-1}. No ligand reduction is indicated by the infrared spectrum for $CuLBF_2CO$. These infrared spectra are shown in Fig. 1. In the carbon-13 nuclear magnetic resonance spectra, the two types of

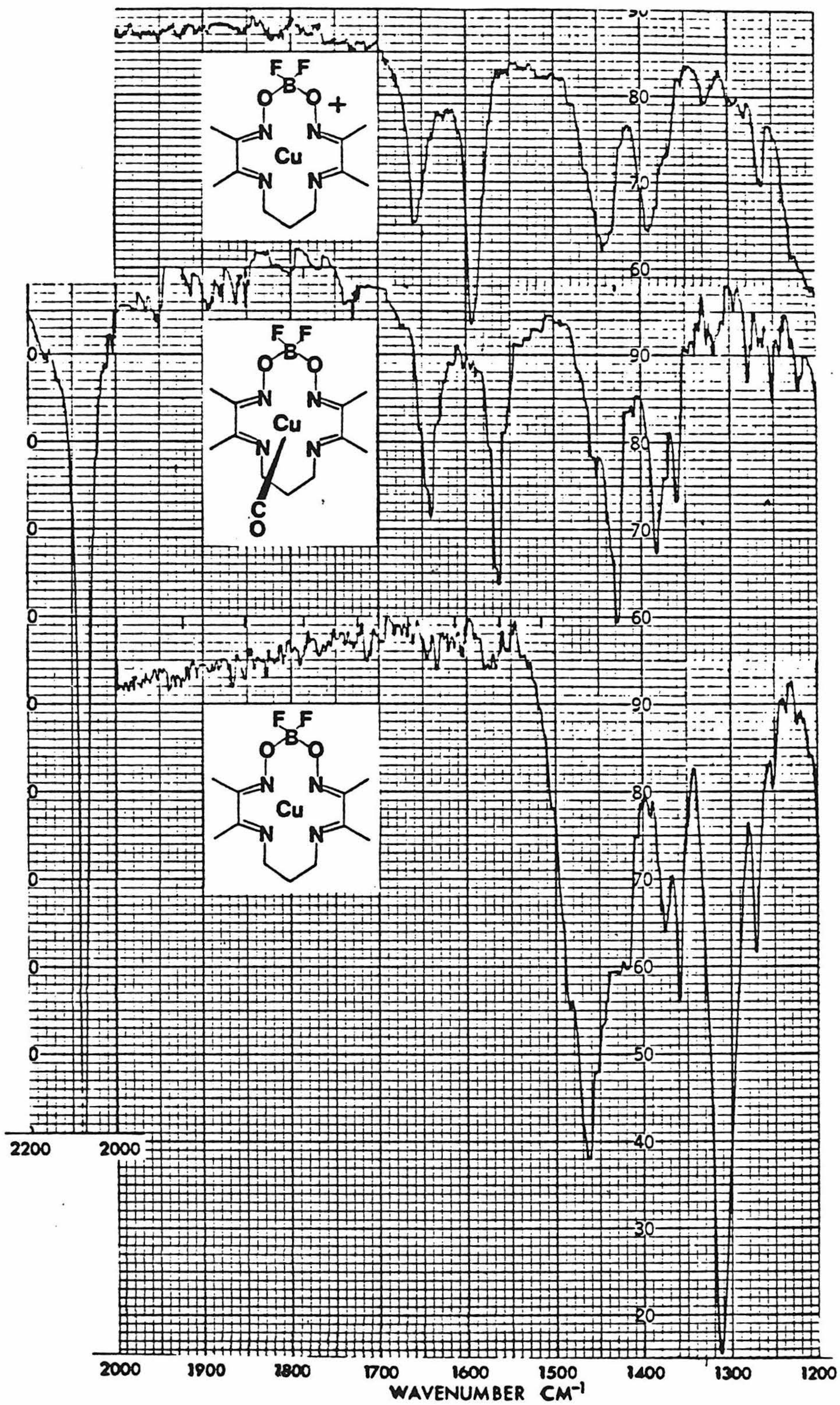

Fig. 1. Infrared spectra in the region 1200 to 2100 cm^{-1} of $Cu(II)\ LBF_2(ClO_4)$ (top), $CuLBF_2CO$ (center), and $CuLBF_2$ (bottom).

imine carbons can be expected to have different chemical shifts. For the Zn(II)LBF$_2$(ClO$_4$) complex[2] the imine chemical shifts differ by 15.1 ppm. In one-electron reduced Cu(II)LBF$_2$(ClO$_4$), the imine chemical shifts are only 4.4 ppm apart. The CuLBF$_2$CO complex again has the normal imine chemical shifts with a 14.2 ppm difference. Data for these and other complexes are in Table 1.

Table 1

Complex	α-diimine infrared bands	^{13}C nmr imine chemical shifts (difference) in CD_2Cl_2	
$CuLBF_2ClO_4$	1660, 1590 cm^{-1}	-- --	
$ZnLBF_2ClO_4$	1665, 1590	167.4, 152.3	(15.1)
$CuLBF_2CO$	1640, 1560	164.3, 150.1	(14.2)
$CuLBF_2PPh_3$	1630, 1550	161.8, 150.3	(11.5)
$CuLBF_2$-py	-- --	160.3, 153.5	(6.8)
$CuLBF_2$N-MeIm	1620, 1540	-- --	
$CuLBF_2$	1470, 1320	160.1, 155.7	(4.4)

The stronger the binding constant of the fifth ligand[3,5] the more the imine spectra (both carbon-13 nuclear magnetic resonance and infrared) resemble those of the copper(II) and zinc(II) complexes. The weaker the binding constant of the fifth ligand, the more the imine spectra resemble those of CuLBF$_2$ with delocalization and spreading of the electron density.

Only one similar study of nuclear magnetic resonance shifts of a macrocycle as a function of additional coordination to the metal has been published. Busch and coworkers[6] found a correlation between the proton chemical shifts of the methyl groups in cobalt(III) macrocycles and the ligand field strength of the coordinated axial ligand. As the axial ligand field got stronger, the methyl group signals shifted to higher field, but the effect was very small.

D. M. Ingle has examined the reduced $NiLBF_2ClO_4$ compounds.[7, 8] $NiLBF_2$ also lacks the normal α-diimine infrared bands while $NiLBF_2CO$ has them. While the $CuLBF_2$ complexes can be studied by nuclear magnetic resonance as above, the $NiLBF_2$ complexes can be studied by electron paramagnetic resonance and the location of the unpaired electron determined. The epr spectrum of reduced $NiLBF_2(ClO_4)$ indicates that the electron goes into the ligand, but the electron is on the metal in $NiLBF_2CO$.

A simple bonding description[9] suggests the orbital scheme shown in Fig. 2. Figure 2A applies to the M(II) complexes [Cu(II) shown, Ni(II) has one less electron]. Addition of an electron somehow lowers the π^* orbital and the result is Fig. 2B ($CuLBF_2$ shown, $NiLBF_2$ has one

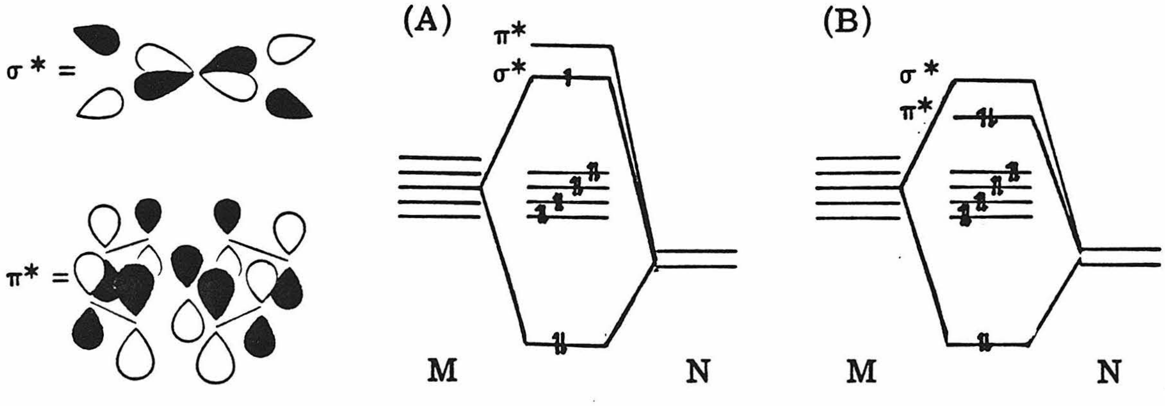

Fig. 2. Interaction of d orbitals with α- diimine orbitals.

less electron). Note that in this description "Cu(I)" is really Cu(III) ligand dianion and "Ni(I)" is really Ni(II) ligand radical anion. Population of the π^* orbital both changes the vibrational frequencies and equalizes the chemical shifts of the imines. Coordination of a fifth ligand changes the geometry and results in an orbital diagram like Fig. 2A ($NiLBF_2CO$ shown, $CuLBF_2CO$ has one more electron). Thus the true metal(I) species are the five coordinate complexes in this bonding description. The designation of the four coordinate species as reduced ligand complexes must be modified by the reminder that they are actually quite covalent in nature. Copper(III) is one extreme and copper(I) is the other. The variation of the infrared and nuclear magnetic resonance parameters with strength of axial ligand binding demonstrates this.

Investigation of additional Ni(I) complexes by D. M. Ingle[8] reveals that the above dicussion is only applicable to ligands containing α-diimine groups. For nonconjugated imines like Me_6-diene or Me_6-tetraene, reduction of the metal(II) complex does yield a true four-coordinate metal(I) complex.

Copper(I) and nickel(I) complexes with nonconjugated imines also form five-coordinate species. The CO binding constants of a number of these complexes have been reported. Table 2 summarizes these, as well as gives the CO binding constants for all new complexes reported in this thesis. This work verifies that the tetraene complexes bind CO much more strongly than the diene complexes.

An interesting comparison is the effect on the reduction potential of adding the two extra methyl groups going from Me_6-diene to Me_8-diene

Table 2

Complex	E_f^{*}	K_{CO}^{**}	Reference
$NiMe_6$-diene$(ClO_4)_2$	-1.241	4.7×10^4	8
$NiMe_8$-diene$(ClO_4)_2$	-1.216	4.8×10^2	this work
$NiMe_8$-tetraene$(ClO_4)_2$	-1.101	2.0×10^4	this work
$NiMe_6$-tetraene$(ClO_4)_2$	-1.081	4.5×10^4	8
$Ni(DMGBF_2)_2$	-0.786	2.8×10^5	8
$NiLBF_2(ClO_4)$	-0.617	2.7×10^3	8
Ni-butyl-$LBF_2(ClO_4)$	-0.798	1.3×10^4	8
10, $CuMe_8$tetraene$(ClO_4)_2$	-0.762	6.1×10^4	this work
8, $CuMe_6$-tetraene$(ClO_4)_2$	-0.683	2.5×10^4	this work
7, $CuMe_6$-diene$(ClO_4)_2$	-0.656	4.7×10	5
9, $CuMe_8$-diene$(ClO_4)_2$	-0.594	< 10	this work
1, $CuLBF_2(ClO_4)$	-0.456	1.2×10^5	5
5, $Cu(DMGBF_2)_2$	-0.438	8.8×10^5	5
3, Cu-butyl-$LBF_2(ClO_4)$	-0.270	1.2×10^3	5

*On Pt or Hg electrode (no significant differences noted) in dimethylformamide. Potentials converted to values versus SHE using ferrocene as an internal standard.[10]

**By the method in reference 5, using the concentration of CO in dimethylformamide[11] under one atmosphere of CO as 4.64×10^{-3} M.

and from Me_6-tetraene to Me_8-tetraene. 1) The reduction potentials of the copper complexes are affected more than those of the nickel complexes. 2) The reduction potentials of the diene complexes are shifted positive. 3) The reduction potentials of the tetraene complexes are shifted negative.

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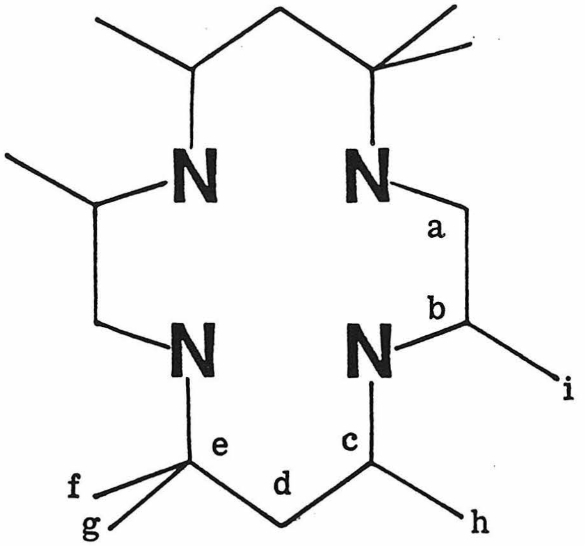
Appendix Three. ^{13}C nmr chemical shifts.*



	c	a	b, d, e	f, g, h	i
Me$_6$-diene(HClO$_4$)$_2$	174.3	40.8	43.1, 46.7, 57.7	20.8, 23.9, 23.9	--
Me$_8$-diene(HClO$_4$)$_2$	173.0	42.1	46.0, 51.7, 57.6	19.6, 24.1, 24.4	18.2
NiMe$_6$-diene(ClO$_4$)$_2$	182.1	43.4	51.2, 52.2, 54.3	22.3, 22.7, 24.4	--
NiMe$_8$-diene(ClO$_4$)$_2$	183.0	49.0	51.0, 52.9, 58.7	21.7, 23.4, 24.1	17.9
NiMe$_6$-tetraene(ClO$_4$)$_2$	186.5	174.1	50.7, 57.7, 64.3	24.5, 25.5, 25.5	--
NiMe$_8$-tetraene(ClO$_4$)$_2$	185.9	176.3	50.2, 57.4, 69.5	23.9, 24.6, 25.6	16.3
CuMe$_8$-tetraene(ClO$_4$)	168.8	164.7	55.6, 57.8, 59.4	23.0, 26.3, 26.5	17.2

*Ppm vs. internal tetramethylsilane. Dimethylsulfoxide-d$_6$ used for Ni compounds and acetone-d$_6$ used for the Cu compound. Spectra of other Cu compounds were not obtainable due to solubility and disproportionation.

Proposals

Proposal I. Synthetic Phosphorus Chemistry

A synthetic organic phosphorus chemistry scheme is suggested whereby the syntheses of the first, all phosphorus donor, binucleating macrocycles are outlined. Mononucleating all phosphorus donor macrocycles have only been prepared for the first time in the last few years, and similar synthetic reactions will be used.

Synthetic Phosphorus Chemistry

Much of the interest in macrocyclic ligand systems has been in the field of cyclic polyethers. These oxygen donor compounds are used for the ligation of the relatively hard alkali and alkaline earth metal cations. Although some softer nitrogen and sulfur containing cyclic ligands have been used for transition metals, only recently have the first tetrakis (*tert.*-phosphino) macrocycles, shown in Fig. 1, been reported. These macrocycles are much more appropriate for ligation of the softer transition metals M(0), Pd(II), Pt(II), Pt(IV), Cu(I), Ag(I), Au(I), Cd(II), Hg(I) and Hg(II). It is proposed that similar

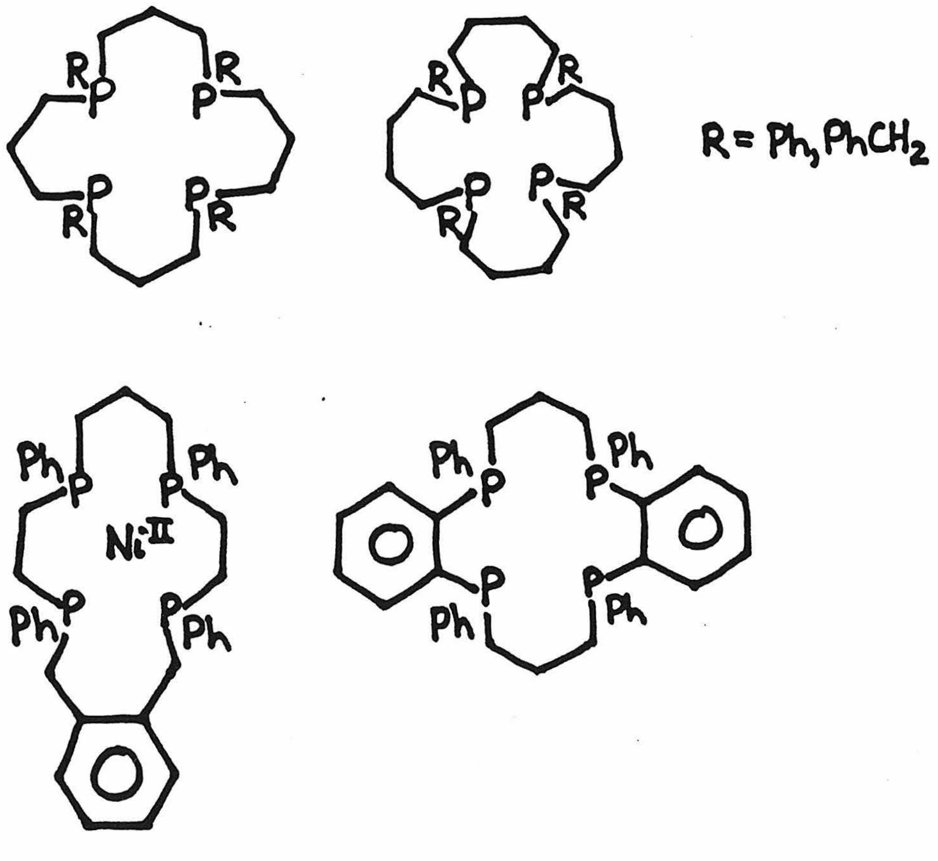


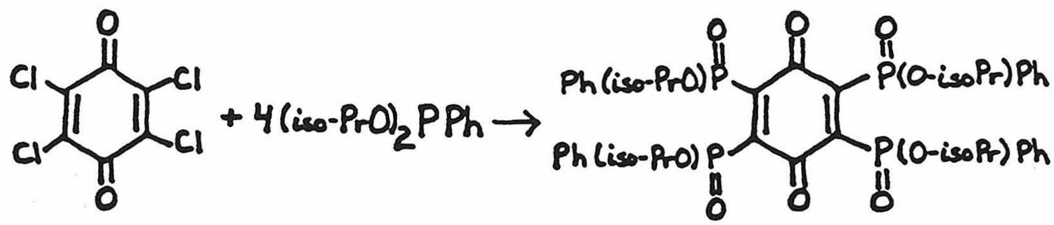
Fig. 1. Known tetrakis (tert.-phosphine) macrocycles.[1-4]

synthetic techniques be used to obtain the first all phosphorus donor macrocyclic complexes capable of complexing two metal ions. While this proposal concerns synthetic phosphorus chemistry, such binuclear metal complexes should exhibit interesting properties based on the greater covalency and extension of the phosphorus ligand orbitals.

Several problems have limited previous work with phosphorus ligands in general. Phosphorus compounds are susceptible to air oxidation and all reactions must be carried out under O_2-free conditions. Tervalent phosphorus compounds with attached alkyl groups are especially sensitive since the electron donating alkyl groups increase the already high electron density on the phosphorus atoms. As Crofts[5] has pointed out, the nauseating smells, tendency to spontaneous inflammability, and toxicity, have not helped to make phosphine chemistry popular. Moreover, few starting materials are commercially available. Synthetic routes must be planned from simple compounds as is done here.

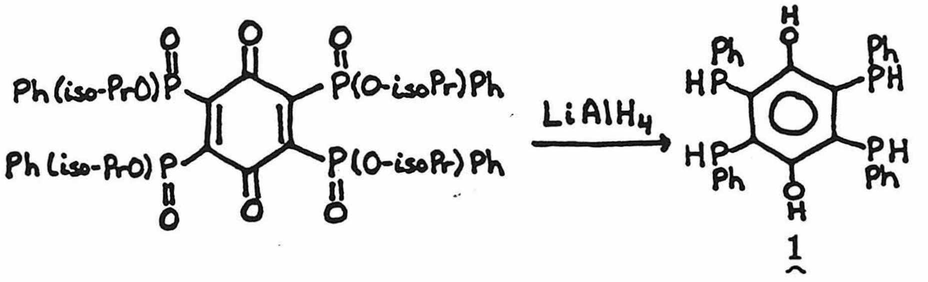
The reaction of chloranil with the commercially available phosphonite $(\text{iso-PrO})_2PPh$ is the beginning of the syntheses proposed here and should give the product shown in Eq. 1. (Powers and Graham[6]

(1)



have previously noted that when chloranil reacts with the tertiary phosphite $(\text{iso-PrO})_3P$, all four chlorine atoms are replaced by phosphonate groups). Tetravalent $R_3P = 0$ compounds can in general be reduced to trivalent phosphorus by treatment with $LiAlH_4$.[7,8] In addition to removal of the =0 by $LiAlH_4$, halogens or -OR groups are exchanged with H. $LiAlH_4$ treatment will also probably result in reduction of the ring to give an aromatic product (Eq. 2). Since phosphines with P-H bonds can be further reacted with alkali metals

(2)

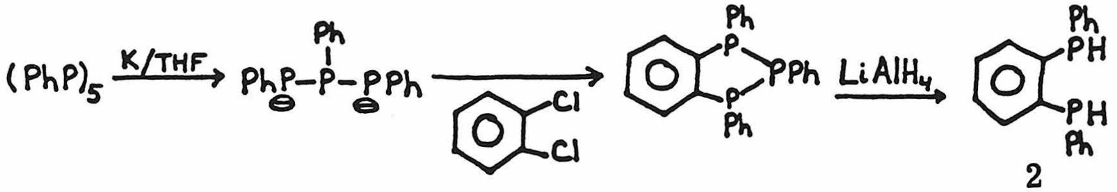


1

or vinyl phosphines, the product, 1, in Eq. 2 is the common key starting material for several new macrocyclic compounds.

Another needed intermediate has been used by Kyba[3] for synthesis of a mononucleating macrocycle and is prepared according to Eq. 3.

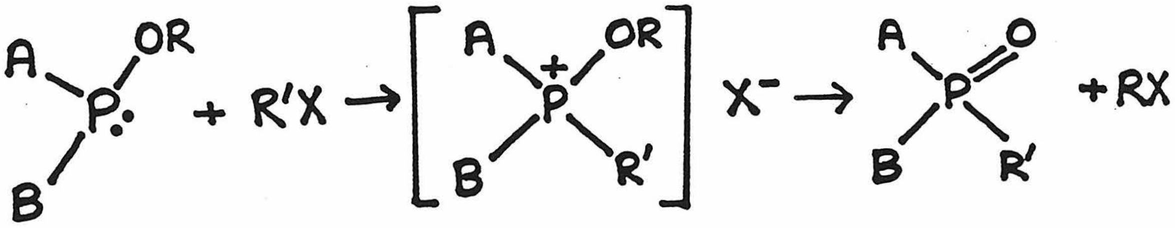
(3)

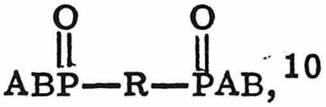


2

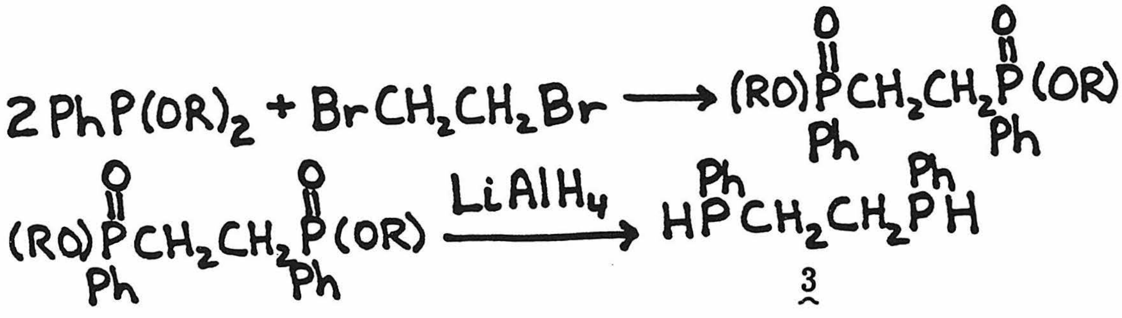
The Arbusov reaction (Eq. 4),[9] where A and B may be alkyl, aryl, alkoxy, or aryloxy groups, is the best studied phosphorus-carbon bond forming reaction. Since the reaction is favored for A and B

(4)



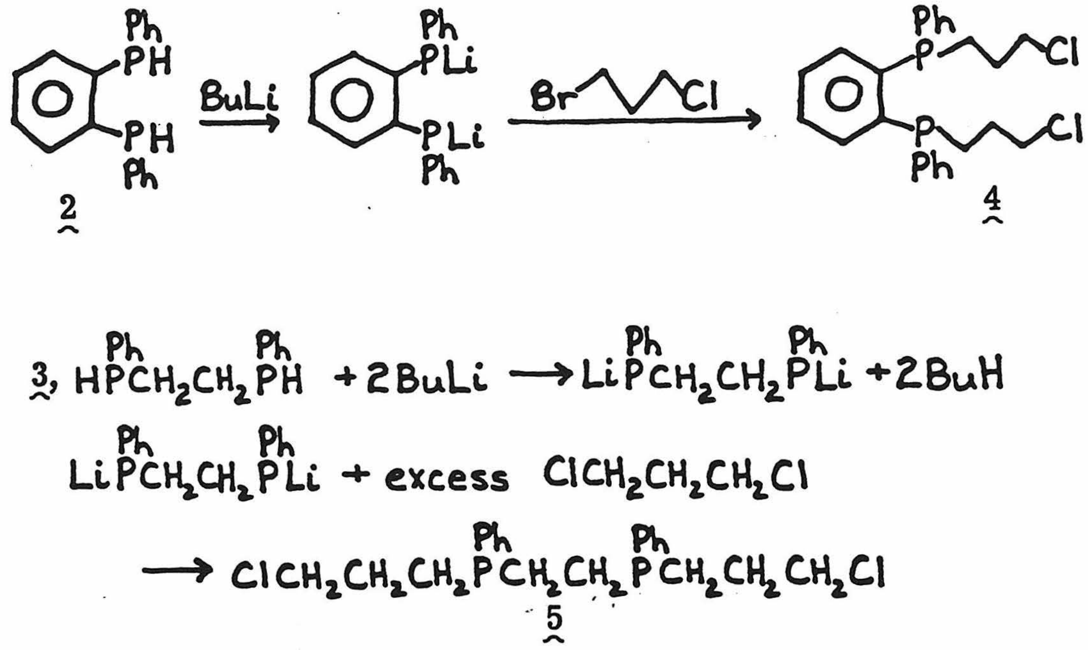
electron donating, the order of reactivity is aryoxy < alkoxy < aryl < alkyl. The usual I > Br > Cl reactivity is found and primary halides work best. Of significant interest in macrocycle synthesis is when XR′X is used to form  $\mathrm{AB\overset{O}{\overset{\|}{P}}{-}R{-}\overset{O}{\overset{\|}{P}}AB}$,[10] followed by $LiAlH_4$ reduction (Eq. 5).

(5)



P–H bonds react with BuLi or PhLi yielding P–Li, which upon reaction with alkyl halide RX gives P–R and net phosphorus carbon bond formation.[3,11,12] Intermediates 2 and 3 would be treated in this way to give 4 and 5 (Scheme I).

Scheme I



$$3,\ \mathrm{H\overset{Ph}{P}CH_2CH_2\overset{Ph}{P}H + 2BuLi \longrightarrow Li\overset{Ph}{P}CH_2CH_2\overset{Ph}{P}Li + 2BuH}$$

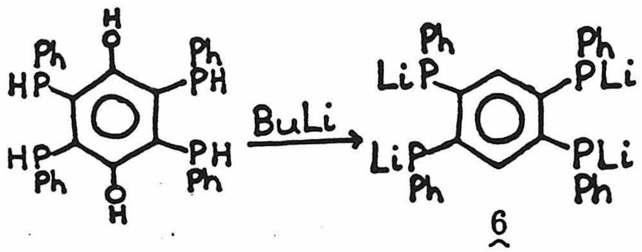
$$\mathrm{Li\overset{Ph}{P}CH_2CH_2\overset{Ph}{P}Li + excess\ \ ClCH_2CH_2CH_2Cl}$$

$$\longrightarrow \mathrm{ClCH_2CH_2CH_2\overset{Ph}{P}CH_2CH_2\overset{Ph}{P}CH_2CH_2CH_2Cl}$$

5

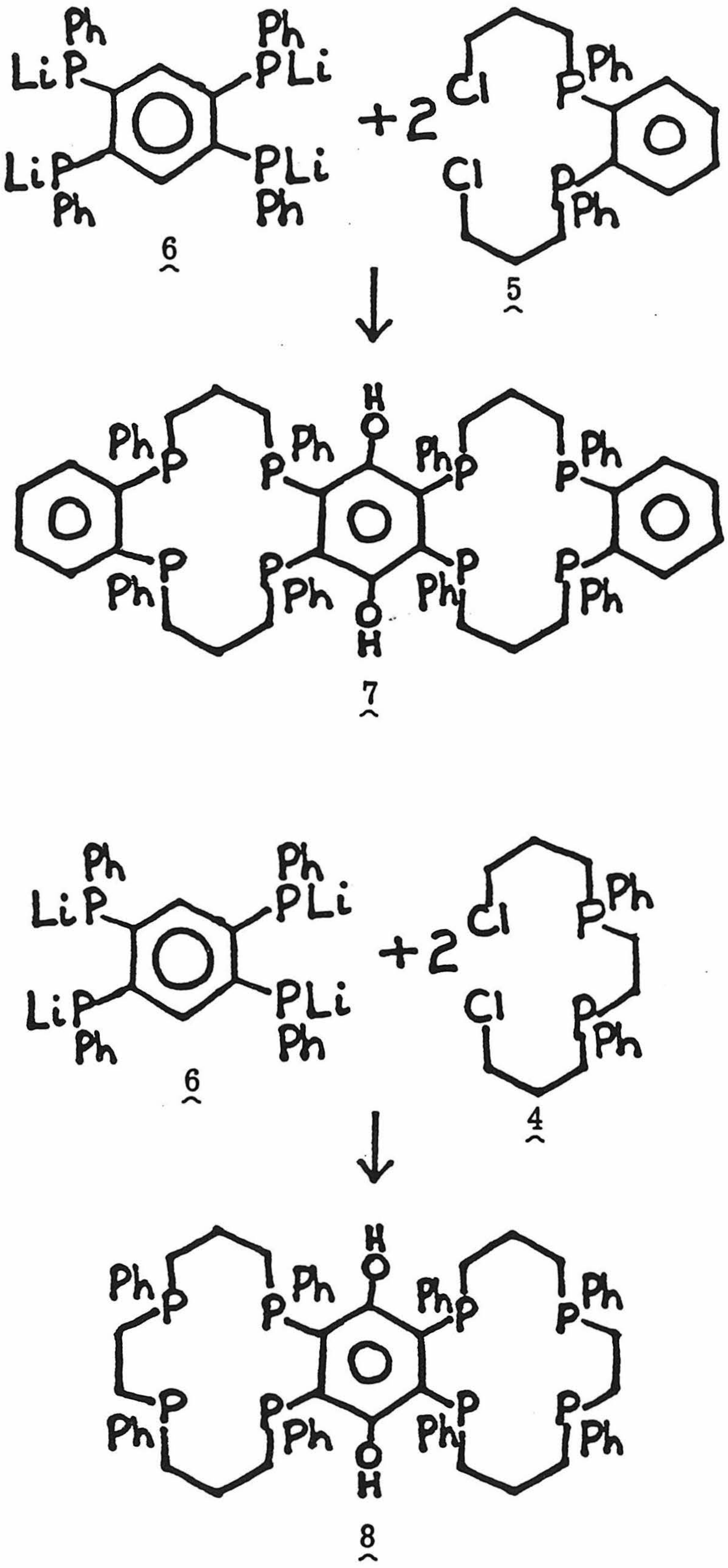
Lastly, 1 could be similarly treated with BuLi (Eq. 6) and then

(6)



reacted with 4 and 5 to give the desired new macrocyclic ligands (Scheme II). Macrocycles related to 7 and 8 could also be prepared by using different legnth alkyl halides in Eq. 5 and Scheme I. In summary, the syntheses outlined here, starting from (iso-PrO)$_2$PPh and (PhP)$_5$, should yield the first all phosphorus donor binucleating macrocycles.

Scheme II



Appendix. Phosphorous compound names.

Trivalent	Tetravalent
Phosphines	Phosphine oxides
R_3P, R_2PH, RPH_2	$R_3P{=}O$, $R_2PO(H)$
Phosphinites	Phosphinates
$R_2P(OR)$	$R_2PO(OR)$
R_2POH phosphinous acid	$R_2PO(OH)$ 2° phosphonic acid
Phosphonites	Phosphonates
$RP(OR)_2$	$RPO(OR)_2$
RPO_2H_2 phosphonous acid	$RPO(OH)_2$ 1° phosphonic acid
Phosphites	Phosphates
3° $P(OR)_3$	3° $PO(OR)_3$
2° $(RO)_2POH$	2° $(RO)_2PO(OH)$
1° $(RO)PO_2H_2$	1° $(RO)PO(OH)_2$
if RO = X, halophosphite	if RO = X, halophosphate

Table after M. Porthault, in "Chimie Organique du Phosphore," Colloques Internationaux du Centre National de la Recherche Scientifique, No. 182 (1970).

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Proposal II. Polypyrrole Coated Electrodes As Diodes

It is proposed to constrct a DC power supply by conversion of an AC source using a polypyrrole coated electrode solution cell in the circuit.

Polypyrrole Coated Electrodes As Diodes

A recent communication[1] concerning electrochemical properties of polypyrrole coated platinum electrodes deserves further inquiry. The published observation is that for coated electrodes, a cyclic voltammogram of ferrocene (E° positive of that of polypyrrole) could be obtained while a cyclic voltammogram of nitrobenzene (E° negative of that of polypyrrole) could not.

First it is proposed to verify these results. The observed differences may have been due to the differing approach of ferrocene and nitrobenzene to the polypyrrole surface. The published conclusion was that current is carried by the electrode only at potentials positive of the polypyrrole oxidation and no current is carried at potentials negative of the polypyrrole reduction. This conclusion is better verified by using one compound with two reversible waves, one positive of polypyrrole and one negative. $Ru(acac)_3$ is one possibility.

It is further proposed to make a solution analogue of a half wave rectifier, by replacing the diode in a normal circuit[2] with a cell containing a polypyrrole coated electrode (Fig. 1). Application of an AC voltage alternating about the polypyrrole E° should result in a DC current output. Observation on an oscilloscope of such a waveform would be conclusive proof of the published hypothesis.

A solution analogue of a full wave rectifier is also possible by adding a second polypyrrole electrode (Fig. 2). The output from this DC power supply might even be filtered somewhat due to the faradaic capacitance of the cell.

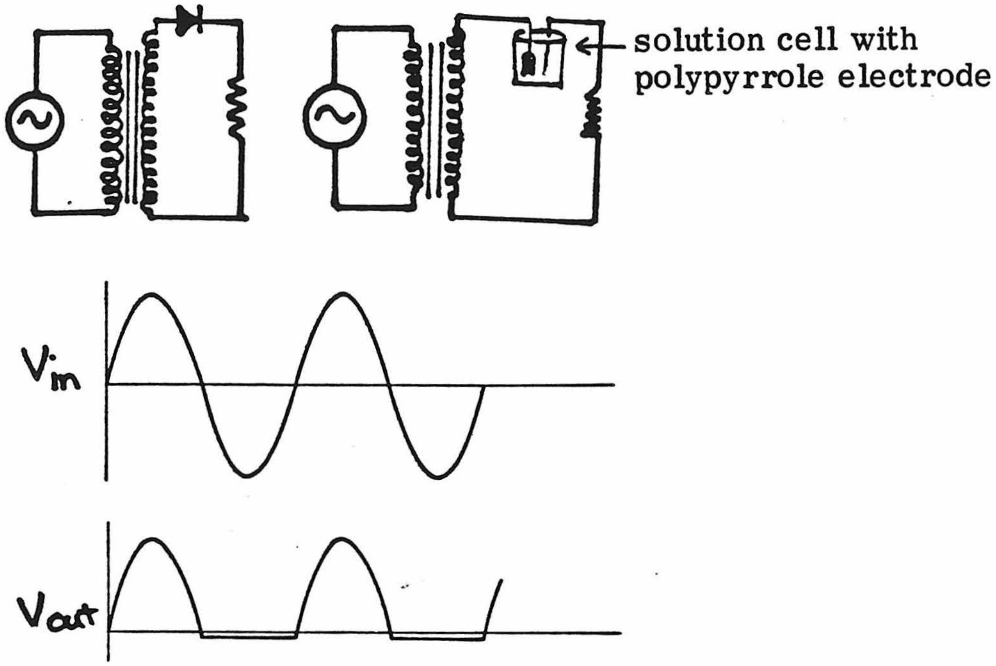

Fig. 1. Half-wave rectifier.

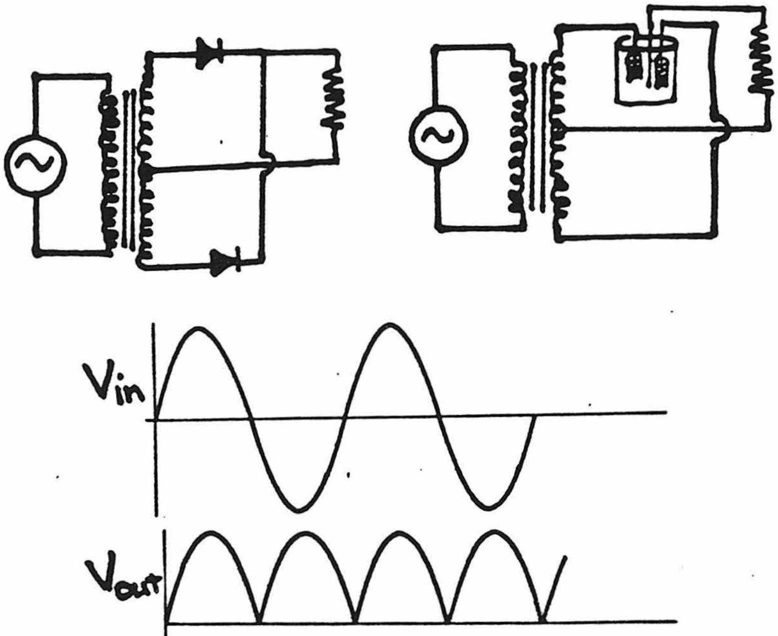

Fig. 2. Full-wave rectifier.

Another proposed area of further inquiry is the amount of current capable of being carried by the oxidized polypyrrole layer. Presumably this can be controlled by changing the size of the electrode area. For large currents (~ 10 Amp or greater) vacuum tubes are still used rather than solid state diodes. There are two distinct disadvantages to use of the vacuum tubes. First, the vacuum tube's filament has high power requirements (~4 Amp at 6.3 V). Second, the vacuum tube requires a vacuum and the glass tube used to maintain that vacuum is fragile. Thus replacement of vacuum tubes in high current power supplies by a polypyrrole solution cell has possible commercial potential.

To adequately evaluate such potential, further experiments are needed to investigate the breakdown voltage of the reduced polypyrrole and the lifetime of such an electrode surface.

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Proposal III. Gas Chromatographic Resolution of Enantiomers

It is proposed that gas-liquid chromatographic separation of enantiomers will be enhanced by use of optically active solid supports loaded with an optically active liquid phase.

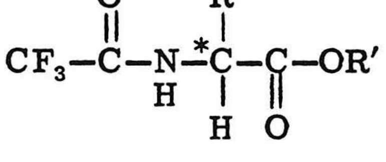
Gas Chromatographic Resolution of Enantiomers

Optical isomers occur widely in nature and are utilized for pharmaceutical purposes, for experimental biochemical studies, and as intermediates in the syntheses of biologically active products. Methods which distinguish or resolve enantiomers are very important, especially in pharmaceutical applications where the two enantiomers can have different biological effects.

The use of gas chromatography to resolve enantiomers has mainly been achieved by conversion of the racemic mixture to a mixture of diastereomers by a suitable chemical reaction with an optically active reagent.[1,2] The diastereomers are then separated by normal gas chromatographic techniques.

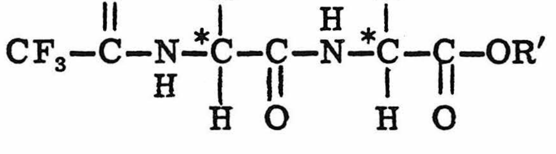
Previous studies of gas-liquid chromatography for the direct separation of enantiomers have centered on the use of optically active liquid phases, most notably N-trifluoroacetyl amino acid esters, and carbonyl-bis (amino acid esters) (Fig. 1).[3] Several observations suggest that more ordered optically active phases increase the

Fig. 1.



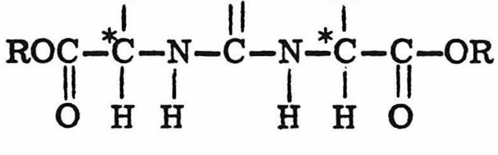
$CF_3-\overset{\overset{O}{\|}}{C}-\underset{H}{N}-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{{}^{*}C}}-\underset{\underset{O}{\|}}{C}-OR'$

N-trifluroacetyl amino acid ester



$CF_3-\overset{\overset{O}{\|}}{C}-\underset{H}{N}-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{{}^{*}C}}-\underset{\underset{O}{\|}}{C}-\overset{H}{N}-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{{}^{*}C}}-\underset{\underset{O}{\|}}{C}-OR'$

N-trifluoroacetyldipeptide ester



$RO\underset{\underset{O}{\|}}{C}-\overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{{}^{*}C}}-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{{}^{*}C}}-\underset{\underset{O}{\|}}{C}-OR$

Carbonyl-bis(amino acid ester)

enantiomeric separation. (1) Corbin and Rogers[4] have discovered that use of a carbonyl-bis(L-valine isopropyl ester) liquid phase in an open column operated below the liquid phase melting point gave greatly enhanced separations. They suggested the enhanced activity resulted from a more fixed interaction geometry. (2) Lochmüller and Souter[5, 6] studied the same carbonyl-bis(L-valine isopropyl ester) as a 5% loading on 100-120 mesh AWDMCS Chromosorb G in a 6 ft × $\frac{1}{8}$" O.D. column. The operation temperature was chosen such that the "liquid" phase was a smectic liquid crystal meso-phase. The largest relative retention ever observed for any gas chromatographic enantiomer separation was obtained. While use of liquid crystal mesophases generally seem to give greater separation than the corresponding isotropic liquids, the operating temperatures are somewhat limited. For the carbonyl-bis(L-valine isopropyl ester) the smectic liquid crystal phase exists in the region 99 to 109° C. Consequently only materials volatile in this narrow range can be examined and much of the utility of gas chromatographic analysis is lost.

It is proposed that optically active solid supports in addition to continued use of optically active liquid phases may enhance enantiomeric separation under a wider range of operating conditions. The underlying theory is that if good separation has been observed for the more ordered chiral "liquid" phases, where presumably the separation is due to a diastereomeric complex formed by solute-solvent interactions, the ordering of the liquid phase could also be accomplished by diastereomeric interactions with the optically active solid support.

Gas liquid chromatography accomplishes a separation by partitioning a sample between a mobile gas phase and a thin layer of nonvolatile liquid held on a solid support. While the solid support is usually considered inert, such is not actually the case. The commonly used diatomaceous supports tend to absorb sample molecules particularly when lightly loaded with liquid phase or when nonpolar liquid phases are used. This is the reason that the silanol groups are often treated with dimethyldichlorosilane to convert them to silyl ethers and reduce surface activity.

Since the nonoptically active solid supports generally used are silicates, use of the optically active silicate quartz (SiO_2)[7] seems a good place to begin this investigation. Quartz is the most important optically active crystal, both because of its widespread occurrence and because of its high optical activity. In quartz crystals the silica groups are joined to each other in left-handed screw arrangements in some crystals and right-handed screw arrangements in others. These two types of crystals would be separated and ground into the usual mesh size for loading into a column. Both optical isomers will be tested with the carbonyl-bis(L-valence isopropyl ester) liquid phase and various degrees of dimethyldichlorosilane pretreatment. The same isomers to be separated as used by Corbin, Rogers, Lochmüller and Souter would be chromatographed to check for enhanced separation. Further inquiry would investigate other optically active solid supports.

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Proposal IV. Synthesis of Linked Macrocyclic Ligands

Synthesis of a tetramine from malonic ester for the purpose of deriving linked macrocyclic ligands is proposed. The ultimate aim is to study metal-metal interactions where the interaction, either direct or through bridging ligands, is along the z axis.

Synthesis of Linked Macrocyclic Ligands

Metal atoms or ions held in close proximity at selected distances are of interest because of possible cooperative chemical and electronic interactions and multiple electron redox processes. Indeed, many proteins and enzymes contain two or more metal atoms in sophisticated systems. Studies of binuclear complexes involve measurement of the electrochemical properties,[1] magnetic interactions,[2] electron paramagnetic spectra and electronic absorption spectroscopy. Most binuclear complexes prepared to date contain metal atoms side-by-side.[3] Fewer binuclear complexes have been examined where the metal-metal interaction is along the z axis, either directly or through bridging ligands, although metal(acetate)$_2$ dimers,[4] some solid state d^8 metal complexes, and the face-to-face porphyrin complexes[5] are notable exceptions (see Fig. 1).

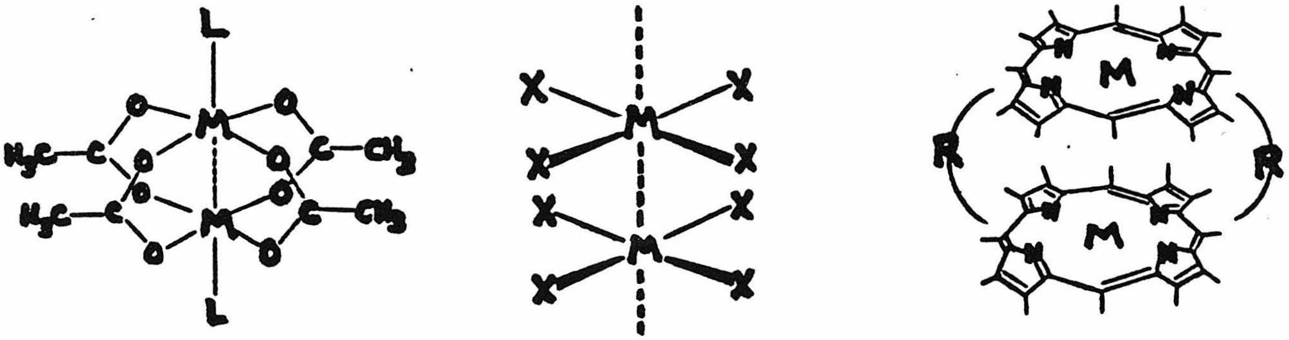
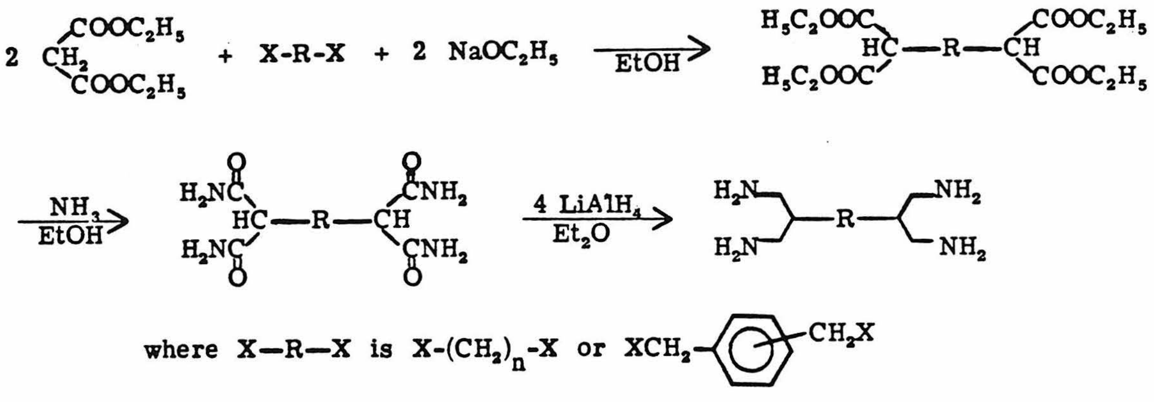


Fig. 1. Metal-metal interaction along the z axis.

A series of ligands that will hold two metal atoms in such a configuration could be derived from the tetramine, $(H_2NCH_2)_2CHRCH(CH_2NH_2)_2$, synthesized as shown in Scheme I.

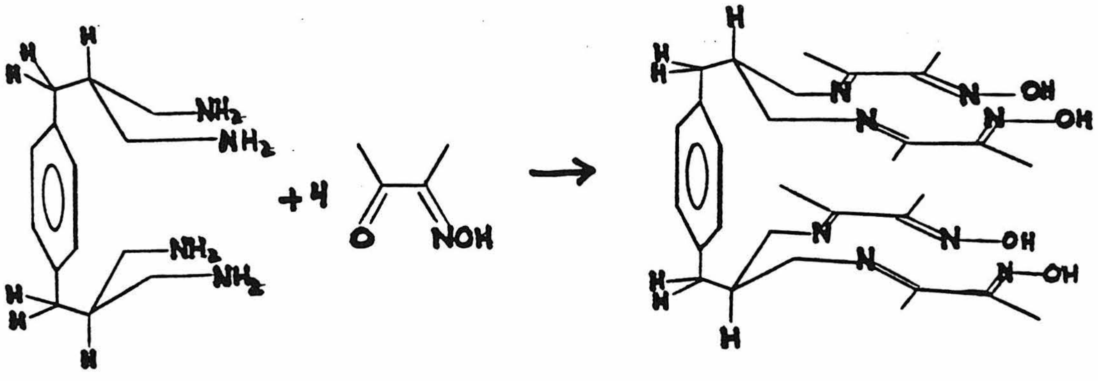
Scheme I



Malonic ester is used as the starting active methylene compound since the mono- rather than di-alkylated product can in general be obtained.[6] With α,ω-dihaloalkanes cyclization could be a problem but even for $Br(CH_2)_3Br$, whose cyclization is normally rapid,[7] yields of greater than fifty percent of the tetraester are obtained when an excess of one equivalent of malonic ester is used.[8] The dihaloxylenes should present no such problem in any case. Formation of the amide and reduction to the amine appears to be straightforward,[9] but alternate routes from the tetraester to the tetramine are also possible.[10]

Once the tetramine has been synthesized, a variety of linked macrocycles are available by Schiff base condensation with aldehydes or ketones. One macrocycle, whose mononuclear version is quite readily synthesized, involves the condensation with 2,3-butanedione-monoxime (Scheme 2).[11] After addition of the metal ion, the oxime bridging hydrogen atom can be replaced by a BF_2 group by treatment with $BF_3 \cdot Et_2O$.[11]

Scheme 2

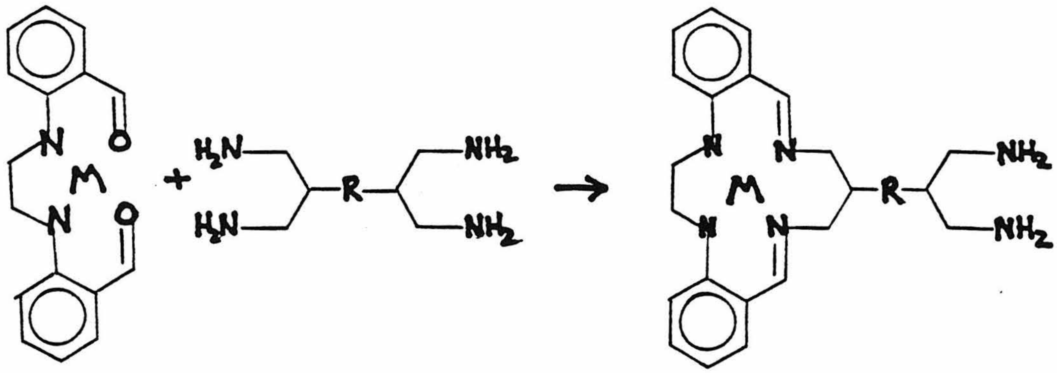


Any metal-metal interaction will be dependent on the length of the link and the conformation of the macrocycles. Molecular models show that all the isomers are interconvertible. Addition of a bridging ligand will tie the metals together in the conformation illustrated above, with one macrocycle lined up vertically over the other. Use of imidazole as a bridging ligand is of interest from the viewpoint of the complex as a model for multi-metal protein centers. Imidazole has been found as a bridging ligand in superoxide dismutase (Cu-Im-Zn)[12] and proposed as a bridging ligand for cytochrome oxidase (Fe-Im-Cu),[13] but few non-polymeric model complexes have been prepared.[14-18] Other bridging nitrogen heterocycles,[19] such as pyrazine,[20] would also be examined. Dioxygen as a bridging ligand is possible when the macrocycle link is short; for face-to-face cobalt porphyrins, Chang has observed[5c] both products in Fig. 2, depending on the link length.

Fig. 2. Face to face cobalt porphyrins

A subject of great interest is when the two metals are different. The first step in such a synthesis of mixed metal linked macrocycles involves condensing an N_2O_2 donor tetradentate ligand with the tetramine, similar to the preparation of a known mononuclear macrocycle (Scheme 3).[21] After isolation of the mononuclear complex with the linked diamine, condensation with a second tetradentate metal complex, where the metal is different, would be accomplished. The bridging ligand would again be added as before. Alternatively, two Jager-type ligands (Fig. 3)[22, 23] could be similarly condensed to form additional mixed-metal linked macrocycles. In the Jager ligand the extra carbonyl functionality is necessary to activate the ligand toward

Scheme 3



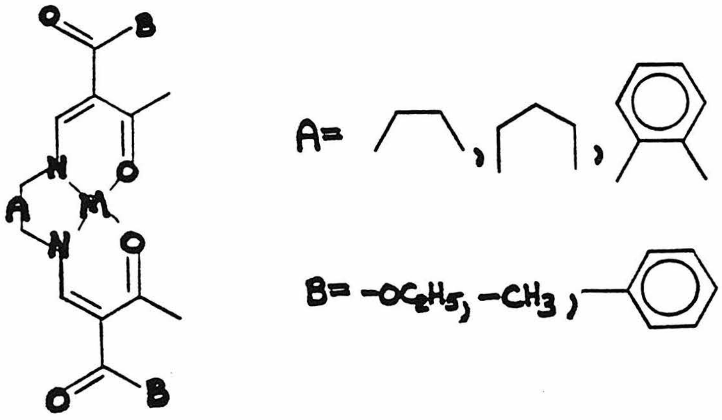
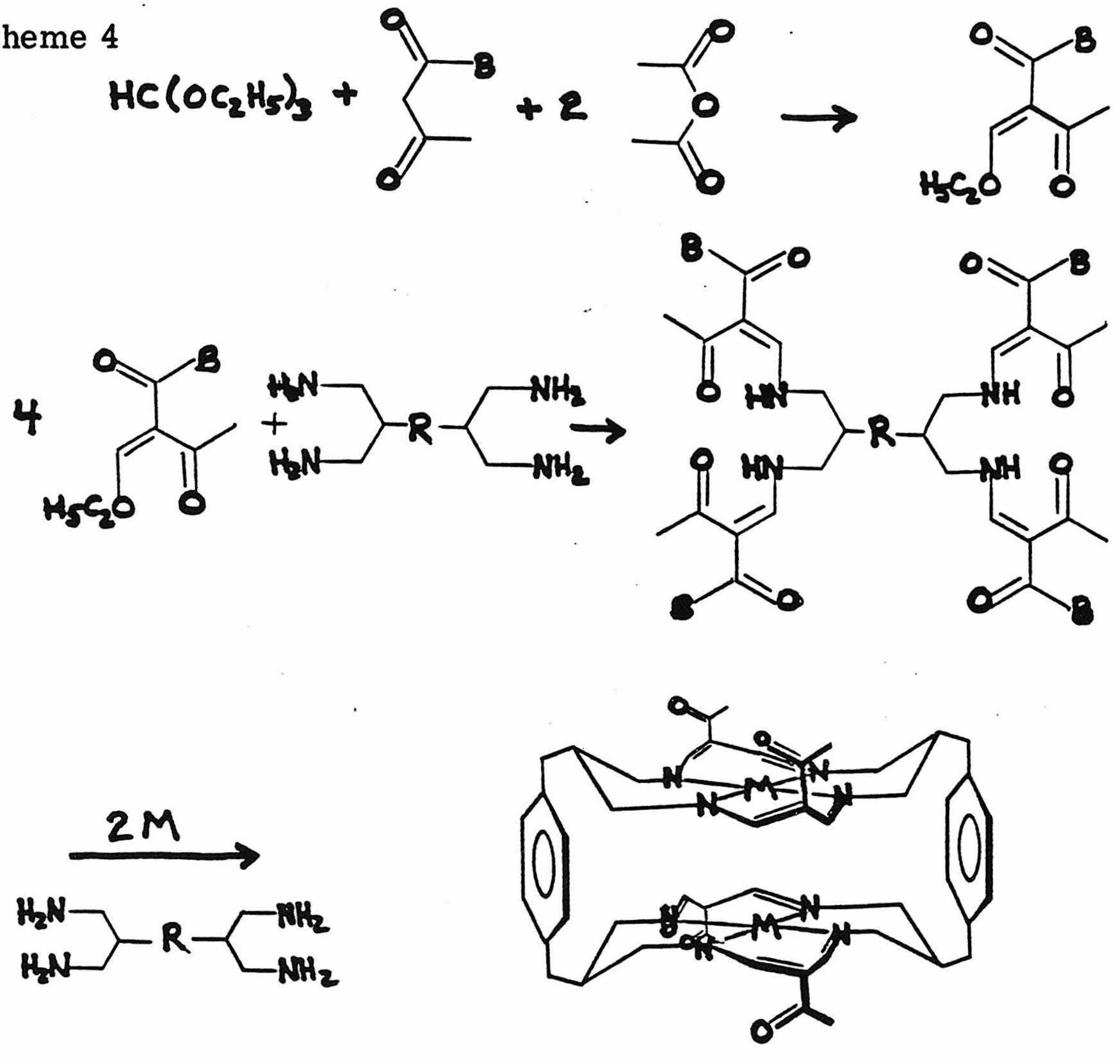


Fig. 3. Jager ligands

further condensation.

It would be highly desirable to synthesize doubly linked macrocycles with the macrocycles face-to-face. The Jager-type ligands could be synthesized using the tetramine for the first condensation, as shown in Scheme 4. Addition of the metal, and use of high-dilution techniques for the addition of a second tetramine, could give the desired product. Synthesis of the doubly linked macrocycle may, however, be a low-yield process with predominantly polymers produced.

Scheme 4



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Proposal V. Substitution Kinetics of Five-Coordinate Complexes

Many kinetic studies have been done on the ligand substitution reactions of four- and six-coordinate metal complexes. Much less studied kinetically are the ligand substitution reactions of five-coordinate complexes. The proposal is made to study the monodentate ligand substitution reactions of M(terpyridine)X_2 and M[(N,N′-di-(3-aminopropyl)piperazine)X]Y. The object is to determine if an associative or dissociative pathway is followed, and if the sixteen and eighteen electron rule applies to ligand substitution in five-coordinate complexes.

Substitution Kinetics of Five-Coordinate Complexes

A large number of studies have been done on the mechanisms of substitution of four- and six-coordinate metal complexes. Square-planar d^8 metal complexes are found to undergo substitution reactions with associative mechanisms involving a five-coordinate intermediate. Six-coordinate complexes substitute ligands by predominantly dissociative pathways, again involving a five-coordinate intermediate.[1] The sixteen and eighteen electron rule, as stated by Tolman,[2] says that diamagnetic organometallic complexes of transition metals may exist in spectroscopically or kinetically detectable concentrations only if the metal's valence shell contains sixteen or eighteen electrons. Thus sixteen electron square planar d^8 systems go through an associative intermediate with eighteen electrons, and eighteen electron octahedral complexes go through a dissociative intermediate with sixteen electrons.

Considerably less work has been done on the substitution reactions of five-coordinate complexes. At first glance, steric considerations would suggest these complexes could undergo substitution with an associative six-coordinate intermediate, or a dissociative four-coordinate intermediate.

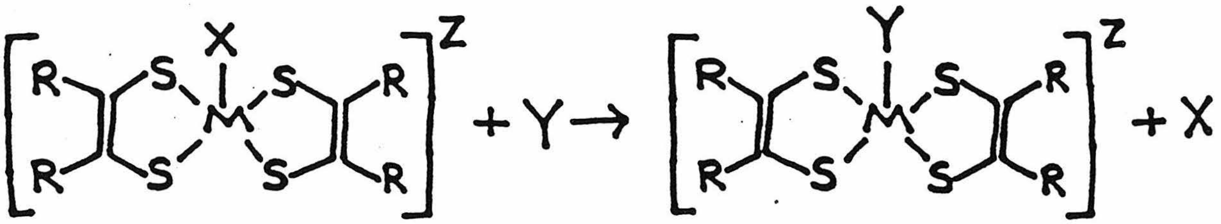
The sixteen and eighteen electron rule for diamagnetic complexes would require that the eighteen electron five-coordinate complexes substitute with a sixteen electron dissociation intermediate. Monodentate diagmagnetic eighteen electron five-coordinate complexes are found to undergo the substitution reaction $MD_4X + Y \rightarrow MD_4Y + X$

with characteristically dissociative kinetics.[3-10] [Co(2, 6-lutidine-1-oxide)$_5$][ClO$_4$] is a seventeen electron species which substitutes dissociatively.[11]

The only sixteen electron five-coordinate series of complexes that has been studied[13] is Mn(NO)(CO)$_3$L. For substitution of CO by phosphine Y, the mechanism depends on L and Y. For L = CO and Y = PPh$_3$ or P(OPh)$_3$ the mechanism is associative with an eighteen electron intermediate as expected. For L = Y = P(OPh)$_3$ the reaction is dissociative with a fourteen electron intermediate. For L = Y = PPh$_3$, the associative and dissociative pathways are both used to the same extent. For L = Y = PBu$_3$ the dissociative pathway is favored, but both mechanisms occur. The dependence on L could be due to the stabilization of the four-coordinate intermediate, or the lack of room for the entering ligand, and the sixteen and eighteen electron rule is not always followed.

Five coordinate compounds with multidentate ligands are even less predictable. The [Ni(o-phenylenebisdimethylarsine)$_2$Br] SCN complex exchanges Br$^-$ for SCN$^-$ dissociatively as expected for an eighteen electron complex.[12] The eighteen electron Pt(II) tris-(o-diphenylarsinophenyl)arsine halide mono-cation and Pt(II) tris-(o-dimethylarsinophenyl)arsine halide mono-cation react associatively through nineteen or twenty electron intermediates.[14, 15]

Another troublesome system has been studied kinetically by Sweigert and coworkers (Eq. 1),[16-20] where X and Y are different phosphine ligands. The complexes themselves, as well as their substitution reaction intermediates, violate the sixteen and eighteen

(1) 

electron rule. They react associatively for (R = Ph, CF_3) fourteen electron (Fe, z=0) and fifteen electron (Co, z=0) systems and by both paths for (R = CF_3, CN) sixteen electron (Co, z=-1) systems.

The substitution kinetics of a five-coordinate high spin seventeen electron iron(III) (p-CH_3-tetraphenylporphyrin) complex have been elegantly studied by LaMar and coworkers and found to be associative with an eighteen electron intermediate.[27-30] This is the only macrocycle whose five-coordinate substitution kinetics have been examined. The reaction is found to proceed with inversion and is studied by observing the averaging of the inequivalent m-H proton nuclear magnetic resonance signals as a function of added X^- concentration (see Fig. 1).

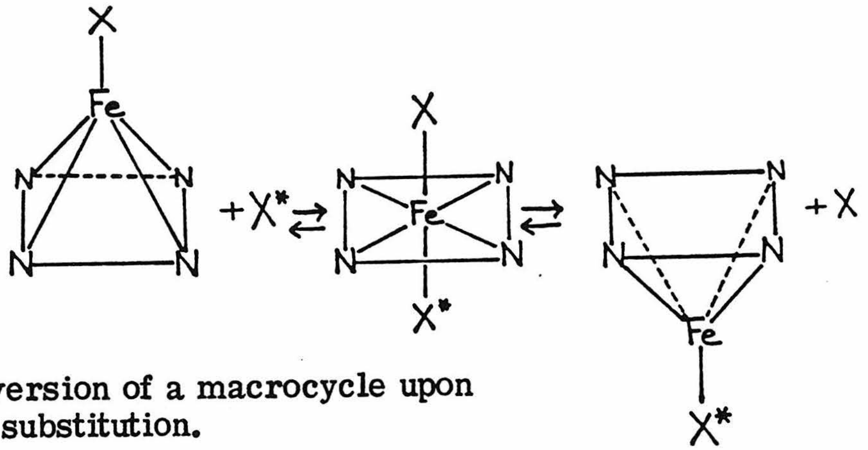


Fig. 1. Inversion of a macrocycle upon fifth-ligand substitution.

The above review of five-coordinate substitution reactions (five-coordinate reactions with bidentate ligands have been ignored) shows several main themes. Eighteen electron diamagnetic monodentate-ligand five-coordinate complexes substitute dissociatively, as expected from the sixteen and eighteen electron rule. The one sixteen electron system that has been studied substitutes by both pathways, which is not expected from the sixteen and eighteen electron rule. With multidentate ligands, more information is needed concerning the kinetics of five-coordinate substitution reactions before further systematization is possible.

I propose to study the substitution kinetics of five-coordinate M(terpyridyl)X_2 and M[(NN′-di-(3-aminopropyl)piperazine)X]Y complexes (Fig. 2). The purpose is threefold: (1) to gain more information about five-coordinate substitutions in general, (2) to learn more about fifth ligand substitution pathways as a function of the metal ion, and (3) to learn more about ligand substitution in high spin complexes.

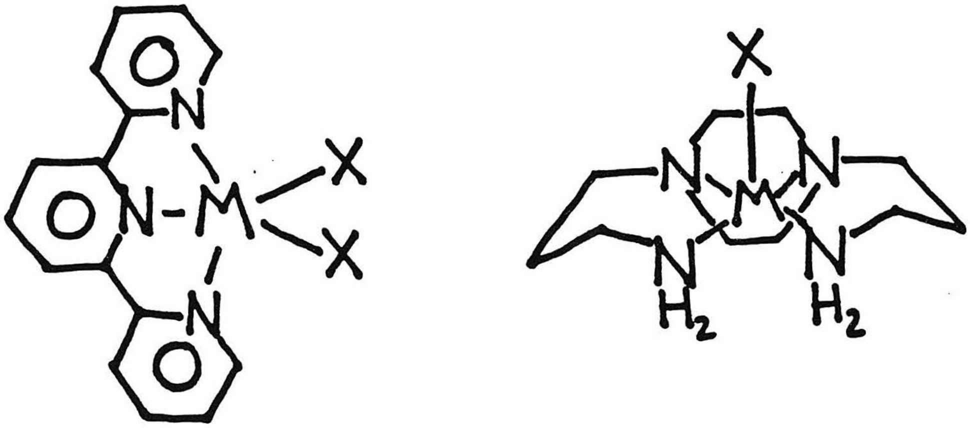


Fig. 2. Five-coordinate metal complexes M(terpy)X_2 (left) and $[M(dapp)X]^+$ (right).

The crystallographically characterized geometry of Zn(terpy)Cl_2 is distorted trigonal bipyramidal,[31,32] while that of [Ni(dapp)Cl] Cl is square pyramidal.[33,34] In both cases a series of complexes with other M and X have been prepared whose X-ray powder patterns indicate isostructural five-coordinate complexes.[31,35,36,38] These complexes are M(terpy)X_2 (for M = Mn, Co, Ni, Cu, Zn, Cd, Hg and X = Cl, Br, and I),[35-37] and [M(dapp)X] Y (for M = Co, Ni, Cu and X = Cl, Br, I, NCS and Y = X, ClO_4, PF_6).[33,38]

Ligand lability is sufficient to achieve substitution reactions, as noted by previous workers as a tendency toward disproportionation in some solvents (notably water).[39] Non-aqueous organic solvents should permit kinetic studies. Given suitable behavior of these complexes in organic solvents, a variety of M and X will be examined for typical associative and dissociative kinetics (see Appendix).

Appendix

Kinetics of the S_N1 Dissociative Mechanism

$$MD_4X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MD_4 + Y$$

$$MD_4 + Y \xrightarrow{k_2} MD_4Y$$

Applying the steady state approximation to the first step yields

$$\frac{d[MD_4]}{dt} = O = K_1[MD_4X] - k_{-1}[MD_4][X] - k_2[MD_4][Y],$$

and rearranging, gives $[MD_4] = \dfrac{k_1[MD_4X]}{k_2[Y] + k_{-1}[X]}$.

Substituting this in the rate expression gives

$$\text{rate} = k_2[MD_4][Y] = \frac{k_1k_2[Y]}{k_1[X] + k_2[Y]}[MD_4X].$$

When $k_2[Y]$ is small compared to $k_{-1}[X]$, the rate will be $k_{obs}\dfrac{[Y]}{[X]}[MD_4X]$. Excess X will retard the rate.

When $k_2[Y]$ is large compared to $k_{-1}[X]$, the rate will be $k_1[MD_4X]$ and a first-order reaction is observed.

For a dissociative mechanism a plot of k_{obs} vs. $[Y]$ will be curved, while a plot of $\dfrac{1}{k_{obs}}$ vs. $\dfrac{1}{[Y]}$ will be linear with a non-zero intercept $= \dfrac{1}{k_1[MD_4X]}$.

Since a dissociative mechanism involves the production two units from one, $\Delta S^\ddagger$ is usually positive. In general the rate will depend on electronic stabilization of the four-coordinate intermediate. Racemization is possible.

Kinetics of the S_N2 associative mechanism

$$MD_4X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MD_4XY \xrightarrow{k_2} MD_4Y + X .$$

Applying the steady state approximation to the first step gives

$$\frac{d[MD_4XY]}{dt} = 0 = k_1[MD_4X][Y] - k_{-1}[MD_4XY] - k_2[MD_4XY] ,$$

and rearranging, gives $[MD_4XY] = \dfrac{k_1[MD_4X][Y]}{k_{-1} + k_2}$.

Substituting into the rate expression results in

$$\text{rate} = k_2[MD_4XY] = \frac{k_1k_2[MD_4X][Y]}{k_{-1} + k_2} .$$

Thus the rate = $k_{obs}[Y][MD_4X]$ and a second-order reaction is observed. Excess X should have no effect on the rate. A plot of k_{obs} vs. [Y] will be linear. Since an associative mechanism involves the production of one unit from two, $\Delta S^\ddagger$ is usually negative. In general the rate will depend on the steric crowding of the complex. The reaction usually proceeds by inversion.

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