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BINUCLEAR TRANSITION METAL COMPLEXES OF FACE-TO-FACE
COMPARTMENTAL BIS(CYCLIDENE) LIGANDS

The Ohio State University

Ph.D. 1984

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BINUCLEAR TRANSITION METAL COMPLEXES OF
FACE-TO-FACE COMPARTMENTAL BIS(CYCLIDENE) LIGANDS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in the Graduate School of
The Ohio State University

By

Naomi Hoshino, M.S.

The Ohio State University

1984

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Chapter 1

INTRODUCTION

There has been a growing interest in multinuclear transition metal complexes in recent years. The increased recognition of the potential importance of such molecules has been reflected in the rapid development of the field of metal cluster chemistry. Polynuclear complexes also hold considerable significance in the area of bioinorganic catalysis. Many proteins and enzymes requiring two or more metal ions have been discovered.

Among a number of biological reactions catalyzed by or involving metallobiomolecules, those which are related to the chemistry of dioxygen are particularly interesting and important. Dioxygen constitutes an essential part of respiratory metabolism serving as the terminal electron acceptor in the electron transport chain. Concomitant reduction of dioxygen to water is responsible for 90% of oxygen consumption. Dioxygen is also activated and utilized in the biological reactions catalyzed by oxygenases. The transport of dioxygen to the site of utilization is another key aspect of the management of dioxygen with metalloproteins. The understanding of the biological transport and fixation of dioxygen is a matter of much consequence because it will benefit the in vitro chemistry of dioxygen in such areas as development of synthetic dioxygen carriers, energy efficient oxygen electrodes for
fuel cells, and industrial application of transition metal catalysts in oxidation of organic compounds.

Table 1 lists examples of dioxygen related metalloproteins with polynuclear active metal centers. The transport proteins hemerythrin and hemocyanin, which are more primitive than hemoglobin and myoglobin, contain iron and copper, respectively, and bind dioxygen at apparent metal to dioxygen stoichiometry of 2:1. Tyrosinase is a copper containing monooxygenase utilizing dioxygen in the hydroxylations of monophenols and further acts as a two-electron oxidase. This enzyme is thought to contain dicopper, oxygen-binding site similar to hemocyanin (Type III Cu).

Laccase is representative of multicopper proteins and contain all three of the well known types (Type I, II, and III) of copper sites. Four copper ions are required for the enzymatic function of reducing dioxygen to water. On the other hand, two heme irons and two coppers, one of which is strongly coupled to one of the hemes, comprise active site of cytochrome c oxidase. That heme protein is found in all higher organisms (animals and plants) as well as lower ones like yeasts and some bacteria. Cytochrome c oxidase catalyzes reduction of dioxygen to water by mediating the transfer of four electrons from a series of redox proteins to the dioxygen.

It is not thought to be accidental that these proteins contain pairs of metals and especially that the oxidases are equipped with four redox-active metal centers. The significance lies in the fact that the full reduction of dioxygen to water requires four electrons and four protons.
Table 1. Examples of Dioxygen Related Metalloenzymes With Multiple Metal Centers.

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Metal Centers</th>
<th>Catalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemerythrin</td>
<td>2 Nonheme Fe</td>
<td>((O_2\ \text{Transport}))</td>
</tr>
<tr>
<td>Hemocyanin</td>
<td>2 Cu</td>
<td>((O_2\ \text{Transport}))</td>
</tr>
<tr>
<td>L-Tryptophan oxygenase</td>
<td>2 Heme Fe 2 Cu</td>
<td>L-Tryptophan (\rightarrow) L-Formylkynurenine</td>
</tr>
<tr>
<td>Tyrosinase</td>
<td>2 Cu</td>
<td>Monophenol (\rightarrow) (o)-Diphenol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(O_2 + o)-Diphenol (\rightarrow) (o)-Diquinone + H(_2)O</td>
</tr>
<tr>
<td>Laccase</td>
<td>4 Cu</td>
<td>(O_2 + p)-Diphenol (\rightarrow) (p)-Diquinone + H(_2)O</td>
</tr>
<tr>
<td>Ascorbate oxidase</td>
<td>8 Cu</td>
<td>(O_2 + \text{Ascorbic acid} (\rightarrow) \text{Dehydroascorbic acid} + H(_2)O</td>
</tr>
<tr>
<td>Cytochrome c oxidase</td>
<td>2 Heme Fe 2 Cu</td>
<td>(O_2 + \text{Cyt c (red)} (\rightarrow) \text{Cyt c (ox)} + H(_2)O</td>
</tr>
<tr>
<td>Superoxide dismutase</td>
<td>2 Cu 2 Zn</td>
<td>(2O_2^− + H^+ \rightarrow O_2 + H_2O^−)</td>
</tr>
</tbody>
</table>
The multiple electron transfer, which the enzyme performs with ease, is not only crucial to circumventing the formation of toxic, partially reduced species such as superoxide $O_2^-$ and peroxide $H_2O_2^-$, but is also efficient in utilizing the maximum oxidizing power of the dioxygen. The common occurrence of pairs of metal atoms at the oxygen binding site in these species facilitates a rapid two-electron donation to oxygen, upon oxygen binding, thereby overcoming the energy barrier associated with the first one-electron step.

The incomplete understanding of these biological systems and the difficulties in elucidation of the mechanism of enzymatic reactions have fueled speculation on the role and nature of the multiatom metal-containing functional units. Since in these systems two metal ions are found in close proximity to each other and usually sharing a bridging ligand, these "connected" metal centers of copper(II) and/or iron(III) (intermetallic distance $\leq 5\AA$) often exhibit unusual magnetic properties that result from a strong metal-metal interaction. The Type III Cu(II) protein escapes detection by electron paramagnetic resonance (EPR) spectroscopy because of the antiferromagnetic coupling of its electron spin. It has been inferred that the characteristics reflected in such a strong metal-metal interaction in the resting enzyme are essential for the function of the reduced enzyme as a multi-electron redox catalyst. Thus a model approach, which is favorably used in the area of bioinorganic chemistry, has acquired more and more research emphasis. That is, low molecular weight polyfunctional ligands which are capable
of fixing two metal ions in close proximity (binucleating ligands) have been designed and the metal complexes with these ligands have been investigated in the hope that the properties and characteristics of these complexes might serve as a test for various possibilities and eventually clarify (and even mimic) the behavior of more complicated and sophisticated natural products.

In the following section recent studies on synthetic binuclear transition metal complexes will be outlined. The examples are selected to provide some experimental background for the study of metal-metal interaction.

1.1 Synthetic Binuclear Complexes.

Since 1970, when Robson introduced the term "binucleating ligand", there has been a steady increase in the number and type of such ligands and the transition metal complexes.

The literature actually offers innumerable examples of dinuclear species that merely contain two metal ions; in many cases, a bridging ligand is shared. These species range from, for example, simple copper(II) salts and chelates containing bridging ligand(s) to somewhat larger macrocyclic complexes bound by a bridging group that ranges from monoatomic ligand to polyatomic organic molecules. The experimental techniques developed to study metal-metal interaction in such dimers are applicable to the binuclear complexes of interest here and will be briefly mentioned below.

When a metal-metal interaction is present in a given binuclear species, the most affected property is its paramagnetism, and,
therefore, magnetic susceptibility measurement and EPR spectroscopy are often used to obtain information on these complexes. The appropriate Hamiltonian for a pair of ions labeled 1 and 2 has the general form:

\[ H = H_1 + H_2 + H_{\text{ex}} + H_{\text{dip}} + H_{\text{syn}} \]  

The \( H_1 \) and \( H_2 \) are assumed to be the same as for each independent ion, while \( H_{\text{ex}} \) and \( H_{\text{dip}} \) represent the exchange and dipolar terms, respectively. The last term arises essentially through differences in the symmetry of the ion sites. When two magnetic ions are in close proximity, exchange need not result but the dipole-dipole coupling will always occur. When the exchange coupling takes place, it is described as a coupling of two spins, written as in equation (ii):

\[ H_{\text{ex}} = -J S_1 \cdot S_2 \]  

(Note that some workers use a different definition, \( H_{\text{ex}} = -2JS_1 \cdot S_2 \)). For the simplest case of two ions, each having one unpaired electron (such as Cu(II)\(_2\)), the coupling constant \( J \) represents the energy difference between singlet and triplet states which arises from the exchange interaction. When \( J \) is negative, the interaction is antiferromagnetic and the singlet ground state results. Magnetic susceptibility measurements yield the value of \( J \), which can also be estimated by temperature dependence of EPR signals.
The dipolar interaction causes a shift in energy of the $M_s = 0$ state from the $M_s = \pm 1$ states in zero-field within the triplet, and can lead to observation of a "triplet" EPR spectrum. Since EPR parameters can be related to the distance between the dipoles, some quantitative information on the metal-metal separation can be obtained in favorable cases.\textsuperscript{13}

The effect of metal-metal interaction on reactivity becomes a major concern when one studies the electrochemical behavior of binuclear species. Electron transfer is an important mode of reaction in the related dioxygen chemistry. When two redox active metals are coupled, the voltammetric redox waves split into two waves and the magnitude of the difference in the two corresponding redox potentials ($\Delta E = E_1 - E_2$) can be related to the stability of intermediate mixed-valence species.\textsuperscript{14} Such splitting could arise solely from simple statistical and electrostatic factors. The theory, which has been developed for and has been applied to a series of $[N_5Ru(II,III)]_2L$, where $N_5$ = ammine or pyridyl ligands and $L$ = organic bridging ligand, relates electronic spectral information (intervalence spectra) to the dynamics of electron transfer between two metal atom sites.

With these considerations in mind, the rest of this section will be devoted to illustrating how a number of synthetic binuclear complexes have been characterized and utilized in various areas of research. The binucleating ligands, which are capable of incorporating two metal ions within a single ligand framework with or without exogenous ligand(s), were conveniently classified by Groh\textsuperscript{15} and Fenton et al.\textsuperscript{16} as follows:
(i) Those containing partially shared donor sets which provide two adjacent coordination sites, oriented in a "side-by-side" manner, in which the center-most donor atom(s) are shared by the metals.

(ii) Those containing isolated donor sets.

(a) Donor sets isolated by intervention of a persistent void.
(b) Isolated donor sets separated by a bridging moiety.
(c) Isolated donor sets within "extendable macrocycles".

Class (i). A variety of examples of this class of ligands are listed in generalized forms on the next page. Syntheses and properties of binuclear complexes derived from these and related ligands have been reviewed elsewhere. All the compounds listed are derivatives of either 2,6-disubstituted phenols or 1,3,5-triketones. The resulting metal complexes involve a mode of metal-metal interaction through in-plane orbitals including those of the bridging oxygen atom(s), although the coordination geometry around each metal may vary from square planar through square pyramidal to pseudo-octahedral. The close proximity of the two metal atoms (3.0-3.2 Å) is also enforced by the ligand structure.

Representative of L1 is Robson's ligand with \( R^1 = R^2 = (CH_2)_3, R^3 = CH_3, \) and \( R^4 = H. \) The ligand L2 is an asymmetric diamide-diamine ligand which is not so different from L1 (\( R^1 = R^2 = (CH_2)_2, R^3 = CH_3, R^4 = H) \) in terms of its ligand field strength. L3 to L6 were termed compartmental ligands by Fenton and possess two dissimilar coordination sites which make it feasible to prepare heterobinuclear complexes. The ligand L3 is, in fact, a precursor to L1 and stepwise metallation followed by the ring closure of L3 yields a heterobinuclear complex of L1 as well. L8 is also a precursor to L2. The term
"compartmental", however, has been used to describe the binucleating ligands and their complexes in which two well-defined coordination sites are separately provided for each metal atom within the molecule.

Magnetic susceptibility studies have been most extensive for these side-by-side binuclear species. Gagné and Hendrickson\textsuperscript{19} investigated a series of homobinuclear complexes with Robson's ligand and found that the net antiferromagnetic exchange interaction increased monotonically as the metal ion was changed in the order of $\text{M(II)}_2$, $(\text{J/cm}^{-1})$: $\text{Mn}_2 (+0.2) < \text{Fe}_2 (-4.2) < \text{Co}_2 (-9.3) < \text{Ni}_2 (-27) < \text{Cu}_2 (-294)$. Throughout this series, the metals occupy 5-coordinate square pyramidal coordination sites with apical chlorides, one each on opposite sides of the ligand plane. When the metals were held in pseudo-octahedral environments, the trend changed very little ($\text{Fe}_2 (-7.5)$, $\text{Co}_2 (-4.1)$, and $\text{Ni}_2 (-23))$.\textsuperscript{20} In a series of heterobinuclear complexes, $\text{CuCl} \cdot \text{MCl} \cdot (\text{L1}) \cdot n\text{H}_2\text{O}$, a trend toward increasing antiferromagnetic exchange interaction was observed; across the series of $\text{Cu(II)M(II)} (\text{J/cm}^{-1})$, $\text{Mn} (-30) < \text{Fe} (-71) < \text{Ni} (-103)$.

In the cases of "asymmetric" heterobinuclear species, in which Cu(II) occupies the inner $\text{N}_2\text{O}_2$ compartment of (L4; $\text{R} = (\text{CH}_2)\text{R}$) and the other metal $\text{M} (= \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{and Cu(II)})$ is placed in O4 site (along with two axial water molecules), Okawa et al. also obtained similar results ($\text{Mn} (-22) < \text{Ni} (-75) < \text{Cu} (-330)$).\textsuperscript{21} Kahn and co-workers also investigated this series and obtained slightly different numbers ($\text{Mn} (-32.5), \text{Ni} (-83.4)$).\textsuperscript{22,23} These authors attempted to rationalize the exchange parameters by a molecular orbital scheme.\textsuperscript{23} Despite the simplifying assumptions they found necessary, the increase in $-\text{J}$ was qualitatively predicted by the theory; $\text{J(}\text{Cu}_2)/\text{J(}\text{CuNi}) > 2$ and
Thus in favorable cases, Kahn's MO scheme of exchange interaction based on the overlap of \( d_{x^2-y^2} \) orbitals of each metal ion can account for the observed antiferromagnetism. Other factors being the same, the more unpaired electrons are involved, the smaller the net antiferromagnetism. The theory, however, applies only to the systems in which orbital angular momentum is quenched. In addition, the possible variation in structural parameters, such as Cu-O-M angle should be considered for a quantitative comparison. This point was well examined in simpler cases as \( \mu \)-dihydroxo-dicopper(II) complexes.\(^{24}\) Sinn and co-workers,\(^{25}\) on the other hand, concluded that in their series of dimeric species (shown below) the \( J \) values correlate with the structural features regardless of the nature of \( M \); this does not coincide with Kahn's argument. The rigidity of the binucleating ligands mentioned above may be advantageous in this regard since in Sinn's dimeric complexes the square planar geometry of copper site is distorted to a
different extent with varying \( M \), thus adding additional unexplained effect.

Lintvedt and co-workers\(^{26}\) have investigated electrochemical behavior of dicopper(II) complexes of \( L_5 \) and the precursor bis(1,3,5-triketonate) complexes. The common feature of the binuclear species studied is the reversible, sequential transfer of two electrons at the same potential.

\[
\begin{align*}
Cu_2(L_5)^{\text{E}_1} & \leftrightarrow Cu_2(L_5)^{\text{E}_2} \\
\end{align*}
\]

The magnetic criterion suggests that the two copper centers are strongly antiferromagnetically coupled (-\( J > 850 \text{ cm}^{-1} \)), and therefore a large separation between \( E_1 \) and \( E_2 \) may be expected. Quite unexpectedly the electrochemistry of these complexes displayed a single two-electron redox wave, regardless of whether the coordination sites containing the two copper(II) ions are identical (in bis(1,3,5-triketonates)) or not (in \( L_5 \)). The authors state that these compounds are viewed as one electroactive center which undergoes two-electron transfer, rather than two metal centers.

On the other hand, Hendrickson and Long\(^{27}\) showed that the dicopper(II) complexes of \( L_1 \) derivative (\( R^1, R^2 = \text{propylene}, 2,2'-\text{dimethylpropylene, butylene, 2,2'-diphenylene, } R^3 = \text{t-butyl, } R^4 = \text{H} \)) exhibit two quasi-reversible one-electron reductions with \( \Delta E_{1/2} = 0.30 - 0.52 \text{V} \). Corresponding comproportionation constants (\( K_{\text{com}} \)) fall in the range \( 4 \times 10^6 - 7 \times 10^8 \).
All seven of the mixed-valence species Cu(I)Cu(II), separately prepared by chemical reduction, exhibited intervalence transfer (IT) bands in the near-infrared region. The room temperature EPR spectra of these mixed-valence species revealed that the unpaired electron is delocalized over two copper sites as evidenced by a characteristic seven-line spectrum $(I_Cu = 3/2)$ in four cases. These results are in accord with Gagné's study$^{28}$ on similar systems and of interest in relation to the so-called "half-met" state (Cu(I)Cu(II)) of dicopper sites in proteins.$^{29}$

The ligands L7 and L8 furnish only one phenoxy oxygen donor to be shared and the binuclear metal complexes always contain exogenous bridging group, Y.

In retrospect, these ligands will allow a wide range of donor group Y to study, while retaining a fairly constant structural framework. Dioxygen and other small molecules are of particular interest. Drago and co-workers$^{30}$ have explored such systems. In the complexes shown below, the bridging group Y was varied from OH$^-$, OEt$^-$, $N_3^-$, Br$^-$, and CN$^-$ to pyrazolate.
These dicopper(II) complexes exhibited moderate to weak anti-ferromagnetic interactions in the above order of Y. The EPR spectra of mixed-valence species Cu(I)Cu(II) indicated that the unpaired electron is localized, whereas the electrochemical results (ΔE$_{1/2}$) gave large $K_{\text{com}}$ values on the order of $10^8$ to $10^{12}$ for Y = OEt$^-$ and $N_3^-$. The authors noted a pronounced solvent effect on electrochemical results and pointed out that the effect of a change in the charge of a species and in its coordination environment on its redox potential should be considered when $K_{\text{com}}$ values are interpreted. Thus they explained the slow electron transfer in the mixed-valence state as probably being due to cleavage of the Cu(I)-Y bond and geometric distortion of the ligand environment around the copper(I) center.

The preceding cases were chosen to illustrate studies that were successful in clarifying the nature of metal-metal interaction. In general this interaction has been shown to arise from exchange, regardless of the magnitude of the process or the characteristic of this particular class of side-by-side binuclear complexes. However, the intrinsic relationship between such exchange coupling and the accompanying intramolecular electron transfer dynamics has not been well delineated. From a bioinorganic standpoint, however, a fairly strong
antiferromagnetic coupling in all the dicopper(II) species reported in this class has demonstrated the ability of bridging oxygen donor(s) (either phenoxy or keto) to foster such a coupling and serves as supporting evidence for the proposed involvement of such phenoxy oxygen bridge in the antiferromagnetically coupled Type III Cu(II) pair in biological systems.\textsuperscript{31}

Class (ii)-(a). Ligands of this subclass contain isolated donor sets separated by a persistent void and are best represented by face-to-face binary porphyrins. The systems described in this thesis also belong to this class. Structures L9 and L10 illustrate β-linked and meso-linked diporphyrin ligands and Table 2 lists specific examples (not all the combinations of R's and metals have been prepared).

The cofacial structure of metal complexes derived from these ligands shown below indicates a particular configuration in which two planar macrocyclic complexes are held face-to-face. They exhibit an intermetallic and/or interporphyrin communication along the axial
Table 2. Examples of β-Linked and meso-Linked Diporphyrins.

### β-Linked Diporphyrins

<table>
<thead>
<tr>
<th>N</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>Metal Complex</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(CH₄)₂COO(CH₂)₃</td>
<td>ethyl</td>
<td>ethyl</td>
<td>Zn₂</td>
<td>32</td>
</tr>
<tr>
<td>2ᵃ</td>
<td>(CH₂)ₙ; n=5,6,8,10</td>
<td>n-octyl, methyl</td>
<td>ethyl</td>
<td>Zn₂</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>(CH₂)ₙCONH(CH₂)ₘ; n=1,2; m=1,2</td>
<td>ethyl</td>
<td>methyl</td>
<td>Co₂,CoPd,Cu₂,</td>
<td>36,37,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CoAg,CoFe,</td>
<td>40-43</td>
</tr>
<tr>
<td>4</td>
<td>CONH(CH₂)ₙ; n=1,2</td>
<td>ethyl</td>
<td>methyl</td>
<td>Co₂</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>(CH₂)ₙCON(n-Bu)(CH₂)ₘ; n=1,2; m=2,3</td>
<td>n-hexyl, methyl</td>
<td>n-pentyl,</td>
<td>Fe₂,Co₂,Cu₂,</td>
<td>44,46-51,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>n-octyl</td>
<td>Cu,FeCu,Zn₂,</td>
<td>52-55</td>
</tr>
<tr>
<td>6</td>
<td>(CH₂)ₙCON Benzyl-</td>
<td>n-hexyl, methyl</td>
<td>-</td>
<td></td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>CH₂CONHCH₂</td>
<td>n-pentyl</td>
<td>methyl</td>
<td>Co₂,Zn₂,FeZn</td>
<td>51</td>
</tr>
</tbody>
</table>

### meso-Linked Diporphyrins

<table>
<thead>
<tr>
<th>N</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>Metal Complex</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SO(CH₂)₃COO</td>
<td>b</td>
<td>H</td>
<td>H</td>
<td>Zn₂</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>SHCONH</td>
<td>phenyl</td>
<td>H</td>
<td>H</td>
<td>Cu₂,Co₂</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>(CH₂)ₙCONR⁵(CH₂)ₘ; n=2,3; m=1,2,3; R₅=H,Me</td>
<td>H</td>
<td>ethyl</td>
<td>methyl</td>
<td>Co₂,CoPd</td>
<td>38,39</td>
</tr>
<tr>
<td>4</td>
<td>(CH₂)₃NMe(CH₂)₂</td>
<td>H</td>
<td>ethyl</td>
<td>methyl</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>(CH₂)₂NHCONH(CH₂)₂</td>
<td>H</td>
<td>ethyl</td>
<td>methyl</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>(CH₂)ₙ; n=4,6</td>
<td>H</td>
<td>ethyl</td>
<td>methyl</td>
<td>Co₂,CoPd</td>
<td>38,39</td>
</tr>
</tbody>
</table>

ᵃ Two R¹ groups may or may not be the same. Two peripheral substituent(s) R² on the same ring can be varied too. R² on the same ring can be varied too.

ᵇ Tetra-meso-(R¹)-strati-bisporphyrin.
direction. It is also noted that the cavity created between two macrocycles of variable sizes can accommodate bridging ligands of different sizes ranging from small dioxygen molecules to a larger organic compound, although little attention has been paid to the latter point to date.

The chemistry of these face-to-face complexes is quite different from the previous case. For instance, the dicopper(II) (and dicobalt(II)) complexes of both L9 and L10, where reported, are all EPR active precluding such a strong antiferromagnetic coupling as in some of the side-by-side counterparts. It is reasonable, in reference to Kahn's theory mentioned before, that there is little or no overlap of the two \( d_{x^2-y^2} \) orbitals on the copper atoms in the cofacial configuration. Thus the triplet EPR spectra of dicopper(II) diophyrins have been assumed to be mostly dipolar in origin and the metal-metal distances have been calculated in some cases \( \text{Cu}_2(\text{L}9-3); \ 4 - 7 \text{Å} \) for four- to six-atom amide linkages, \( \text{Cu}_2(\text{L}9-5); \ 4.2 - 6.4 \text{Å} \) for four- to seven-atom amide linkages, \( \text{Cu}_2(\text{L}10-2); \ 6.3 \text{Å} \). The EPR spectra of dicobalt(II) complexes proved to be more difficult to analyze on the basis of dipolar interaction alone and the necessity of including exchange interaction was suggested. The interaction between cobalt(II) atoms should be stronger in the axial direction, since the magnetic orbital is now \( d_{z^2} \).

The source of interest in these cofacial binary porphyrins is not their magnetic properties, but their electronic spectral features and their chemical reactivity toward dioxygen. With respect to the first point, one of the areas of research utilizing these diophyrins is associated with model studies on the chlorophyll dimers involved in
bacterial photosynthesis and related light-induced electron transfer reactions. Early examples of cyclophane porphyrins were synthesized by Ogoshi and by Kagan (L9-1 and L10-1, respectively) for the purpose of covalently linking two porphyrin rings in a stacking position. The absorption spectra of cofacial diporphyrins and their zinc complexes commonly exhibit blue shifts in their Soret bands and varied alterations in the visible region as compared to monomeric porphyrins. Chang has interpreted this phenomenon as exciton interaction. These spectral characteristics, together with sharpness of proton-NMR signals, can be used as a qualitative measure of the magnitudes of interporphyrin separation and cofaciality. The shear displacement or "slippage" from a completely parallel position has been examined by x-ray crystal structural analysis for some cases. In Cu2(L9-5; n = 2, m = 3) and Cu2(L10-3; n = 3, m = 2) the interplanar distances are as close as 3.52Å and 3.87Å, respectively, while intermetallic distances of 5.22Å and 6.33Å indicate a lateral displacement between porphyrin centers of 3.80Å and 4.95Å, respectively. Although the crystal structure is not always retained in solution, such deviation from cofaciality seems to take place commonly in the complexes included in Table 2. Chang's recent communication on a strictly cofacial "pillared diporphyrin", linked by a biphenylene unit, is quite interesting in this regard.

Chang's diporphyrin, L9-5; n = 1, m = 2, and R² = n-octyl, has found a unique application in picosecond photochemical studies. Using the magnesium complex of this ligand, in which one porphyrin ring remains unmetallated, Netzel and associates obtained optical
spectral evidence for a photo-driven electron transfer from magnesium porphyrin to a free base porphyrin:

$$[\text{Mg} - \text{H}_2] \xrightarrow{h\nu \text{ (ps)}} [\text{Mg} - \text{H}_2^-]$$

This process mimics photosynthetic charge separation despite the relatively short lifetime of the charge transfer product. A heterobinuclear analogue Zn(II)Fe(III)Cl(L2-5) was also shown to undergo similar internal electron transfer upon photoexcitation to form $[\text{Zn} - \text{Fe(II)}]\text{Cl}$ despite of a change in the nature of excited state. In addition, the back reaction of this process bears some resemblance to another primary event in bacterial photosynthesis; i.e., reduction of the bacteriochlorophyll dimer by ferrous cytochrome $c$. It should be noted that binucleating ligands have contributed tremendously to the study of electron transfer reactions, optical or thermal, eliminating the complications due to the otherwise bimolecular nature of the process.

Another major source of interest in this class, (ii)-(a), of ligands comes from the potency of the resulting binuclear metal complexes as multielectron redox catalyst. Collman and Anson recognized the possibility of modifying an electrode with these complexes to achieve electrocatalytic four-electron reduction of dioxygen. The development of an electrode material at which the rapid four-electron reduction of dioxygen to water proceeds, at or near the reversible potential ($+1.23\text{V vs. NHE}$), would constitute a major advance in fuel cell technology. Primary goals are (1) to decrease the unfavorable
overpotential associated with current technology, and (2) to deliver four electrons efficiently to form water and not hydrogen peroxide (two-electron process). Binuclear catalysts were thought to provide an advantage over their mononuclear counterparts, especially when the two metal atoms are so closely located as to "trap" the dioxygen substrate. Presumably this would lead to simultaneous two-electron transfer and this idea is reminiscent of the enzymatic action mentioned before. The dicobalt(II) porphyrins were chosen because Co(II/III) couple was the most anodic among the metalloporphyrins with demonstrated affinities for dioxygen. The expected catalytic activity is depicted below:

\[
\begin{align*}
(Co(III)_2) & \rightarrow 2e^- (Co(II)_2) \\
2H_2O & \rightarrow 4H^+ + O_2 \\
2e^- & \quad (Co(III)O_2^- - Co(III))
\end{align*}
\]

Collman, Anson, and their co-workers have extensively investigated the electrocatalysis of several dicobalt(II) species coated on a graphite electrode by means of rotating ring-disk voltammetry. They demonstrated that Co2(L9-3; n = 1, m = 1), which has the shortest four-atom linkages with estimated metal-metal distance 4Å, achieved a four-electron reduction at +0.7V, which is impressingly anodic and close to the reversible potential. Quite surprisingly an analogous system Co2(L9-4; n = 2) and Co2(L9-4; n = 1), with even shorter linking groups, did not effect the four-electron process at all and produced only hydrogen peroxide. Other species with five- and six-atom linkages also
proved to be poor catalysts. The extreme sensitivity of the catalytic activity to the intimate geometry of the binuclear complex has been noted by Chang et al., as well, among their dicobalt complexes $\text{Co}_2(L^9-5)$. Mechanistic studies led these authors to interpret these results in terms of the stability of the key intermediate ($\text{Co}(\text{III})-\text{O}_2^{2-}-\text{Co}(\text{III})$) and proton transfer to this $\mu$-peroxo species (vide infra). A thorough elucidation of the events at the electrode surface is very difficult to achieve and awaits further investigation. Yet it is clear that, for the purpose of electrochemical application of these binuclear species in this particular catalysis, it is necessary to control rather intricate geometric factors and that these render a majority of the diporphyrins unappealing.

Noting the relatively short history (beginning in 1977), it is not surprising that the two areas of research mentioned above are still expanding. Another possible application of face-to-face complexes might use the persistent cavity in the molecule for specific inclusion of organic molecules. Guest-host chemistry of this sort, involving binuclear transition metal complexes, is still unprecedented.  

**Class (ii)-(b).** This subclass, binucleating ligands with isolated donor sets separated by a bridging moiety, can be as broad as is the definition. Selected examples are given on the next page. (Double bonds are left out for clarity in L13 and L15). As can be seen, two metal complexation sites, which are typically square planar or tetragonal with the exception of L16, are "hinged" together by various groups and the resultant orientation of coordination spheres can be either coplanar (L11, L12), roughly cofacial (L13, L14), or intermediate
(L15, L16). The mode of metal-metal interaction varies with the details of the structure.

The ligands L13 and L14 are similar to the subclass (ii)-(a) mentioned just before, except that the diporphyrins are more rigidly cofacial. Both L13 and L14 have vertically stacked (as drawn) and offset (nonstacked) forms. In a stacking position the binary porphyrin L13 fixes two metal ions at a separation of about 6Å and has been regarded as model species in the area related to photosynthesis. The ligand L14 is a synthetic modification of such ligands as L13 and still a rare example of a cofacial Schiff base ligand. In the stacked form of Cu(II)2(L14) both magnetic and EPR data suggested a weakly ferromagnetic interaction. The electronic spectra and the unusual redox properties have been interpreted in terms of electron delocalization through π-π interaction between [CuN4O2] chromophores.

In the coplanar systems M2(L11) and M2(L12), the metal-metal interaction may be mediated by the aromatic moiety between the metals. Hendrickson et al. showed that Cu(II)2(L11; R = benzene) exhibited an antiferromagnetic interaction (J = -12.2 cm⁻¹) which they interpreted as arising from spin polarization propagated through the benzene ring; a contribution of the π system to the exchange interaction was implied.

An interesting case has been made by Lippard and co-workers in the light of mediated antiferromagnetism using various complexes containing [Cu(II)2(im)] core, where im designates an imidazolate bridge between the copper(II) ions. Their goal was to test the postulate that a derivatized bovine erythrocyte superoxide dismutase (Cu2Cu2BESOD) contains a bimetallic site of the form [Cu2(im)] by using synthetic model
systems. Lippard's compounds all contain a [Cu(II)$_2$(im)] core within a binucleating ligand. They have provided supporting evidence for this suggestion since these compounds indeed exhibited an antiferromagnetic behavior ($J = -17 - -88$ cm$^{-1}$)$^{61}$ which mimics that of Cu$_2$Cu$_2$BESOD ($J = -26$ cm$^{-1}$). The variation in the magnitudes was found to correlate well with the basicity of the ligand, indicating predominance of a $\sigma$-super-exchange pathway.$^{61}$

The gable porphyrin (L15; $R^1 = 1,3$-benzene, $R^2 = $ phenyl) was synthesized by Tahushi and Sasaki,$^{62}$ originally to simulate a heme-heme interaction found in cytochrome $c_3$. The dicobalt(II) complex of this ligand, however, showed a rather interesting phenomenon; that is, a cooperative dioxygen binding$^{62b}$ at $-20^\circ$C in the presence of a bridging base. When a DMF solution of this complex containing excess diimidazolymethane was exposed to various partial pressures of dioxygen, the absorbance spectral change was observed to follow a Hill plot with a coefficient $= 1.5$. Steady-state dioxygen binding equilibria were analyzed to yield $K_1 = (2.1 \pm 0.1) \times 10^{-3}$ torr$^{-1}$ and $K_2 = (18 \pm 1) \times 10^{-3}$ torr$^{-1}$. The authors explained that the enhanced affinity for the second oxygen molecule was due to the release of strain in the deoxygenated complex.

Similar singly-bridged cobalt porphyrins were prepared by Vida et al.$^{63}$ They communicated the finding that these dicobalt(II) complexes (Co(II)$_2$(L15; $R^1 = \sigma-\text{d}-O(\text{CH}_2)_{3}-\text{d}$, $R^2 = \sigma$-tolyl), for instance) catalyze the oxidation by dioxygen of 3,5-di-$t$-butylcatechol to an $\sigma$-quinone. They have proposed that the species depicted below is a key intermediate for this catalysis.
Apparently the binuclear nature of the catalyst is advantageous since a monomeric counterpart does not have this catalytic efficiency. The flexible polyatomic linkage may play a role in a specific interaction with the substrate.

The ligand L16 is unique in that it allows a coordination geometry of trigonal, or lower, symmetry and is perhaps more representative of the class (ii)-(b) in the flexibility with which its pair of metal sites can be rearranged. The recent trend in copper protein modeling seems to point to the synthetic modification of binucleating ligands to allow more flexibility in coordination geometry and metal-metal distance. Such an attitude is justified by the fact that in a Type III copper site the metal-metal distance changes between deoxy and oxy forms. Karlin and his associates, for instance, have been successful in mimicking some of the dioxygen binding and activation behavior of binuclear copper proteins using \text{Cu(II)}_2(L16; X = 2-pyridyl). This complex was found to undergo a hydroxylation of the ligand upon oxygenation as shown below.

\[ \text{Co} \quad \text{OH} \quad \text{OH} \quad \text{Co} \]

\[ \text{Co} \quad \text{R} \]

\[ \text{X} \]
It was confirmed that the source of oxygen atoms in the product was indeed the dioxygen. The hydroxylated ligand, which has some resemblance to L7 in the class (i), was isolated and recombined with copper(I). This new complex binds dioxygen by forming a μ-peroxo-copper(II) species of the type long postulated for oxyhemocyanin. A number of claims had been made prior to this report on (almost) reversible dioxygen binding of copper(I) dimers, with no spectroscopic evidence for μ-peroxo nature of the bound dioxygen, however.

Thus, the diversity of the chemistry of complexes with class (ii)-(b) ligands, as exemplified above, owes it to various types of "hinges". The structural flexibility of the ligands, that is desirable in certain cases, will be further emphasized in the next case.

Class (ii)-(c). The last category of binucleating ligands include macrocyclic ligands which accept two metals in a less constrained manner than do other classes. Some of these ligands are illustrated on the next page.

Agnus' macrocycle L17 was designed to model a Type III copper site. Incorporation of sulfur donors is in accord with the fact that the multicopper proteins contain reversible electrochemical systems that perform multielectron transfers at positive potentials, indicating the
stabilization of the copper(I) state. In addition, the intermetallic distances in $M_2(L_{17})$ complexes can vary from 3.5 to 8Å due to the enormous flexibility of pentamethylene chains between NS$_2$ sites. As in Karlin’s ligand, L$_{16}$, the three-atom donor sites are designed to leave the copper atom coordinatively unsaturated in order to provide the desired reactivity toward exogenous ligands, including dioxygen. For example, in Cu(II)$_2$(N$_3$)$_4$(L$_{17}$; $R$ = H) coordination in a basal plane is the same for both copper(II) ions and it involves tetragonal copper ions with two end-to-end bridging azide ions, one terminal azide, and the secondary amine nitrogen. Two sulfur atoms loosely interact with each copper ion in the axial sites. It is thought that this compound dissociates the end-on azide ligands upon dissolution in DMSO and that a bridging azide is also cleaved upon reduction to produce tetrahedral geometry around the copper(I).

![Chemical structure](image)

The solid sample shows a magnetic behavior indicative of a very strong antiferromagnetic coupling as in the Lintveit’s previously mentioned side-by-side complex, but the electrochemical behaviors differ significantly. Thus the apparent splitting in the redox potentials ($\Delta E_{1/2}$) of -60 mV in the case of Cu(II)$_2$(N$_3$)$_2$(L$_{17}$; $R$ = H), as opposed
to zero for a two-electron redox center, is explained by such a structural change upon reduction.

The ligand L18 is a similar polyamine type ligand. The work by Lippard et al. using these ligands \( Y = 0 \) or \( \text{CH}_2 \) was initiated in the course of the model studies for bovine erythrocyte superoxide dismutase alluded to in the previous subsection. First it was shown that these macrocyclic ligands greatly enhanced the stability of the \([\text{Cu}_2(\text{im})]\) core in solution, as compared to other binucleating chelates. The analogous complexes \( \text{Cu}(\text{II})_2(\text{OH})(\text{Cl}_3)\text{L}_{18}(Y = 0) \) and \( \text{Cu}(\text{II})_2(\text{CH}_3\text{COO})_2-(\text{L}_{18}; Y = 0) \) in which the imidazolate ligand was replaced by \( \text{OH}^- \) and \( \text{CH}_3\text{OH}^- \), respectively, were shown by crystal structures to adopt markedly different conformations of the 24-membered aliphatic ring, depending on the bridging ligand. The \([\text{Cu}_2(\text{im})]\) lies in a flat ring macrocycle conformation, whereas \([\text{Cu}_2(\text{OH})]\) core is encapsulated in a U-shaped macrocycle conformation and in the \([\text{Cu}_2(\text{CH}_3\text{COO})]\) complex the macrocycle adopts an S-shaped conformation. The \([\text{Cu}_2(\text{OH})]\) complex exhibits a strong antiferromagnetic coupling between coppers \((J = -4.78 \text{ cm}^{-1})\). Taken together with other reports on similar complexes containing such mono-\( \mu \)-hydroxo \([\text{Cu}_2(\text{OH})]\) unit, it seems that a geometry suited to good overlap of magnetic orbitals on copper and oxygen atoms can be ensured by the geometrically less demanding class (ii)-(c) ligands.

Nelson’s group has been utilizing the Schiff base ligands \( \text{L}_{19} \) and \( \text{L}_{20} \) for the same type of study. Their synthetic procedure allows one to vary the \( R^1 \) group from a polymethylene chain to an ether, thioether, or amine derivative (in \( \text{L}_{19} \)) and also to hydrogenate or methylate the
imine functionality to form L20. The mode of metal coordination to these variable donor sets is quite diverse. The dicopper(II) complexes have been viewed as hosts with variable volumes that can encapsulate one or two small bridging guest molecules or ions, such as OH\(^-\), OR\(^-\), halide, pseudohalide, pyrazolate, imidazolate, and pyrazine.\(^{71b}\) The properties of resulting bridged dicopper(II) complexes are more or less typical of class (ii)-(c) species. Nelson et al. have also been investigating the reactivity of dicopper(I) complexes. The Cu(I)\(_2\)(L20; \(R^1 = (\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\), \(R^2 = \text{H}\)) was shown to possibly be subject to proton (\(=\text{R}^2\)) transfer after dioxygen uptake.\(^{71a}\) This and other studies\(^{64}\) of reactivity of binuclear species have set a direction for future research in the copper protein modeling.

The last example of this class are polynuclear cryptates L21 and L22; both of them are polycyclization products of L18. The "strapping" in L21 may lead to locking in a certain conformation of the 24-membered saturated macrocycle. The bis-tren derivative (L21; \(Y = \text{H}_2\), \(Z = \text{H}\))\(^{72a}\) is thus expected to impose a geometry of two coaxially arranged tripod ligands, and L22\(^{72b}\) assumes a face-to-face configuration. Martell, Lehn, and co-workers have pursued the mono- and binuclear complexation in solution and further the formation of a bridged cryptate in which a substrate species is fixed between the two metals. The dicobalt(II) cryptate was found to react with dioxygen and form a dioxygen cryptate containing peroxo and hydroxo bridges, Co\(_2\)(O\(_2\))(OH)(L21; \(Y = \text{H}_2\), \(Z = \text{H}\)).

In summarizing the class (ii)-(c) ligands, the concept of substrate binding to the binuclear metal sites has been advanced further in this class. This is because the coordination unsaturation within the
binucleating ligand alone requires the metals to pick up other ligands and also because the ligand is designed to accommodate those ligands between the metals. With an appropriate spacing between two donor sets, even a tetraaza macrocycle leads to a dibridged binuclear species.\textsuperscript{73}

Cytochrome c Oxidase Models. In summarizing this section, an historical perspective of bioinorganic model studies for cytochrome c oxidase will be briefly described in order to illustrate the evolution of binuclear model compounds for a certain target system. The area is still open to much debate as the protein\textsuperscript{74} itself remains enigmatic. It has been established, however, that dioxygen interacts with a pair of heme iron and copper atoms, designated as heme a\textsubscript{3}/Cu\textsubscript{B}, and the other heme (heme a) and copper (Cu\textsubscript{A}) act as an electron shuttle. In the resting state of the enzyme, the active site heme a\textsubscript{3} - Fe(III)/Cu\textsubscript{B}(II) unit exhibits properties revealing that the two metal centers are strongly antiferromagnetically coupled (\(-J > 200\ \text{cm}^{-1}\)). This large coupling phenomenon has inspired a number of proposals suggesting an inidazolate,\textsuperscript{75} oxo,\textsuperscript{76} mercapto,\textsuperscript{77} or others, as a bridging group between heme iron and copper. The three representative models are depicted below and introduction of examples of synthetic model complexes in accord with each structure will follow.

![Chemical Structures](image-url)

(1) \hspace{2cm} (2) \hspace{2cm} (3)
The imidazolate bridged structure (1) was postulated by Palmer et al.\textsuperscript{75} in 1976. The model assumes that the nitrogenous axial ligand of heme \( a_3 \), suggested by EPR data\textsuperscript{78} for the reduced protein, can be an imidazole moiety, which further bridges to the copper, thereby explaining at the same time the strong antiferromagnetism. Such coupling would result in the ground state having total spin of 2 (\( S_T = 2 \); high spin heme \( a_3 \) - Fe(III), \( S = 5/2 \), and Cu\( \text{II} \), \( S = 1/2 \)) and is consistent with the magnetic data for the protein. The model also leaves the sixth coordination site of the heme, in a reduced state of the enzyme, for dioxygen to bind.

Quite a few synthetic binuclear systems have subsequently been reported to support this model. Most of them have involved an associative process through axial coordination of an imidazole/copper moiety to a square planar macrocyclic iron complex, and not a binucleating ligand.\textsuperscript{79} One such example was published by Wilson and his co-workers.\textsuperscript{79b}

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{tppstructure.png}
\end{figure}

Based on the magnetic susceptibility (15 to 300K) and Mössbauer and EPR spectroscopic result with the complex shown above and its FeZn analogue,
the authors speculated that the iron(III) porphyrin existed in both high-spin (S = 5/2) and low-spin (S = 1/2) forms at 20:80% ratio. Strong coupling to the copper(II) is assumed for both isomers in order to generate $S_T = 2$ and 0 states.

A majority of the species having imidazolate and other heterocycle bridges have turned out to discount the possibility that such ligands may foster a strong antiferromagnetic coupling. As mentioned earlier for class (i) and (ii)-(b) complexes, even in the case of two copper(II) ions, the coupling constant does not exceed 90 cm$^{-1}$ and the combination of iron(III) and copper(II) tends to produce weaker coupling due to the mismatch of the magnetic orbitals. Moreover, stronger axial coordination to the iron porphyrin in synthetic models often causes spin pairing, leading to either intermediate- or low-spin states; these states do not simulate the high-spin heme properly. Thus the interest in model(1) has shifted in search of alternative bridging groups.

The oxo-bridged model (2) was presented by Wilson and his co-workers in 1980. They postulated a catalytic redox model which includes a five-coordinate heme iron with an imidazole ligand on the side opposite the copper. Oxygenation leads to the formation of an Fe(III)-O-O-Cu(II), μ-peroxo species which is converted to μ-oxo species, (2), by extruding one oxygen atom in the form of water. Evidence based on $^{18}O_2$ labeling experiments has indicated, however, that the reduced enzyme converts dioxygen completely to water and that no oxygen atom is incorporated in the oxidized enzyme. Thus model (2) may not be appropriate for the resting enzyme but still is attractive in
explaining the magnetic coupling. The ability of oxygenous bridges to mediate a generally stronger antiferromagnetic coupling than imidazolate has been demonstrated among class (i) and class (ii)-(c) binuclear complexes. The authors draw analogy to the known chemistry of iron porphyrins that bind dioxygen. A well known μ-oxo dimer ([(TPP)Fe]₂O, for instance) is believed to form through the μ-peroxo dimer as a result of dioxygen fixation by [(TPP)Fe(II)]. There is an analogy from the postulated involvement of such μ-peroxo species M-O-O-M in oxyhemocyanin. In the complete catalytic scheme they postulated, reduction of the μ-oxo species leads to cleavage of the bridge to reform the oxygen-active iron(II) center. Reductive cleavage of the μ-oxo bridge in [(TPP)Fe]₂O was shown to lead to [(TPP)Fe(II)] and [(TPP)Fe(II)(OH)]⁻ by Kadish in electrochemical studies⁸² and served as supporting data for the scheme.

The model (2) is in clear contrast to (1) in that the role of copper ion is not only as a redox center but also as a participant in dioxygen binding.

A number of synthetic binuclear species⁸³ support model (2). The best characterized system was reported by Chang et al.⁸³a It involves the binucleating ligand shown below.

![L23](image-url)
The ligand was carefully designed so that the "strap" would allow sufficient flexibility to the copper coordination geometry so as to accommodate the Fe-O-Cu unit in the pocket. The β-strapping was also superior to meso-linkages in that iron is more likely to maintain its high-spin state. The isolated complex, Fe(III)OCu(II)(H₂O)(CH₃COO)(L23) showed an IR peak consistent with the μ-oxo formulation and the magnetic susceptibility of this complex was fitted to an \( S_T = 2 \) state for an antiferromagnetically coupled Fe(III)/Cu(II) pair with \( -J = 44 \text{ cm}^{-1} \) (the energy splitting between \( S_T = 2 \) and \( S_T = 3 \) states is \( 3J = 132 \text{ cm}^{-1} \)). This is the first case of a synthetic model for cytochrome oxidase for which the magnetic behavior can be interpreted qualitatively in a manner consistent with that of the natural system.

The ligand L23 represents a new type of binucleating ligand which is particularly well suited for cytochrome oxidase model studies. Several species with similar design principles have been reported. They are commonly porphyrin-type ligands with appended coordination sites. These ligands are more or less a hybrid of all three subclasses (ii)-(a), (b), and (c), described above, in terms of the ligand architecture. That is, the iron and copper coordination sites ought to have some characteristics of subclass (ii)-(a) and (ii)-(c), respectively, and they have to be combined in an orthogonal manner in order to achieve a strong coupling between the metals. In addition, the two coordination sites have to be very selective for each ion to ensure the formation of heterobimetallic species. In this regard, pyridyl or amino groups in the appendage are not preferable since these are
likely to coordinate intermolecularly to the iron center in the porphyrin unit.

Recent studies of the prosthetic groups in cytochrome c oxidase by means of iron and copper EXAFS led Powers and Chance to put forth specific proposals for the ligands of copper and heme groups and their arrangement in space. The model (3) is a part of these proposals and somewhat resembles model (2). The major finding in the EXAFS experiments was the occurrence of a bridging sulfur donor in coordination sphere of both heme $a_3$ - Fe(III) and CuB(II). Upon reduction, the Fe-S bond is cleaved and the iron(II) of the heme $a_3$ binds dioxygen in a manner similar to hemoglobin. The mechanistic aspects of the reactions following this event, according to these authors, are more or less like those associated with model (2). Thus the role of such sulfur bridges seems to be the delivery of electrons to the two metal sites. It implies that there is good overlap of iron, sulfur, and copper orbitals, which would be manifested in the form of strong magnetic coupling. However, there is no precedent for such a strong antiferromagnetism mediated by a sulfur-containing ligand. Therefore, synthesis of appropriate model systems to test this proposal has been awaited.

With regard to this difficulty in fitting the EXAFS results to the conventional view of antiferromagnetism, Elliott and Akabori presented an alternative explanation for the EPR silence and magnetic behavior of the heme $a_3$/CuB pair. These workers pointed out that a combination of dipolar coupling and only a small exchange coupling between copper(II) and a rapidly relaxing iron(III) with intermediate-spin state $S = 3/2$
can explain the EPR silence or extensive broadening. Their model compound$^{87a}$ (related to model (3)) gives spectral and structural evidences$^{87b}$ for $S = 3/2$ state for the iron(III) and little coupling to Cu(II) and yet the EPR spectrum is very broad with little temperature dependence.

Thus the understanding of the structure of the active site in cytochrome c oxidase still remains one of unfulfilled goals of bioinorganic model studies. In reviewing this area, the functional aspects of the model systems have yet to be explored.$^{88}$ The emphasis on the significance of an apparent magnetic interaction in the heme $a_3/Cu_B$ unit has drawn a lot of attention to the possibility of its relationship to enzymatic function. However, the enzyme may well be equipped with other devices that facilitates efficient electron transfer. Therefore studies of the reactivity of binuclear complexes which are capable of interacting with dioxygen, regardless of magnetic coupling, would be of considerable value.

1.2 Mechanistic Aspects of Reduction of Dioxygen.

1.2.1 Enzymatic Reaction. The overall picture of the catalytic reduction of dioxygen to water by enzymes is far from clear, but a considerable amount of kinetic work has accumulated on cytochrome c oxidase. The literature is extremely confusing due to ambiguities in the chemical identification of the intermediate species involved in the reaction of the enzyme with dioxygen. The complete catalytic cycle includes substrate (cytochrome c) binding, dioxygen binding, electron transfer, and proton translocation, but kinetic investigations have
focused on the dioxygen binding step. The method combines rapid mixing and flash photolysis and uses carbon monoxide binding in order to protect the reduced enzyme from dioxygen. The CO is photolyzed off to initiate the reaction of the enzyme with dioxygen. The subsequent events are monitored by absorption and/or EPR spectral changes.

Gibson and Greenwood have resolved the spectroscopic events in the reaction of the fully reduced enzyme with dioxygen at room temperature in terms of oxidation of cytochrome a (3 x 10^4 sec^-1), copper oxidation (7 x 10^3 sec^-1), and cytochrome a oxidation (7 x 10^2 sec^-1). No direct evidence has been found for an O2-bound species.

Low temperature experiments, however, have revealed the presence of O2-bound intermediates. Most notable was the resolution of a dioxygen complex of the ferrous heme a3, termed Compound A by Chance, as the primary intermediate trapped at -114°C. This species was formulated as CuB(I)-a3Fe(II)-O2, in which the oxidation states of the metal ions are assumed to be as written. As the temperature was raised, new species called Compounds B were observed. Chance and coworkers formulated these species as products of internal electron transfer from the metals to the bound dioxygen, judging from absorption spectra consistent with partial oxidation of the iron and copper component. The diagram shown below summarizes their findings and proposals. The other two components of the enzyme (cytochrome a and CuA) are included in the scheme. The U-peroxo formulation for the Compound B2 is more or less speculative. The formation of these species was observed at temperatures below -60°C and the authors assume that further transfer of electrons and protons to the bound dioxygen species would take place at higher temperatures.
A partially reduced enzyme can also be prepared. This mixed-valence enzyme was shown to contain cytochrome $a$ and $\text{Cu}_A$ in their oxidized states and reduced cytochrome $a_3$, with CO bound, and $\text{Cu}_B$ in the cuprous state. Yoshikawa and Caughey$^{91}$ pointed out that under turnover conditions no detectable amount of the fully reduced or the fully oxidized form of the enzyme is present and that the mixed valence state is very sensitive to respiratory inhibitors. Thus there is no apparent need for the full reduction of the oxidase prior to reaction with oxygen. Some of the electrons needed to reduce dioxygen may be received after an $O_2$ adduct is formed. Results of low temperature studies similar to those mentioned above but with the mixed valence enzyme are summarized below.
Newly detected species were termed Compounds C and formulated as superoxo- (C₁ and C₂) and μ-peroxo- (C₃) complex of ferriheme similar to the Compounds B.

Hill and Greenwood⁹² have identified species equivalent to the Compounds A and C at room temperature recently and presented kinetic data for the reaction sequence.

\[
\begin{align*}
\text{Cu}^{2+}_{A} + \text{Cu}^{2+}_{B} & \rightarrow \text{Cu}^{2+}_{A} + \text{Cu}^{2+}_{B} + \text{O}_2 \\
\text{Fe}^{3+}_{a} + \text{Fe}^{2+}_{a} & \rightarrow \text{Fe}^{3+}_{a} + \text{Fe}^{2+}_{a} + \text{CO} \\
\text{Fe}^{3+}_{a} + \text{Fe}^{2+}_{a} & \rightarrow \text{Fe}^{3+}_{a} + \text{Fe}^{2+}_{a} \cdot \text{O}_2 \\
\text{Fe}^{3+}_{a} + \text{Fe}^{2+}_{a} & \rightarrow \text{Fe}^{3+}_{a} + \text{Fe}^{2+}_{a} \cdot \text{Fe}^{3+} \cdot \text{(607 nm Compound)}
\end{align*}
\]

The authors proposed the release of peroxide only to explain their spectrophotometric kinetics but the relatively slow rate of this step implies that this event may not occur in the actual catalysis. It is noted that the bridging mode of coordination of the dioxygen between cytochrome a₃-Fe and Cu₆, which has been regarded advantageous in the light of facile two-electron transfer, may not be a requirement and
close proximity of Cu$_B$ may be sufficient. Perhaps the U-peroxo bridge is important for the subsequent cleavage of the O-O bond before or after proton transfer.

It is emphasized that there is no direct evidence for exact structure of Fe/Cu/O$_2$ species in these intermediates and the assignment of the oxidation state for each component is quite ambiguous without knowledge of the nature of Fe-O$_2$ bond in the dioxygen adduct of this particular heme.$^{93}$

Valentine and McCandlish$^{94}$ have surveyed known examples of oxygen adducts of metal complexes and presented sixteen conceivable structures for functional intermediates in the reaction of cytochrome c oxidase with dioxygen. These include new possibilities (a) that the dioxygen ligand may be protonated and (b) that the O-O bond may be cleaved. Thus it is relevant to consider metal-oxo and hydroxo formulations.

It is conceivable that the heme component in cytochrome c oxidase binds dioxygen to form an adduct not unlike one in hemoglobin or myoglobin but the dioxygen bound in the oxidase is reduced very rapidly. In their report on reductive titration of the oxidase, Palmer et al.$^{95}$ indicated an interaction between two hemes involving shifts in redox potential for each of the two such that a change in oxidation state for one of the hemes lowers the redox potential of the other. Yoshikawa and Caughey$^{96}$ suggested, on the basis of their study on carbon monoxide binding by the enzyme, that dioxygen could bind to the oxidase in any of the four oxidation states of the whole enzyme. Perhaps the dioxygen ligand binds to heme a$_3$ as soon as its iron is reduced to
divalent state and triggers an electron flow from cytochrome c into the oxidase and then to itself.

1.2.2 Electro-catalytic Reduction of Dioxygen. As mentioned in the previous section, Collman, Anson, and Chang have approached the four-electron reduction of dioxygen by electrochemical means. In this in vitro system, dioxygen interacts with the dicobalt(II) porphyrin catalyst and receives electrons from the electrode. Collman et al.\textsuperscript{42} have postulated the catalytic cycle of the heterogenous reaction in acidic media shown below.
The observation that an appreciable current flow due to dioxygen reduction to water occurs after both cobalt atoms are reduced to their divalent states (at potential $E_2$) indicates that species B is the active catalyst. The dioxygen adduct C is believed to be the key species leading to D because only one catalyst with the precisely required metal-metal separation was found to be efficient in producing water. The species with three-atom linkages is thought to have too small a cavity for dioxygen to enter on the basis of EPR measurements. This and other catalysts with larger cavities would generate dioxygen adducts such as F and H, which would lead to formation of hydrogen peroxide.

The rapid formation of the ($\mu$-hydroperoxo)dicobalt(III) complex, E, is proposed in order to account for the pH dependence of the electrochemical behavior. The possibility of the formation of an isomer E' is included based on a precedent for such a complex which is more easily reducible.

There is little doubt about the importance of the $\mu$-peroxo species D. The above scheme was proposed as an electrode surface event and therefore the lower porphyrin ring is envisioned as being adsorbed on graphite. Thus an intermolecular $\mu$-peroxo species, conceivably derived from such species as F and H in solution, is not considered in this process. At any rate stereochemical requirements for the catalyst to ensure the inclusion of dioxygen, as in C or G, are quite demanding. If the requirements are met, however, there must be enough driving force for dioxygen to go into the cavity instead of binding to the upper cobalt on the surface as in F and H.
EPR studies on the reaction of dicobalt(II) porphyrin in a solution phase have confirmed the formation of a (\(\mu\)-peroxo)dicobalt(III), corresponding to D, in the presence of imidazolyl axial base.\(^{37}\) In this case the axial positions outside the molecule are occupied by the added base. However, a recent report by Collman, Britt, and co-workers\(^ {97}\) disclosed the formation of (\(\mu\)-superoxo)dicobalt(III) species in the oxygenation of both dicobalt(II) and dicobalt(II/III) species in solution.

It is not clear whether dioxygen oxidizes the starting dicobalt(II) complex directly or whether it first forms a (\(\mu\)-peroxo)dicobalt(III) species. If the latter should be the case, the implication to the electrode process may be that the catalytic efficiency may lie in the subsequent steps rather than in the stability of the \(\mu\)-peroxo inclusion complex.

Chang and co-workers\(^ {50,55b}\) pointed out that the symmetry of such (\(\mu\)-peroxo)dicobalt(III) complexes is related to the electrocatalytic performance of dicobalt(II) complexes. A comparative study of EPR
signals of (μ-superoxo)dicobalt(III) species led them to deduce that the best catalyst would form cis-Co-O_2-Co species whereas other diporphyrins with a "slipped" ring conformation would generate trans-Co-O_2-Co analogue.

They argue that the cis configuration would make the peroxo intermediate more accessible to nearby solvent molecules and facilitate the desirable multiple proton transfer and concomitant cleavage of the O-O bond necessary to complete the four-electron pathway.

The two cases mentioned above are not directly related but are commonly described as involving inner sphere electron transfer to dioxygen from a binuclear complex. The transfer of the third and fourth electrons and four protons to the peroxo intermediate have never been described in substantial detail.

1.3 Binuclear Complexes of Synthetic Nonporphyrin Ligands of Class (ii)-(a); Bis(cyclidene) Complexes.

The research undertaken by Busch and associates has involved the extensive investigation of totally synthetic heme protein models which are capable of reversibly binding dioxygen. The iron(II) and cobalt(II)
complexes of the lacunized macrobicyclic ligands, I, have been shown to vary in such capabilities depending upon the various substituent groups on the macrocyclic periphery, temperature, and solvent system. Remarkable progress has been made in fine tuning these factors in order to increase dioxygen affinity and stability of the resultant dioxygen adduct.\textsuperscript{98}

The basic strategy was to design the ligand so as to create a small cavity above the metal ion by bridging the macrocyclic unit by the $R^1$ group. The dioxygen molecule is incorporated in this cavity and protected by the $R^1$ group from exposure to other molecules. The coordinated dioxygen ligand is believed to be in a reduced state and susceptible to further reactions, which might decrease the stability of 1:1 metal oxygen adduct.

\[
M(\text{II}) + O_2 \longrightarrow M(\text{II} + \delta) - O_2^{-\delta-}
\]
One of these reactions is the formation of a μ-peroxo dimer. One role of the \( R^1 \) group is to prevent such dimerization from occurring. In retrospect, however, the concept of dioxygen activation may utilize this process, as shown in the previous section.

\[
\text{M(III)-}O_2^- + \text{M(II)} \rightarrow \text{M(III)-}O_2^{2-}\text{-M(III)}
\]

The procedure for the synthesis of the lacunar complex I also permits formation of a binuclear complex II.

The latter have provided a unique opportunity to study the effect of having another redox active metal ion in a predictable position within the molecule on the behavior of a metal dioxygen adduct. The overall face-to-face configuration of this macrotricyclic ligand makes it representative of a novel nonporphyrin binucleating ligand of class (ii)-(a). The established need for investigation of the nature of the
interaction between binuclear transition metal complexes and dioxygen has prompted research involving diiron(II) and dicobalt(II) complexes.

From studies on the diiron(II) complexes, Herron et al. have concluded that these complexes generally behave like unbridged monomeric complexes and that the two metal ions independently undergo one-electron oxidation through an outer sphere mechanism. The overall reaction led, however, to formation of hydrogen peroxide and was surprisingly reversible.

One of the goals of this thesis research involving the dicobalt(II) analogue of II was to define the mode of intermetallic communication and its relationship to the behavior of the binuclear species towards dioxygen. The interaction between the two metal sites is expected to be greatly affected by the nature of the persistent void between the two coordination spheres and this is associated with the flexibility of the ligand framework.

The vaulted complex III, synthesized first by Takeuchi, has opened a new research area in which the enlarged cavity above the metal has been used for specific inclusion of organic compounds.
Similarity in the size of the void in II and III suggests that the same possibility exists in II but the nature of the guest-host association should differ due to the presence of two metal ions in II. Inclusion within the cavity of both coordinating and noncoordinating guest molecules has been explored in this thesis research.

In the following chapter, results of these studies will be presented and discussed. Throughout the chapter the binuclear complex of the structure II is designated as 

\[ [M_2(R^3N)_2(R^1N)]_2([0\text{cyclidene}]_2)^{2n^+} \]

in which "cyclidene" denotes the macrocyclic unit, either 14-membered (0 = 14) or 16-membered (0 = 16). In general, the abbreviation specifies the metal, groups that link two cyclidene units, the type of cyclidene, and the charge (or counterion).

\[ Y = (CH_2)_{2,3} \]

Cyclidene
Chapter 2
RESULTS AND DISCUSSION

The work described in this chapter includes synthesis, purification, and characterization of binuclear transition metal complexes derived from nonporphyrin face-to-face compartmental ligands of the cyclidene type, \([M_2\{(Me_2(NR^2)R^1)_2[Q]cyclidene_2}\}]^{n+}\). In the first section, synthetic procedures for the homobinuclear cyclidene complexes are discussed starting with parent dinickel(II) complexes followed by dicobalt(II) and dicopper(II) derivatives. Preparation of heterobinuclear (bis)cyclidene complexes with copper-nickel and chromium-nickel pairs is also described. Section 2.2 is devoted to characterization of these transition metal bis(cyclidene) complexes. In the first three subsections solid state data concerning the molecular formulation and structure are discussed. The following subsection utilizes NMR data for a series of dinickel(II) bis(cyclidene) complexes to demonstrate the flexibility of the macrotricyclic molecules. Properties that are more characteristic of the central transition metal atom (redox and magnetic properties) are discussed in the last two subsections using electrochemical and EPR data.

One of the goals of this thesis research is to study the dioxygen reactivity of binuclear bis(cyclidene) complexes and relate it to the properties inherent in the binuclear nature. This was done with
dicobalt(II) derivatives with different linking groups $R^1$; the results are discussed in section 2.3.

A study of guest-host complexation involving the transition metal bis(cyclidene) species comprises the last section; the first part is devoted to a dicobalt(II) system incorporating a bridging coordinating ligand while the second discusses interaction of noncoordinating organic guest compounds.

2.1 Syntheses of Homo- and Heterobinuclear Compartmental Bis(cyclidene) Complexes.

2.1.1 Dinickel(II) Complexes.

All the complexes used in this work were prepared by template synthesis using nickel(II) ion. There are two routes to the binuclear species, as shown in Schemes 1 and 2. Scheme 1 yields both the mononuclear lacunar complex (I) and the binuclear bis(cyclidene) complex (II) simultaneously. The dinickel(II) complexes having $R^1 =$ dimethylene, trimethylene, heptamethylene, and m-xylyl groups ($R^2 = H$ and $R^3 = \text{CH}_3$) were prepared by this route, and separated from the mononuclear co-product by means of CM-Sephadex chromatography. Use of bulky substituent $R^3$ and N,N'-dimethyldiamines ($R^2 =$ methyl), however, increases relative yield of lacunar complex. This is especially true when the $R^1$ group is hexamethylene, which appears to have the optimum length to span the macrocyclic [16]cyclidene unit. Kojima$^{101}$ has shown that the product is almost exclusively monomeric in this case.

The reaction in Scheme 2, on the other hand, favors the formation of binuclear complexes and permits their synthesis with a wider variety
Scheme 1

Scheme 2
of R^1 groups. In the first step the substitution of each methoxy group in the starting material by diamine is forced by the presence of 4-10 fold excess of the diamine. The product is isolated and then used as a nucleophile in the second step. The unbridged aminoalkylethylidene derivatives (III), [Ni(Me_2(NHR^1NH_2)_2[Q]cycloidene)]^{2+}, can exist in different configurations with respect to the orientation of R^1NH_2 group on the nitrogen in solution as evidenced by multiple carbon-13 NMR signals, leading to formation of undesired coupling products including oligomers in considerable amounts. Another factor to be considered is that the too large excess of the diamine causes difficulties in isolating the bis(amoalkylethyldiene) derivative, while the presence of excess diamine is necessary to form the unbridged complex III. Using typically 10-fold excess of ethylenediamine, the R^1 = dimethylene derivative of III was isolated in good yield. For 1,4-diaminobutane, 1,5-diaminopentane, and m-xylylenediamine, however, solid product was also isolated in fairly good yields but chemical analyses showed that N/Ni ratio was commonly lower than 8, that which is expected for the structure III. The chemical analyses were fitted to a mixture of III and other products such as I and II (both have N/Ni ratio = 6) which amounted to 40-50%, for R^1 = tetramethylene and pentamethylene. Purification was effected by chromatography on alumina; side products I and II were easily and exclusively eluted with acetonitrile. The remaining was then eluted with 3% ethanol in acetonitrile. In the case of R^1 = m-xylylene, this procedure was useful in removing some of the excess diamine as well. The products of the second reaction in Scheme 2 were worked up commonly by both alumina and CM-Sephadex ion exchange
chromatographies. Overall yields for dinickel(II) complexes having $R^1 = \text{dimethylene, pentamethylene,}$ and $m$-xylylene links prepared following Scheme 2 were comparable to those in Scheme 1.

Two new members of compartmental bis(cyclidene) complexes were synthesized by the route in Scheme 2. When piperazine was used in place of the primary diamine, the binuclear product $[\text{Ni}_2((\text{Me}_2\text{pip})_2([16]\text{cyclidene})_2)](\text{PF}_6)_4$ was isolated as a powdery yellow solid scarcely soluble in acetonitrile. A 14-membered derivative of dimethylene-linked bis(cyclidene), $[\text{Ni}_2((\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2)_2([14]\text{cyclidene})_2)]^{14+}$, was obtained by starting with the [14]cyclidene precursor. The yields for these two compounds were very low (5%). Notable darkening of Sephadex column was observed after lengthy use for these complexes; this may have been due to decomposition of the unreacted nucleophile III.

A new N-methylated derivative was also prepared. The dimethylene-linked bis(cyclidene) complex having $R^2 = \text{CH}_3$ was prepared by deprotonation of $R^2 = \text{H}$ analogue followed by N-methylation (Scheme 3).

An example of rather unique retro-bridged bis(cyclidene) complex of dinickel(II) was also prepared following Scheme 4. The deprotonated precursor of nickel(II) cyclidene species were reacylated with acid chloride, thereby bridging the two macrocyclic units. The neutral complex thus obtained was methylated at the carbonyl groups and then converted to the N-dimethyl derivative of the bis(cyclidene) complex, $[\text{Ni}_2((\text{NMe}_2)_2\text{CH}_2)_4([16]\text{cyclidene})_2)](\text{PF}_6)_4$, by usual means. The yield was, however, discouragingly low; one of the more favored by-products of the above reaction was identified as the singly bridged species depicted below.
2.1.2 Dicobalt(II) and Dicooper(II) Complexes.

Preparation of binuclear complexes with metals other than nickel(II) has been carried out by demetallation of the dinickel(II) precursor, described above, followed by insertion of the desired metal ion (Scheme 5). The ligand remains intact through these reactions as confirmed directly by X-ray structural determination on one dicobalt(II) complex (vide infra) and also by other inferential data. The protonated ligands, IV, having $R^1$ = dimethylene (both $R^2$ = H and CH$_3$), trimethylene groups were isolated as hexafluorophosphate salts, by metathesizing either the tetrachlorozincate or the chloro-hexafluorophosphate using NH$_4$PF$_6$ in water. However, while the tetrachlorozincate of the ligand with $R^1$ = m-xylylene was easily isolable, its aqueous solution yielded only an oily material upon addition of NH$_4$PF$_6$ even at 0°C. This oil, solidified by stirring in isopropanol, proved to be satisfactory for synthesis of dicopper(II) derivative. However, cobalt insertion required a more pure ligand salt, and, therefore, for this ligand HBr was used instead of HCl, whereby the ligand bromide salt was isolated in good yield. Use of HBr for the dimethylene- and trimethylene-linked bis(cyclidene) ligand led to isolation of bromo-hexafluorophosphate.
salts. Some of the dicobalt(II) complexes were found by analysis to contain the halide, which was carried along with the ligand. These observations are in accord with likely association of the halide ions to N-H (R²) residues.

![Scheme 5](image)

The piperazine-linked his(cyclidene) ligand was also prepared and insertion of cobalt(II) was attempted. Under the reaction conditions shown in Scheme 5, however, no apparent reaction took place and even after an overnight reflux only a trace amount of yellow-orange species formed; the small amount was not isolaible. A stronger base is probably required to free the ligand for metal insertion.
2.1.3 Heterobinuclear Complexes.

The reaction in Scheme 5 allows one to prepare heterobimetallic complexes of the face-to-face bis(cyclidene) ligands by using a mixture of two metal ions, M and M'. Since the two metal complexation sites are equivalent in these ligands, however, selective metallation is difficult. The product mixture of MM, MM', and M'M' was, instead, subject to CM-Sephadex chromatography.

Two reactions were carried out for M = Ni and M' = Cu. When the reaction mixture of the ligand having R¹ = dimethylene and R² = H and both nickel and copper acetate was chromatographed, slow elution with aqueous 0.2 M NaSO₄, which is normally used to elute divalent cations, resulted in separation of a broad yellow band. Gradual increase in concentration of sodium sulfate through 0.3 M to 0.4 M effected separation of the other two red bands. EPR results indicated that the second band contained a CuNi species (axial EPR signal for the Cu(II) moiety), whereas the slowest-moving band was the Cu₂ fraction (EPR indicative of magnetic interaction between the two copper(II) centers). The first band was mostly the Ni₂ component but was considerably contaminated by the following copper-containing fraction.

When the ligand had R¹ = m-xylylene groups, however, the reaction product, though similar in appearance, did not chromatograph as nicely as the R¹ = dimethylene derivative. The multiple bands were quite broad and not well separated from each other. Nevertheless the 0.3 M fraction was collected and used for an NMR study discussed in Section 2.4.2. The chemical analysis was fitted to 36% CuNi and 64% Ni₂. The reason for the poor separation is not clear. Attempts to remove bromide that may
be coordinated to the copper atom and/or to use a different eluent may be helpful.

Attempted syntheses for the combination of $M = \text{Ni}$ and $M' = \text{Cr(III)}$ were generally unsuccessful. First of all, a mixture of nickel(II) and chromium(II) ions using common salts such as nickel acetate and $\text{Cr(II)Cl}_2(L = \text{pyridine or acetonitrile})$ could not be obtained due to the redox reaction forming nickel(0) and chromium(III) ion. When the two solutions were added to a ligand solution separately ($R^1 = \text{dimethylene}$ and $R^2 = \text{H}$), the reaction in Scheme 5 did seem to occur but $0.4\text{M NaSO}_4/H_2\text{O}$ effected elution of only the $\text{Ni}_2$ component. The remaining reddish material came off as one band with $1.0\text{M NaCl}$ solution.

In another attempt to prepare and isolate a half-metallated material, half a mole of $\text{Cr(py)}_6\text{Br}_2$ was added to the ligand ($R^1 = \text{trimethylene}$). The isolated species proved to be a dichromium(III) complex. This example illustrates the difficulty in controlled stepwise metallation.

It is noted that the reactions of Scheme 2 is conceivably a superior way to synthesize heterobinuclear species since two metals can be incorporated into separate cyclidene ligands prior to the coupling reaction. At present, however, the methylated starting material is available only as the nickel(II) complex and the unbridged bis(diamine)-macro cyclic complexes of other metal ions of interest, such as iron(II), cobalt(II), have not been obtained due to the tendency of these metal ions to be either 5- or 6-coordinate, which leads to intra- or intermolecular coordination of the terminal amino groups. A similar
phenomenon has been encountered in a study by Gunter et al. using a porphyrin ligand having appended pyridyl groups.

It is also noted that the functionalization of the macrocyclic periphery represented by the first reaction in Scheme 2 is quite versatile and has opened a pathway to a different type of binuclear complex, suited particularly to a range of heterobinuclear species. This possibility has been pursued with the group.

\[
\text{A synthesis attempted in this work using } [\text{Ni} \{\text{Me}_2(\text{NHCH}_2\text{CH}_2\text{NH}_2)_2[16]\text{-cyclidene}]\}}^{2+} \text{ and cupric chloride hydrate yielded a species in which a small amount of copper was incorporated. The reaction was, however, no simpler than other syntheses of mixed-metal binuclear complexes.}
\]

2.2 Characterization of Homobinuclear Compartmental Bis(cyclidene) Complexes of Dinickel(II), Dicobalt(II) and Diicopper(II).

The binuclear complexes prepared in this work were routinely characterized by elemental analysis and other spectroscopic means. Characterization of some of the dinickel(II) and diiron(II) complexes have been published by Busch et al. and therefore only new findings will be described in this section. It must be emphasized that
the chromatographic separation of the parent dinickel(II) complexes had not been used extensively prior to this work.

2.2.1 Mass Spectral Confirmation of the Binuclear Formulation.

Apart from the X-ray crystal structure determination of \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{mxy}l\}_2\{[16]\text{cycloidene}\}_2\}(PF_6)_4\) by Zimmer, attempts by previous workers to establish the binuclear structure have been limited to such physical measurements as molecular weight and conductance.\(^{103}\) The conductance measurements were, however, not conclusive due to the suspected ion pairing association and molecular weights were determined by vapor osmometry on neutral derivatives formed from the tetrapositive complexes by deprotonating the ligand.

In the present work Laser desorption/ionization (Laser DI) and fast atom bombardment (FAB) mass spectrosocopies proved to be useful. Despite the highly involatile nature of the tetravalent species, both \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2\}_2\{[16]\text{cycloidene}\}_2\}]^{4+}\) and \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{mxy}l\}_2\{-([16]\text{cycloidene}\}_2\}]^{4+}\) gave reasonable mass spectra as shown in Figures 1 and 2, respectively. These complexes appear to lose protons from the ligands, and then attach a potassium ion from the matrix material (potassium bromide) under laser desorption/ionization conditions. Thus the positive pseudomolecular ions of \(m/z=865\) for dimethylene(R\(^1\))-bridged species and \(m/z=1018\) for \(m\)-xyylene-bridged species are consistent with the formulation \([\text{Complex} - n\text{H}^+ + \text{K}]^+\) (\(n = 2\) and 1, respectively).

The FAB technique is somewhat milder than this and the ionization of the \(m\)-xyylene bridged species was not effected. The three positive molecular ions derived from \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2\}_2\{[16]\text{cycloidene}\}_2\}]^{4+}\) were formulated as \([\text{Complex} - \text{H}]^+ = 827\), \([\text{Complex} - 4\text{H} + \text{H}_2\text{O}]^+ = 842\)
Figure 1. Laser DI Mass Spectrum of

\[ \text{[Ni}_2\{(\text{Me}_2\text{NH})_2\text{moxyl}\}_2\{\text{[16]cyclohexene}\}_2\}]\text{(PF}_6\text{)}_4. \]
Figure 2. Laser Di Mass Spectrum of

\[ \text{Ni}_{2} \left( \text{Cffe}_2\text{NH}_2\text{C}_6\text{H}_4\text{NMe}_2\right)_{16} \text{Co}
\]
Figure 3. FAB Mass Spectrum of
[\text{H}_2\text{O}_2\text{HN}_2\text{CH}_2\text{CH}_2\text{C}(\text{NH})\text{C}_6\text{H}_4\text{Me}]^{+}\text{Cl}^{-}.
and \([\text{Complex} - 2\text{H} + \text{Cl}]^+ = 861\) (Figure 3). The water molecule and the chloride ion (counter ion) in the heavier species may be involved in hydrogen bonding to the \(N-H(R^2)\) site permitting it to vaporize together with the complex.

Although the fragmentation patterns were not studied in detail, the two examples shown above clearly indicated that the binuclear species were indeed separated cleanly from the mononuclear products.

2.2.2 X-ray Crystal Structure Determination on \([\text{Co}_2(\text{Me}_2(\text{NH})_2\text{mxyol})_2(\text{[16]cyclidene})_2]\)Cl\(_4\cdot2\text{CH}_3\text{OH}\).

After the binuclear formulation has been established, the next concern is naturally the stereochemistry of the molecule. In addition, the class of face-to-face binuclear cyclidene complexes has a characteristic molecular cavity between the two metal sites that is of potential use in metal ion promoted reactions. Therefore it is important to define the dimensions of such cavities between metal ions in order to assess the possibilities for a given complex. Since only one single crystal structure has been previously solved for a dinuclear cyclidene complex \([[\text{Ni}_2((\text{Me}_2(\text{NH})_2\text{mxyol})_2(\text{[16]cyclidene})_2)](\text{PF}_6)_4]\) and since that structure was only poorly refined due to a disorder problem, two more attempts were made in this work.

The first attempt was with the dinickel(II) complex having dimethylene links, \([[\text{Ni}_2((\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2(\text{[16]cyclidene})_2)](\text{PF}_6)_4\cdot\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}\) and a similar problem was encountered; attempts at the refinement have not led to convergence. Nonetheless, the approximate Ni-Ni distance has been
estimated to be 10Å. This is considerably shorter than the corresponding value of 13.6Å obtained for the \( m \)-xylylene linked complex. This suggests that the range of metal-metal distances for a group of \([M_2((Me_2(NH)_2R')_2(16)cyclidene)_2]^{n+}\) complexes would be some 9Å or longer and this precludes the possibility of detectable metal-metal electronic coupling in the solid state. Another structural relationship suggested by this preliminary solution is concerned with what may be described as an offset/eclipsed configurational isomerism. Because the linking groups rise from atoms that are off center with regard to the parent macrocycles, the links may orient the two macrocycles either in an offset array or more nearly over each other (Structures VI and VII).

Note that these two structures assume "lid-on" configurational isomers (vide infra), in which the linking groups \( R^1 \) are projecting perpendicular to the \( N_4 \) macrocyclic planes. While the \( m \)-xylylene linked macrocycles were found to be in the offset arrangement, the partial structure determination suggests that the dimethylene links might lead
to the eclipsed isomer. Due to other forces, however, the two cyclidene units appeared to be displaced from the ideal structure as drawn above in a somewhat folded conformation.

In contrast to the problems associated with the X-ray structures of the two dinickel(II) complexes, the crystal structure of 
\[ \text{[Co}_2((\text{Me}_2\text{NH})_2\text{oxyl})_2(\text{[16]cyclidene})_2)\text{]}\text{Cl}_4 \cdot 2\text{CH}_3\text{OH} \] was solved without much difficulty. Data collection and structure solution and refinement were performed by Dr. J. Gallucci and Dr. A. Jircitano in the following manner (Table 3 summarizes all the information concerning the procedure).

Red plate-like crystals were grown by slow evaporation from methanol. A suitable crystal was mounted inside a glass capillary tube of a 0.5 mm diameter under nitrogen and glued with epoxy resin. Crystal data information is included in Table 3. Preliminary measurements indicated monoclinic symmetry with systematic absences, h0l, l = 2n; 0k0, k = 2n, unequivocally indicative of space group \( P2_1/c \). Unit cell parameters were determined by accurate centering of 15 reflections well-distributed in reciprocal space. Data were collected using the 0-2\( \theta \) technique, with a variable scan rate ranging from 2° to 12°/min., depending upon the intensity of a 2 second pre-scan. The scan range was 1.0° below the \( K_{\alpha 1} \) peak to 1.0° above \( K_{\alpha 2} \), with background counts taken with background-to-scan ratio of 0.5 at the beginning and end of each 20 scan. Intensities and standard deviations were calculated according to the formula \( I = r(S-\text{RB}) \) and \( I^2 = r^2(S + r^2\text{B}) \), respectively, where \( r \) is the scan rate in degrees/min., \( S \) is the total scan count, \( R \) is the scan-to-background time ratio, and \( \text{B} \) is the total background count. Six
standard reflections monitored every 100 reflections showed only random fluctuation over a 0.01% range. The data were corrected for background, and Lorentz and polarization factors were applied to obtain structure factors. Programs used were the XRAY70 and CRYM packages. Wilson's method was used to bring $F^2$ to a relatively absolute scale. The $I^2$ were scaled by increasing the $I^2$ obtained from counting statistics by $PI^2$, where $P$ was chosen as the rms deviation of the standard reflections. Scattering factors were obtained from references indicated in Table 3.

The position of the heavy atom was ascertained from a Patterson map, and the positions of the remaining non-hydrogen atoms were revealed by subsequent Fourier maps. Refinement was performed using full matrix least squares techniques during which the function $\sum(w(|F_o| - |F_c|))^2$ was minimized. The data were weighed according to $1/(\sigma_F)^2$. Residuals were calculated as $R = \sum ||F_o| - |F_c||/\Sigma |F_o|$, and $R_w = (\sum w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2)^{1/2}$. Isotropic refinement resulted in convergence at $R = 0.073$. At this point the thermal parameters of the cobalt and chlorine were allowed to vary anisotropically because of the limited data. Subsequent full matrix least-squares refinement resulted in convergence at $R = 0.070$ and $R_w = 0.080$. In the final cycle of refinement, no atom shifted by more than 0.08 of its esd. A final difference map was featureless. Final positional parameters are given in Table 21 in the Appendix A.

Figure 4 shows the ORTEP diagram of the complex for both front and side views. The macrocyclic moieties around the cobalt atoms are constrained by the centrosymmetry as are the two $m$-xyylene groups. The numbering scheme is given in Structure VIII.
Table 3. Summary of the Crystallographic Data for
[Co₂{(Me₂(NH)₂mxyl)₂(16cycloiden)e}_2]Cl₄·2CH₃OH.

**Formula** \( \text{Co}_2\text{C}_{52}\text{H}_{44}\text{N}_{12}\text{Cl}_4·2\text{CH}_3\text{OH} \)

**FW** 1180.95

**Cell Parameters**

\[
\begin{align*}
a/Å & = 11.121(1) \\
b/Å & = 13.738(3) \\
c/Å & = 20.185(2) \\
α/deg & = 90 \\
β/deg & = 99.15(1) \\
γ/deg & = 90 \\
V/Å³ & = 3044.6
\end{align*}
\]

**Z** 2

**Space Group** \( P2_1/c \)

**Systematic Absences** \( h0l, l = 2n; 0k0, k=2n \)

**Fooo** 1202.0

**Dcalc, g cm\(^{-3}\)** 1.287

**Dobs, method** 1.30(1), flotation CCl₄/Heptane

**Crystal size and shape, mm** 0.10x0.20x0.27; red plates \( \{110\}, \{002\} \)

**Absorption coefficient, cm\(^{-1}\)** 7.89

**Lattice parameters 20 for fit** 15

**General positions** \( \hat{C}; x,y,z; \hat{X}, 1/2 + y, 1/2 - z \)

**Radiation and λ** MoK\(_{α}\)

**Temperature** 70°F

**Diffractometer** syntex P2₁

**Scan Type** 0 - 20

**Scan Speed** 2-12°/min

**Scan Range** 1.0° K\(_{α1}\), 1.0° K\(_{α2}\)

**Background-scan time** 0.5
Table 3. Continued

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<tr>
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<td>Absorption correction, min.</td>
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<tr>
<td>max.</td>
<td>none</td>
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<tr>
<td>Method</td>
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<tr>
<td>Refinement based on</td>
<td>$F$</td>
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<tr>
<td>Number of parameters</td>
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<tr>
<td>Anisotropic convergence, $R$</td>
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<td>(Co, Cl only)</td>
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<td>$R_w$</td>
<td>0.080</td>
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<td>Goodness of fit (GOF)</td>
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<td>Maximum shift error, average</td>
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<td>Final difference map, featureless</td>
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<td>Scattering factors, $f'$, $f''$ References</td>
<td>104(H) and 105 (all others)</td>
</tr>
<tr>
<td>Computer programs</td>
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Figure 4. ORTEP Diagrams of 

$\text{Co}_2[(\text{Me}_2\text{NH})_2\text{mxyl}]_2([16]\text{cyclidene})_2]\text{Cl}_4\cdot2\text{CH}_3\text{OH}$. 
As shown in the ORTEP diagrams, the complex retains the basic structural characteristics of (a) the dinickel(II) analogue in the overall ligand configuration (lid-on and offset) and (b) the lacunar family of cyclidene compounds in terms of the nature of the macrocyclic periphery. Notably different is the fact that two cobalt ions are weakly coordinated by chloride anions (Co-Cl = 2.55 Å). Accordingly, the two saturated 6-membered chelate rings (Co, N1, C12, C11, C10, N4 and Co, N2, C4, C5, C6, N3) are both in chair conformations. This is in
contrast to the dinickel(II) analogue in which the ring near the m-xylylene groups is in a boat form. Such a flipping of the chelate ring was observed in the crystal structures of iron(II)-chloro (lacunar) complexes\textsuperscript{106} and a cobalt(III) bis(thiocyanato) lacunar complex\textsuperscript{107} as well.

The large horizontal displacement of the two macrocyclic units (shear displacement 6.24Å) causes the two cobalt atoms to be 12.38Å apart while the vertical interplanar separation is only 10.70Å. The shape of the cavity is therefore better described in terms of a parallelogram as a cross section rather than a tall rectangle. The distortion of the shape of the cavity is less severe in the dinickel(II) cation (Ni-Ni=13.6Å, plane-plane = 12.8Å and shear displacement = 4.6Å).

The most remarkable feature in the ORTEP is the extensive hydrogen bonding chain that spans between pairs of bridge nitrogens, N5 and N6. The uncoordinated chloride anion and the methanol of crystallization are both involved. They more or less block one side of the cavity and arch out from the cavity. Figure 5 describes the dimension of this hydrogen bonding arch. The N5-O, O-C12, and C12-N6 lengths (2.88Å, 3.01Å, and 2.97Å, respectively) are all consistent with literature values of 2.57 - 3.22Å for nitrogen-H-oxygen, 2.86 - 3.21Å for oxygen-H-halide, and 2.91 - 3.52Å for halide-H-nitrogen bondings.\textsuperscript{108} As a result of these hydrogen bonding bridges the N5-N6 distance is significantly elongated (6.66Å) compared to that in the dinickel(II) species (5.74Å), in which such a hydrogen bonding did not occur. The distortion in the cavity shape in the dicobalt(II) complex is associated with two major
Figure 5. Dimension of the Hydrogen Bonding Arch in
\[ \text{[Co}_2\{\text{Me}_2\text{(NH)}_2\text{methyl}\}_2\{[16]\text{cyclidene}\}_2\}\text{Cl}_4\cdot2\text{CH}_3\text{OH}. \]
structural changes, apart from different crystal packing: weak coordination of the chloride to the cobalt resulting in the chair conformation of both chelate rings in the middle of the macrocycle, and occurrence of the two extensive hydrogen bonded arches midway along the cavity. The chloride ions are undoubtedly responsible for these features. It is important to note, on the other hand, that the ligand structure is flexible enough to respond to such changes in environment. Additional bond length and bond angle data are listed in Tables 4 and 5.

The implication one can gain from these crystallographic results is that the N-H(=R2) groups could make the molecular cavity much less hydrophobic than would otherwise be suspected. The design of a series of N-alkylated lacunar dioxygen carriers was developed to create a dry hydrophobic cavity to prevent the bound dioxygen substrate from interacting with solvent. Thus the dioxygen bound to these dicobalt(II) N-protonated complexes are expected to be more susceptible to solvolysis, if not reactive with this proton itself. From the viewpoint of dioxygen cleavage, however, such a functionality may be useful; it could provide the protons necessary to form water, if the dioxygen substrate can somehow be brought to the reduced state.
### Table 4. Bond Length and Other Distance Data for [Co₂((Me₂(NH)₂mxy1)₂([16]cycloidene)₂)]Cl₄·2CH₃OH.

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<tr>
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<tr>
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<tr>
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<td>1.485(21)</td>
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<tr>
<td>N2–C3</td>
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2.2.3 Infrared Spectral Study of the Ligand Structure.

2.2.3.1 Dinickel(II) Complexes. The Infrared (IR) spectra of the binuclear cyclidene complexes are generally very similar to those of corresponding mononuclear lacunar complexes and give little information on the detailed molecular structure. Nonetheless a use of IR spectral data is exemplified by the series of spectra shown in Figure 6 which follows the course of Scheme 2 (Section 2.1.1) for the synthesis of \[\text{[Ni}_2\left(\text{Me}_2\text{(NH)}_2\text{mxyI}\right)_2([16]\text{cyclidene})_2]\text{(PF}_6\text{)}_4\]. The spectrum (a) of the starting methoxy derivative \[\text{[Ni}\left(\text{Me}_2\text{(OMe)}_2[16]\text{cyclidene}\right]\text{(PF}_6\text{)}_2\] possesses peaks at 1630 cm\(^{-1}\) and 1580 cm\(^{-1}\) ascribed to conjugated imine (\(\nu(\text{C} = \text{N})\)) and alkene (\(\nu(\text{C} = \text{C})\)) stretching modes, as well as peaks due to the ether linkage (1283 cm\(^{-1}\) and 1028 cm\(^{-1}\)) and hexafluorophosphate anion (840 cm\(^{-1}\) and 560 cm\(^{-1}\)). The spectrum (b) of the unbridged complex \[\text{[Ni}\left(\text{Me}_2\text{NHmxyI NH}_2\right)_2[16]\text{cyclidene}\]\text{(PF}_6\text{)}_2\] indicates that the methoxy groups have been replaced in this material since the peaks due to the alkene-substituted ether are absent while bands due to the hexafluorophosphate anions are retained. In the N-H stretching region are seen two broad absorptions centered around 3280 cm\(^{-1}\) and 3390 cm\(^{-1}\) which are ascribed to the terminal and substituted amino groups, respectively. The former broad absorption disappears and the other peak sharpens up following the second reaction in Scheme 2, as shown in the spectrum (c) of the resulting binuclear complex, \[\text{[Ni}_2\left(\text{Me}_2\text{(NH)}_2\text{mxyI}\right)_2-([16]\text{cyclidene})_2]\text{(PF}_6\text{)}_4\]. It is noted that in both spectra (b) and (c) the absorption around 1600 cm\(^{-1}\) appears as one broad peak. Since the N-H deformation mode of secondary amines (1650 - 1550 cm\(^{-1}\)) is usually weak and the stretching mode of the benzene ring (1600 - 1580 cm\(^{-1}\))
Figure 6. An IR Spectral Description of the Reaction Scheme 2 for the Synthesis of $[\text{Ni}_2((\text{Me}_2(\text{NH})_2\text{mxy})_2(\text{[16]cyclo})_2)](\text{PF}_6)_4$.

(a) $[\text{Ni}(\text{Me}_2(\text{O}Me)_2(\text{[16]cyclo})_2)](\text{PF}_6)_2$,

(b) $[\text{Ni}(\text{Me}_2(\text{NH}mxy\text{NH}_2)_2(\text{[16]cyclo})_2)](\text{PF}_6)_2$, and

(c) $[\text{Ni}_2((\text{Me}_2(\text{NH})_2\text{mxy})_2(\text{[16]cyclo})_2)](\text{PF}_6)_4$. 
seems to contribute little in this region (the spectral pattern persists in analogous systems with \( R^1 = \) polymethylphen), the spectral change in this region from (a) to (b) and (c) is taken as an indication of changes in conjugation in the ligand framework \( \nu(C=N) \) and \( \nu(C=C) \).

The spectra (b) and (c) are very similar to each other, except that spectrum (b) is somewhat broader; the only notable difference is in the C-H bending mode around 700 cm\(^{-1}\), reflecting a slight difference in local symmetry of the benzene ring in the two species.

Table 6 summarizes selected IR frequencies for binuclear bridged complexes. In general the dinickel(II) compartmental complexes of interest exhibit two or three peaks in the skeletal region, which often appears as one broad absorption with the central peak being most intense. The hexafluorophosphate salts display two peaks arising from the anion and also a sharp N-H stretching absorption when \( R^2 = H \). A small absorption at ca. 3500 - 3600 cm\(^{-1}\) due to ethanol of crystallization is also commonly observed. The chloride salts, on the other hand, display a very broad absorption in the N-H and O-H stretching region, suggesting the involvement of the N-H(= R\(^2\)) moiety in hydrogen bonding to chloride and/or water (chloride salts are very hygroscopic). The 14-membered macrocyclic analogue \([\text{Ni}_2((\text{Me}_2\text{NH})_2-\text{CH}_2\text{CH}_2)_2([14]\text{cyclidene})_2)](\text{PF}_6)_4\) is exceptional in that the region beyond 3200 cm\(^{-1}\) is not as sharp as the 16-membered counterpart. Synthetic procedures for this material were found to be more moisture sensitive.

The N-H stretching absorption can be used to monitor an alkylation reaction on the bridge nitrogen (Scheme 3, Section 2.1.1). The absence
Table 6. Selected IR Frequencies\(^a\) for Dinickel(II) Compartmental Bis(cyclidene) Complexes, [Ni\(_2\)\{(Me\(_2\)(NR\(_2\))\(_2\)R\(^1\)\}_2([Q]cyclidene)\(_2\)]X\(_4\).

<table>
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<tr>
<th>Q</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>X</th>
<th>(v(O-H))</th>
<th>(v(N-H))</th>
<th>(v(C=N))</th>
<th>(v(C=C))</th>
<th>(v(P-P))</th>
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<td>H</td>
<td>PF(_6)</td>
<td>3645(^w)</td>
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<td>16</td>
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<td>H</td>
<td>PF(_6)</td>
<td>3570(^w), 3500(^w)</td>
<td>3380</td>
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<td>H</td>
<td>PF(_6)</td>
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<td>3455</td>
<td>1610(^{sh}), 1580</td>
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<td>1576, 1540(^{sh})</td>
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<tr>
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<td>3370(^{br}), 3200(^{sh})</td>
<td>1610(^{sh}), 1570</td>
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<tr>
<td>16</td>
<td>pip</td>
<td>-</td>
<td>PF(_6)</td>
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<td>---</td>
<td>1670(^w), 1608</td>
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<td>CH(_3)</td>
<td>PF(_6)</td>
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<td>-</td>
<td>-c</td>
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<tr>
<td>16</td>
<td>-</td>
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<td>-d</td>
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<td>---</td>
<td>1608</td>
<td>1561</td>
<td>840, 557</td>
</tr>
</tbody>
</table>

\(^a\) cm\(^{-1}\).

b. [Ni\(_2\)\{(adip)\(_2\)(Me\(_2\)[16]tetraenatoN\(_4\))\(_2\)].

c. [Ni\(_2\)\{((OMe)\(_2\)(CH\(_2\))\(_4\))\(_2\)([16]cyclidene)\(_2\)](PF\(_6\))\(_4\).

d. [Ni\(_2\)\{((NMe)\(_2\)(CH\(_2\))\(_4\))\(_2\)([16]cyclidene)\(_2\)](PF\(_6\))\(_4\).
of (N-H) stretching mode in the IR spectrum of \([\text{Ni}_2\{(\text{Me}_2\text{NMe})_2\text{CH}_2\text{CH}_2\}_2-([16]\text{cyclidene})_2\}]\text{(PF}_6\text{)}_4\) indicates that the deprotonation and methylation sites were indeed the bridging nitrogen atoms.

Another distinct IR spectral change that accompanies this reaction is observed in the \(\nu(C = N)\) and \(\nu(C = C)\) region. Figure 7 compares the IR spectra of (a)N-H and (b)N-CH\(_3\) derivatives of dimethylene linked complexes in this region. The broad absorption centered at 1580 cm\(^{-1}\) in spectrum (a) splits into two distinct widely separate peaks (1618 cm\(^{-1}\) and 1548 cm\(^{-1}\)) upon N-methylation (b). Referring again to the large family of mononuclear lacunar complexes, the corresponding spectral change may be taken as an indication of lid-on/lid-off isomerism, which is a configurational isomerism arising from the arrangement of \(R^1\) and \(R^2\) groups around the bridge nitrogen (Structures IX and X). The lid-on isomer has the linking group \(R^1\) projecting perpendicular to the \(N_4\) macrocyclic plane, whereas the \(R^1\) group is situated at the side of macrocyclic unit in the lid-off isomer.

![Diagram of lid-on and lid-off isomers]

On the basis of carbon-13 NMR spectra in solution, all of the binuclear species with \(R^2 = H\), \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2R^1\}_2([16]\text{cyclidene})_2\}]^{4+}\), have been assigned to the lid-on structure, whereas all of the lacunar
Figure 7. Comparison of IR Skeletal Stretching for 

$$[\text{Ni}_2\{\text{Me}_2(\text{NR}^2)\text{CH}_2\text{CH}_2\}_{\text{2}}(\text{[16]cyclohexene})_{\text{2}}]\text{(PF}_6\text{)}_{\text{4}}.$$ 

(a) $R^2 = \text{H}$ and (b) $R^2 = \text{CH}_3$. 
complexes prepared and characterized to date have been found to be lid-off isomers, regardless of the \( R^2 \) group, except for (NH)\(_2\)mxyl,\(^{106}\) (NH)\(_2\)cyhex (derived from 1,3-bis(aminomethyl)cyclohexane)\(^{109}\) and (NH)\(_2\)fl (derived from 9,9-bis(3-aminopropyl)fluorene) complexes, which have the lid-on structure.\(^{103}\) No example of an N-alkylated lid-on isomer is known.

In the present case the N-methylated binuclear complex, [Ni\(_2\)\((\text{Me}_2(\text{NMe})_2\text{CH}_2\text{CH}_2)_2([16]\text{cyclidene})_2\)]\(^{4+}\) cannot be unequivocally assigned to either isomeric form on the basis of the NMR data (vide infra). The isomeric structures of two other known example of N-methylated compartmental complexes of this family, [Ni\(_2\)\((\text{Me}_2(\text{NMe})_2\text{duryl})_2([16]\text{cyclidene})_2\)]\(^{4+}\) and [Ni\(_2\)\((\text{Me}_2(\text{NMe})_2\text{pxyl})_2([16]\text{cyclidene})_2\)]\(^{4+}\), prepared by Zimmer,\(^{106}\) are also ambiguous because the NMR criterion is not clear, although he has classified these species as lid-on isomers together with other binuclear complexes having \( R^2 = \text{H} \).

If one examines the two IR frequencies reported as \( \nu(\text{C} = \text{N}) \) and \( \nu(\text{C} = \text{C}) \) for nickel(II) complexes, a trend is apparent; the lacunar complexes known to be lid-off isomers and the N-methylated compartmental complexes exhibit two intense peaks with a separation from 50 to 80 cm\(^{-1}\), while the lid-on complexes, both lacunar and compartmental, show essentially one broad peak. When one or two peaks are resolved as shoulder-like peaks, the apparent difference between reported values does not seem to exceed 40 cm\(^{-1}\).

Thus the IR spectral change from (a) to (b) in Figure 7 can be tentatively interpreted as due to the change from the lid-on to the lid-off configuration. Possibly the examination of an extended series of N-
alkylated binuclear complexes whose $R^1$ group have no methyl residues might yield less ambiguous NMR evidence for the suspected lid-off structure.

It is still not clear how this stereochemical difference brings about the different IR spectral patterns. Inspection of available crystallographic bond distance data for a pair of iron(II)-chloro lacunar complexes reveals that there is no drastic difference in alkene C=C and imine C=N bond lengths between lid-on and lid-off isomers. The family of nickel(II) vaulted complexes introduced in Section 1.3, in which the lid-on/lid-off isomerism does not occur, exhibit a two-peak pattern in the 1530-1610 cm$^{-1}$ region, with a frequency separation of 65-80 cm$^{-1}$. Thus the difference in overall geometry of the molecules rather than in conjugation within the ligand framework may be important in determining the IR absorption intensities of certain stretching modes. Nevertheless the IR spectral pattern at around 1600 cm$^{-1}$ can be used as a criterion for lid-on/lid-off isomerism for the solid state complementing the carbon-13 NMR criteria for the solution phase.

2.2.3.2 Dicobalt(II) and Dicopper(II) Complexes. Figure 8 compares IR spectra of a series of binuclear cyclidene complexes containing different transition metals, $[M_2((Me_2(NH)_2(CH_2)_3)_2([16]cyclidene))_2]^{4+}$; $M=$Co(II), Ni(II) and Cu(II). It can be seen that a change in the coordinated metal ion results in little change in the corresponding IR spectra.

Selected IR frequencies are listed in Table 7 for the bis(cyclidene) complexes of metals other than nickel. One notices that the $[Co_2((Me_2(NH)_2CH_2CH_2)_2([16]cyclidene)_2)]^{4+}$ species exhibit two
Figure 8. IR Spectra of 

\[ \text{[M}_2(\text{Me}_2\text{NH})_2(\text{CH}_2)_3\text{Cl}_2(\text{[16]cyclidine})_2]](\text{PF}_6)_4 \cdot \]

(a) M=Co(II), (b) M=Ni(II) and (c) M=Cu(II).
Table 7. Selected IR Frequencies\textsuperscript{a} for Binuclear Complexes, 
\[ M_2\{\text{Me}_2\text{(NR}_2\text{)}_2\text{R}_1\}_2\{[16]\text{cyclidene}\}_2\}X_4. \]

<table>
<thead>
<tr>
<th>M</th>
<th>R\textsuperscript{1}</th>
<th>R\textsuperscript{2}</th>
<th>X</th>
<th>(\nu(O-H))</th>
<th>(\nu(N-H))</th>
<th>(\nu(C=N))</th>
<th>(\nu(C=C))</th>
<th>(\nu(P-P))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co ((CH_2)_2)</td>
<td>H</td>
<td>Cl/PF\textsubscript{6}</td>
<td>---</td>
<td>3373, 3319</td>
<td>1605\textsuperscript{sh}, 1586</td>
<td>1539</td>
<td>839, 553</td>
<td></td>
</tr>
<tr>
<td>Co ((CH_2)_3)</td>
<td>H</td>
<td>PF\textsubscript{6}</td>
<td>---</td>
<td>3390</td>
<td>1616,</td>
<td>1577</td>
<td>840, 559</td>
<td></td>
</tr>
<tr>
<td>Co mxyl</td>
<td>H</td>
<td>PF\textsubscript{6}</td>
<td>---</td>
<td>3418</td>
<td>1617\textsuperscript{sh},</td>
<td>1572</td>
<td>835, 552</td>
<td></td>
</tr>
<tr>
<td>Co ((CH_2)_2)</td>
<td>CH\textsubscript{3}</td>
<td>PF\textsubscript{6}</td>
<td>---</td>
<td>---</td>
<td>1610</td>
<td>1545</td>
<td>835, 558</td>
<td></td>
</tr>
<tr>
<td>Cu ((CH_2)_2)</td>
<td>H</td>
<td>PF\textsubscript{6}</td>
<td>3640\textsuperscript{W}</td>
<td>3390</td>
<td>1622,</td>
<td>1580</td>
<td>840, 558</td>
<td></td>
</tr>
<tr>
<td>Cu ((CH_2)_3)</td>
<td>H</td>
<td>PF\textsubscript{6}</td>
<td>3675, 3590</td>
<td>3390</td>
<td>1620,</td>
<td>1580</td>
<td>840, 560</td>
<td></td>
</tr>
<tr>
<td>Cu mxyl</td>
<td>H</td>
<td>PF\textsubscript{6}</td>
<td>3650\textsuperscript{W}</td>
<td>3395</td>
<td>1618,</td>
<td>1575</td>
<td>833, 559</td>
<td></td>
</tr>
<tr>
<td>Cu mxyl</td>
<td>H</td>
<td>Cl</td>
<td>3370\textsuperscript{br}, 3220\textsuperscript{br}</td>
<td>1625</td>
<td>1582</td>
<td>---</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} cm\textsuperscript{-1}.  


\( \nu(N-H) \) peaks and two intense peaks for \( \nu(C=N) \) and \( \nu(C=C) \) stretches (1539 cm\(^{-1}\) and 1586 cm\(^{-1}\), with a shoulder at 1605 cm\(^{-1}\)). Elemental analysis has revealed that the complex should be formulated as a chlorotris(hexafluorophosphate) salt and therefore it is conceivable that the chloride is coordinated to one of the cobalt(II) ions, making the cobalt unequivalent in the solid state.

2.2.4 NMR Spectral Characterization of Dinickel(II) Compartmental Bis(cyclidene) Complexes.

Both proton and carbon-13 NMR spectra of the diamagnetic dinickel(II) compartmental cyclidene complexes have been used to assess the overall conformations of the tricyclic ligands in solution. Selected examples will be described to illustrate the tremendous flexibility of the ligands and fluxional behavior of some of the protons.

Interpretation of carbon-13 spectra is relatively straightforward. Figure 9 shows a broadband proton-decoupled (a) and DEPT (Distortion Enhancement by Polarization Transfer) (b) carbon-13 spectra of \([\text{Ni}_2((\text{Me}_2(\text{NH})_2\text{mxy})_2([16]\text{cyclidene})_2)]^{4+}\) obtained in DMSO-\(d_6\) at room temperature. The DEPT technique allows one to identify methyl, methylene, and methine carbons unequivocally as shown in the set of spectra (b). A conventional off-resonance technique was applied to the same solution for comparison and the results are shown in Figure 10.

The number of carbon signals on the broadband proton decoupled spectrum is consistent with the presence of two symmetry elements. In reference to the crystal structure of this complex\(^{103}\) alluded to in the previous section, one of these symmetry elements must be an inversion
Figure 9. Broadband Proton-Decoupled and DEPT Carbon-13 NMR Spectra of [Ni$_2$((Me$_2$(NH)$_2$mxyl)$_2$([16]cyclidene)$_2$)]$^{4+}$.

(In DMSO-d$_6$ at room temperature)
Figure 10. Broadband Proton-Decoupled and Off-Resonance Carbon-13 NMR Spectra of $[\text{Ni}_2(\text{Me}_2\text{NH})_2\text{mxy}l)_2(\text{[16]}\text{cyclidene})_2]^{4+}$.

(In DMSO-d$_6$ at room temperature)
center relating the two metal coordinating cyclidine groups and the two linking groups. The other element is probably a mirror plane through both macrocycles containing the metal centers and carbons \( I \) and \( J \). The latter symmetry element is absent from the crystal structure due to the horizontal displacement of the two macrocycles with respect to each other. The motions allowed by the linking groups is fast on the NMR time scale in this solvent, resulting in the overall mirror symmetry. This situation is illustrated below.

When the same complex is dissolved in a different solvent, a pronounced solvent effect is observed. The carbon-13 chemical shifts of this complex are given in Table 8 for different solvents. Most notable is the observation that the two methyl carbons \( M \) and \( N \) appear at virtually the same position (ca. 20 ppm) in DMSO-\( d_6 \), whereas pairs of corresponding peaks are found some 5 ppm apart (20.8 ppm and 15.6 ppm) in acetonitrile-\( d_3 \) and nitromethane-\( d_3 \). According to the previous arguments, the former feature indicates the lid-off configuration around the bridge nitrogen, whereas the latter is found among the lid-on
Table 8. Carbon-13 NMR Data for
\[ \text{[NL}_2\{(\text{Me}_2\text{NH})_2\text{methyl}\}_2\{\text{[16]cyclohexane}\}_2\}^{4+} \]

In Various Solvents.

<table>
<thead>
<tr>
<th>Carbon (^a)</th>
<th>Chemical Shifts/ppm (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMSO-d(_6)</td>
</tr>
<tr>
<td>A</td>
<td>169.4</td>
</tr>
<tr>
<td>B</td>
<td>166.4</td>
</tr>
<tr>
<td>C</td>
<td>159.7</td>
</tr>
<tr>
<td>W</td>
<td>138.0</td>
</tr>
<tr>
<td>Y</td>
<td>129.9</td>
</tr>
<tr>
<td>Z</td>
<td>128.8</td>
</tr>
<tr>
<td>X</td>
<td>126.6</td>
</tr>
<tr>
<td>D</td>
<td>109.3</td>
</tr>
<tr>
<td>K</td>
<td>54.4</td>
</tr>
<tr>
<td>E</td>
<td>50.2</td>
</tr>
<tr>
<td>F</td>
<td>48.7</td>
</tr>
<tr>
<td>I</td>
<td>29.1</td>
</tr>
<tr>
<td>J</td>
<td>28.7</td>
</tr>
<tr>
<td>M</td>
<td>21.0</td>
</tr>
<tr>
<td>N</td>
<td>20.6</td>
</tr>
</tbody>
</table>

\(^a\) See Figure 9 for signal assignment.  
\(^b\) Referenced to solvents; (CD\(_3\))\(_2\)SO, CD\(_3\)CO, CD\(_3\)NO \(_2\), and CD\(_3\)CN.  
\(^c\) Sample contained ethanol of crystallization.  
\(^d\) Indistinguishable.  
\(^e\) Superimposed on solvent peaks.  
\(^f\) Tetrachloride salt.
isomers. Since the present complex was determined to be in the lid-on configuration and it is not likely to convert to the lid-off form under mild conditions, the above data are interpreted as a solvent effect involving hydrogen bonding. It is suggested that DMSO is strongly hydrogen bonding and, when bound to the $R^2$ protons, influences the environment of the methyl carbon $M$ as does the $R^1$ group in lid-off species. Another notable feature associated with the hydrogen bonding is the departure of the imine carbon $B$ from $C$ by about 7 ppm in the spectrum in DMSO-$d_6$.

In order to confirm that the (m-xylylene) lid-on structure is retained in these solutions, fully proton coupled spectra were obtained for both DMSO-$d_6$ and nitromethane-$d_3$ solutions. On the basis of Herron's argument, the three-bond carbon-proton coupling constant, $^3J_{C-H}$, for the methyl carbon $N$ and the $R^2$ proton, can be used to evaluate the lid-on/lid-off isomer type. In the lid-on configuration the two nuclei are oriented trans to each other and the coupling constant should be greater than that of the lid-off (cis) counterpart.

Known examples of lid-on isomers displayed coupling constants in the range of 6.1-7.8 Hz, while a lid-off isomer yielded $^3J_{C-H} < 1.5$ Hz. In the present case the corresponding coupling constants were...
evaluated to be ca. 2 Hz and 2.7 Hz for the DMSO-$d_6$ and nitromethane-$d_3$ solutions, respectively. These values apparently fall in the range between those for known lid-on and lid-off isomers. It is noted that the value obtained for the nitromethane-$d_3$ solution is much smaller than that reported (6.5 Hz) by Herron et al. The present sample contains ethanol of recrystallization and it is likely that the ethanol molecule remains hydrogen bonded to the $R^2$ proton in solution. It appears that the orientation of the $R^2$ proton relative to the vinylc methyl carbon is much less trans-like when the proton is involved in the hydrogen bonding.

The last entry in Table 8 compares the carbon-13 NMR spectrum of the sample containing no ethanol in acetonitrile-$d_3$. The number of carbon signals roughly coincides with a structure having only one symmetry element, probably the inversion center. Thus in the absence of a strongly hydrogen bonding solvent, the $m$-xyylene linked complex apparently assumes the lower symmetry, "slipped" conformation, as in its crystal structure.

It is not clear how the hydrogen bonding interaction to the $R^2$ proton promotes the interconversion among the different conformers, leading to the apparent $C_{2h}$ molecular symmetry. In practice, most of the binuclear complexes studied have been recrystallized from acetonitrile and/or ethanol solvent, and therefore the overall symmetry of these complexes in common solvents, such as acetonitrile at room temperature, can be approximated as $C_{2h}$ (or $C_{2v}$ for the eclipsed isomer).

The above example serves to demonstrate the flexibility of the bis-(cyclidene) ligand in which the molecular symmetry can vary considerably. Figure 11 compares the carbon-13 NMR spectra (acetonitrile-$d_3$) of
a series of dinickel(II) compartmental cyclidene complexes with different linking groups \( R^1 \). All the signals are commonly broad compared to the sharp signals due to ethanol (58.0ppm and 18.8ppm), but the spectrum (a) of \([\text{Ni}_2\left(\text{Me}_2\text{NH}\right)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\left(\text{[16]}\text{cyclidene}\right)_2]\)\(^4^+\) with short dimethylene links displays some of the signals broadened more extensively than others. The broader signals are assignable to the carbons \( A \)(imine), \( D \)(\(\gamma\)-carbon), \( K \)(methylenec next to the bridge nitrogen) and \( N \)(vinyllic methyl), while the rest of the signals arise from atoms of the cyclidene moieties. This trend suggests that the source of such broadening is the rotational motion around the entire alkyl \( \text{bis}(\text{aminoethyldiene}) \) linking groups. When \( R^1 \) groups are elongated from two-atom to five-atom linkages, the carbon signals \( A, D, K, \) and \( N \) progressively sharpen up (spectra (b), (c)), indicating that the longer polymethylene chain can rotate more freely, averaging the carbon environments into an overall conformation with higher symmetry. Replacement of the middle methylene group of the \( R^1 = (\text{CH}_2)_5 \) by sulfur atom results in broadening of the carbon signals \( D, K, \) and \( N \) and partial resolution of the signal \( A \). Incorporation of heteroatoms into a linear alkyl chain usually increases the freedom of rotation of the chain, but in the present case the sulfur atom may cause a certain folded structure of the \( R^1 \) group unlike the straight pentamethylene chain. The \( m \)-xylylene link provides another five-atom linkage with a constraint imposed by the benzene ring. The same broadening pattern of the carbon-13 signals is observed for the \( m \)-xylylene linked species.

An example of a binuclear complex in which the conformational motion around the linking groups is restricted is given in Figure 12.
Figure 11. Carbon-13 NMR Spectra of a Series of

\[ \text{[Ni}_2((\text{Me}_2\text{NH})_2\text{R}^1)_2(16\text{cyclidene})_2]^4^+ \].

(a) \( \text{R}^1 = (\text{CH}_2)_2 \), (b) \( \text{R}^1 = (\text{CH}_2)_3 \), (c) \( \text{R}^1 = (\text{CH}_2)_5 \),
(d) \( \text{R}^1 = (\text{CH}_2)_2\text{S}(\text{CH}_2)_2 \), and (e) \( \text{R}^1 = m\text{-xylylene} \).

(In acetonitrile-d$_3$, at room temperature)
Figure 12. Carbon-13 NMR Spectra of
(a) $[\text{Ni}_2\{\text{Me}_2\text{pip}\}_2\{[16]\text{cyclidene}\}_2]\text{]^{4+}$ in Nitromethane-$d_3$ and
(b) $[\text{Ni}\{\text{Me}_2\text{NMMe}_2\text{CH}_2\text{CH}_2\}_2\{[16]\text{cyclidene}\}_2]\text{]^{4+}$
in Acetonitrile-$d_3$. (at room temperature)
The complex \([\text{Ni}_2\{(\text{Me}_2\text{Pi})_2\{[16]\text{cyclidene}_2\}]^{4+}\) differs structurally from \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2\}_2\{[16]\text{cyclidene}_2\}]^{4+}\) by the additional dimethylene link substituting for the \(R^2\) protons. The expected rigidity of the double dimethylene link and, perhaps, the higher molecular symmetry are reflected in the sharpness of all the signals, the number of which corresponds to the \(C_{2h}\) point group for the molecule. The nonequivalence of the carbons \(K\) and \(K'\) in the bridging units indicates that the two dimethylene groups are, as anticipated, not interconverting.

The N-methylated dimethylene-linked complex exhibits a carbon-13 NMR spectrum consistent with the lid-off configuration and with roughly equivalent cyclidene units (Figure 12(b)). Every peak shows considerable broadening. It appears that the structural change upon N-methylation results in the lowered symmetry.

Carbon-13 chemical shifts data for the complexes included in Figures 11 and 12 are summarized in Table 9.

Proton NMR spectra of the dinickel(II) compartmental cyclidene complexes are more difficult to analyze since the proton environments are more sensitive to structural asymmetry (absence of a particular symmetry element) and generate numerous unresolved signals. The proton signals easiest to assign are vinyl protons (7.4 - 7.9 ppm) and \(R^2\) protons (6.3 - 6.8 ppm). When the symmetry allows, two sharp singlets may be identified in the region 2.0 - 2.5 ppm for two methyl groups.

An example given in Figure 13(a) is the proton NMR spectrum of \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2\}_2\{[16]\text{cyclidene}_2\}]^{4+}\) in acetonitrile-d₃ recorded at room temperature. Both the vinyl and \(R^2\) protons are resolved into three separate peaks, one of which is apparently twice as intense as the
Table 9. Carbon-13 NMR Data for Selected Dinickel(II) Bis(cyclidene) Complexes.

| Carbon | Chemical Shifts  
|--------|------------------
|        | $R^2 = H$          | $R^2 = CH_3$       |
|        | $R^1 = (CH_2)_2$ | $R^1 = (CH_2)_3$ | $R^1 = (CH_2)_5$ | $R^1 = (CH_2)_2$ | $R^1 = pip$ | $R^1 = (CH_2)_2$ |
| A      | 168.7           | 168.3            | 168.3             | 168.5, 168.6   | 171.4       | 175.1, 174.2   |
| B      | 161.3           | 160.1            | 160.1             | 160.5, 169.3   | 168.6, 167.7 |
| C      | 160.8           | 160.1            | 160.1             | 160.5, 162.3   | 162.1, 160.5 |
| D      | 118.3           | 112.8, 112.5     | 112.6             | 112.5, 113.0   | 112.5       |
| E      | 56.7            | 56.3             | 56.3              | 56.4           | 57.8        | 53.6, 52.3     |
| F      | 51.5            | 51.5             | 51.5              | 51.7           | 54.0        | 51.7, 50.8     |
| K      | 45.9b           | 42.5             | 45.7              | 45.0b          | 52.6        | 44.7, 38.6     |
| L      | 30.2            | 30.7             | 30.7              | 30.6           | 30.9        | 30.6           |
| J      | 30.2            | 30.0             | 30.2              | 30.0           | 30.8        | 29.5           |
|        | 30.0            |                  |                   |               | 29.6        |                 |
| (R$^1$ β-methylene) (R$^1$ β-methylene) |          |                   |                   |               |             |                 |
| N      | 21.0            | 20.8             | 20.7              | 21.3           | 20.5        | 21.7, 20.8     |
| N      | 15.5           | 15.1             | 15.5, 15.3        | 15.6, 15.5b    | 18.5        | 19.7           |

a. Referenced to solvent; CD$_3$CN (and CD$_3$NO$_2$ for R$^1$, R$^2 = pip$).
b. Broad.
c. Indistinguishable.
d. Very broad signal at ~33ppm assignable to R$^1$ methylene group next to sulfur.
Figure 13. Proton NMR Spectra of 
\[\text{[Ni}_2\{(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2\}_2([\text{16} \text{cyclidene})_2]\}^{4+}\] in Acetonitrile-d$_3$.

(a) At 299K, (b) the Spectral Change in the Region 6-8 ppm upon Cooling.
others. Thus it appears that there is no combination of symmetry elements that relates all four of these protons on the molecule. The slightly different local environment, to which the carbon-13 nuclei are less sensitive, is reflected in the separation of these proton signals.

In order to confirm that such asymmetry arises from different conformers, the temperature dependence of the proton NMR spectrum was studied. As shown in Figure 13(b), as the temperature is lowered to 233K, all four peaks of both vinyl and R2 protons are resolved. Without a complete assignment of each signal to specific protons, it is not possible to describe the functional behavior unambiguously. Nonetheless over the temperature range of 233K - 299K there does not seem to be a drastic change in the molecular symmetry. At temperatures above room temperature, however, it was observed in DMSO-d6 solvent that the four signals from initially unequivalent protons particularly on the R2 position merge into one peak at 339K (Figure 14). The temperature at which such coalescence is observed is, however, not reached in other measurements and therefore the proton environment in this complex can be generally regarded as nonequivalent under normal conditions.

The above example was described in order to demonstrate the molecular functionality reflected in the proton NMR spectra. Such behavior is more or less common to all the dinickel(II) compartmental cyclidine complexcs studied here.

With regard to the effect of hydrogen bonding solvents on the proton NMR spectra, certain methyl proton signals commonly exhibit fairly large downfield shifts upon addition of ethanol to their acetonitrile-d3 solutions. It is difficult to relate such shifts to molecular dynamics
Figure 14. Proton NMR Spectra of

\[ \text{[Ni}_2\text{((Me}_2\text{NH})_2\text{CH}_2\text{CH}_2)_2([16]cyclidene)_2)]^{4+} \text{ in DMSO-d}_6. \]

(a) At 300K, (b) the Spectral Change in the Region

6 - 9 ppm upon Warming.
without knowledge of which proton(s) undergo change. The overall molecular symmetry, however, appears not to be greatly affected by the addition of ethanol, since the number of peaks appearing in the spectrum does not change.

In summary, the application of NMR spectroscopy to the dinickel(II) compartmental cyclidene complexes has revealed a tremendous flexibility of the ligand structure in solution. As a result of motion about the linking groups, the carbon environment is averaged to the apparent $C_{2h}$ (or $C_{2v}$) symmetry, while such an averaging does not necessarily apply to the proton environment. A typical source of asymmetry seems to be the sliding motion of the two macrocyclic rings, eliminating a mirror symmetry element. Such molecular dynamics may play an important role in catalysis since substrate inclusion and product extrusion may be kinetically assisted.

2.2.5 Electrochemical Characterization of Redox Properties of Binuclear Compartmental Bis(cyclidene) Complexes.

The redox behaviour of the binuclear compartmental cyclidene complexes was studied by cyclic voltammetry and differential pulse polarography in acetonitrile solvent. Of primary concern was whether or not two redox processes characteristic of metal-metal coupled systems are observed for the bis(cyclidene)complexes. The NMR results have revealed that the ligands are generally very flexible and therefore the average metal-metal distances in solution may be quite different from those shown in the crystal structures, and possibly considerably shorter than them. In fact, some of the bis(cyclidene) complexes having short linking groups have yielded unexpectedly large separation of two
redox waves. The nature of the metal-metal interaction reflected in the electrochemical behavior is discussed in this section.

The dinickel(II) complexes generally display reversible to quasireversible oxidation waves at 0.71-0.98 volts vs. Ag/AgNO$_3$ on the cyclic voltammograms. No apparent correlation between the $E_{1/2}$ values and the linking group $R^1$ has been observed by previous workers. As mentioned earlier, the primary interest in the electrochemistry of binuclear species lies in $\Delta E_{1/2}$ values, which were expected to be small in the present dinickel(II) complexes. Two examples of cyclic voltammetric traces are given in Figure 15 for bis([16]cyclidene) compounds with $R^1 = \text{m-xylylene}$ and dimethylene, respectively. In both cases, the oxidation wave at 0.8 - 0.9V was assigned to two metal redox couples on the basis of coulometry and EPR identification of electrolysis products.

Figures 16(a) and 16(b) show the EPR spectra of one-electron and two-electron electrolysis products of $[\text{Ni}_2\{(\text{Me(NH)}_2\text{mxylyl})_2([16]-\text{cyclidene})_2\}]^{4+}$, respectively. The two spectra are identical and the intensity merely doubles upon removal of the second electron. The axial signal (parallel component) arising from the $d^7$ nickel(III) exhibits a well resolved quintet due to the superhyperfine coupling of two nitrogens ($I=1$) of the acetonitriles ($g = 2.00$, $A_N = 20.0$ gauss), indicating the 6-coordinate structure of the nickel(III) species. The identical shape of the signals (a) and (b) also indicate that the two nickel sites are independent of each other and that each metal can be oxidized to 6-coordinate solvated species without affecting the other.
Figure 15. Cyclic Voltammograms of Dinickel(II) Bis[cyclidene] Complexes Having Relatively Long Linking Groups.

(a) [Ni₂{(Me₂(NH)CH₂CH₂)₂([16]cyclidene)₂}]^{4+} and

(b) [Ni₂{(Me₂(NMe)₂CH₂CH₂)₂([16]cyclidene)₂}]^{4+}.

(In acetonitrile containing 0.1M TBAB, at room temperature, scan rate 100 mV/sec.)
On the other hand, the one-electron and two-electron oxidation products of the complex with shorter bridge \([\text{Ni}_2\{(\text{Me}_2\text{NMe})_2\text{CH}_2\text{CH}_2\}_2\text{([16]cycloidene)}_2\}]^{\text{II}}\) exhibit slightly different EPR spectra. The spectrum (b) of the two-electron oxidation product in Figure 17 possesses an additional component marked by an asterisk, which is absent from the partially oxidized product. The broadness of the signal at \(g = 2\) precludes an organic radical as the source of these signals, but neither is any nitrogen nuclear hyperfine coupling observed. Therefore it is most likely that the dimethylene linked complex does not have a cavity large enough to accommodate two solvent molecules to form a 6-coordinate nickel(III) species as in \([\text{Ni}_2\{(\text{Me}_2\text{NH})_{2\text{mxy}}\}_2\text{([16]}\text{cycloidene)}_2\}]^{5+,6+}\) and consequently the oxidized species must assume very distorted 5- or 6-coordinate geometries. The difference in spectra (a) and (b) may reflect variations in their distortion in the first and the second coordination sites.

The EPR signals (b) in both Figures 16 and 17 were found to decay, when the solution was warmed to room temperature, with apparent half-lives of 15-40 minutes. This behaviour parallels Chavan's finding\(^{11}\) with a series of lacunar complexes having \(R^2 = R^3 = \text{CH}_3\) and \(R^1\) varying from a long dodecamethylene to a short trimethylene chain and including an unbridged \([\text{Ni}\{(\text{Me}_2\text{NMe})_2\text{[16]cycloidene)}\}]^{2+}\) complex. He observed that the electrode products of his lacunar complexes vary from a normal 6-coordinate nickel(III) species to a ligand radical, depending on the size of the cavity.

However, the electrochemical behavior of these nickel(II) lacunar complexes has been found to be curiously insensitive to such a variation
Figure 16. EPR Spectra of $[\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{MXV}_1\}_2\{[16]\text{cyclohexene}\}_2]\}^{n+}$

Obtained by Controlled Potential Electrolysis.

(a) $n = 5$ and (b) $n = 6$. (Electrolyzed at 1.0 V, see Figure 15(a), EPR recorded at 77K)
Figure 17. EPR Spectra of $[\text{Ni}_2\{(\text{Me}_2\text{NMe})_2\text{CH}_2\text{CH}_2\}_2\{\text{16}\text{cyclidene}_2\}]^{n+}$

Obtained by Controlled Potential Electrolysis. (a) $n = 5$, (b) $n = 6$.

(Electrolyzed at 0.95 V, see Figure 15(b), EPR recorded at 77K)
in the nature of the electrode products. Thus the $E_{1/2}$ values of the reversible oxidation waves all fall between 0.74 and 0.79 volts vs. \( \text{Ag/AgNO}_3 \) in acetonitrile solvent. If such insensitivity holds for both nickel sites in the present binuclear series, the two $E_{1/2}$ values (and $\Delta E_{1/2}$) might not correlate with the $R^1$ group in this case either.

However, the cyclic voltammograms obtained for \([\text{Ni}_2(\text{Me}_2\text{pip})_2^-([16]\text{cyclidene})_2])^{4+}\) (Figure 18(a)) clearly indicates departure of one redox couple from the other. Another example of such a weakly split redox wave was observed for \([\text{Ni}_2((\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2)_2([14]\text{cyclidene})_2])^{4+}\) and is shown in Figure 18(b). These compounds are expected to have a short metal-metal separation and the electrochemical behavior of the dinickel(II) bis(cyclidene) complexes does appear to correlate with the metal-metal distance.

Differential pulse polarography was applied, therefore, in order to obtain quantitative data for $\Delta E_{1/2}$. Sample traces of the polarograms of \([\text{Ni}_2((\text{Me}_2\text{NH})_2\text{mxyl})_2([16]\text{cyclidene})_2])^{4+}\) and \([\text{Ni}_2((\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2)_2([14]\text{cyclidene})_2])^{4+}\) are shown in Figure 19 for comparison. The separation of the two $E_{1/2}$ values is still not visible (the potential at the peak of $\Delta i/i_d$ vs. \( V \) curve corresponds to $E_{1/2}$) for some cases and therefore the $\Delta E_{1/2}$ values were calculated from half-width of the polarogram using Richardson and Taube's working curve. After $\Delta E_{1/2}$ is calculated, the two $E_{1/2}$ values were obtained from the following equation:

$$E_{1/2}^2 = E_c + (\Delta E_{1/2} + E_{pul})/2$$

in which $E_{pul}$ denotes pulse amplitude (= 10 mV in this study). The results are given in Table 10.
Figure 18. Cyclic Voltammograms of Dinickel(II) Bis(cyclidene)
Complexes Having Relatively Short Linking Groups.
(a) $[\text{Ni}_2((\text{Me}_2\text{pip}))_2([16]\text{cyclidene})_2]^{4+}$ and
(b) $[\text{Ni}_2((\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2)_2([14]\text{cyclidene})_2]^{4+}$.
(In acetonitrile containing 0.1 M TBAB, at room temperature,
scan rate 100 mV/sec.)
Figure 19. Differential Pulse Polarograms of
(a) [Ni₂{(Me₂(NH)₃mxyl)₂[[16]cycloidene]₂}]⁺⁺ and
(b) [Ni₂{(Me₂(NH)₂CH₂CH₂)₂[[14]cycloidene]₂}]⁺⁺.
(In acetonitrile containing 0.1M TBAB, at room temperature,
scan rate 2 mV/sec., "drop time" 0.5 sec.)
Table 10. Differential Pulse Polarographic Data for a Series of Dinickel(II) Complexes \([\text{Ni}_2\{(\text{Me}_2\text{NR})_2\text{R}^1\}_2([\text{Q}]\text{cyclidene}_2)]^{4+}\).
(In acetonitrile containing 0.1M TBAB, at room temperature)

<table>
<thead>
<tr>
<th>(\text{R}^1)</th>
<th>(\text{R}^2)</th>
<th>(\text{Q})</th>
<th>width/mV</th>
<th>(\Delta E_{1/2}/\text{mV}^a)</th>
<th>(E_c/\text{V})</th>
<th>(E_{1/2}^1/\text{V})</th>
<th>(E_{1/2}^2/\text{V})</th>
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<tr>
<td>mxyl</td>
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<td>16</td>
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<td>0.879</td>
<td>0.929</td>
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<td>61.3</td>
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<td>0.891</td>
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<td>14(^b)</td>
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<td>0.812</td>
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<td>((\text{CH}_3)_2)</td>
<td>-</td>
<td>16(^c)</td>
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<td>0.733</td>
<td>0.713</td>
<td>0.762</td>
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<td>([\text{Ru(NH}_3)_5\text{(py)}]^{2+})</td>
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<td>-</td>
<td>98.8</td>
<td>42.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a. Table 1, pp. 1280 in reference 112.
b. No ligand oxidation was observed.
c. Mononuclear unbridged complex, \([\text{Co}\{(\text{Me}_2\text{N})_2\}_2[16]\text{cyclidene}]\^{2+}\).
As can be seen, although the $\Delta E_{1/2}$ values are all small and represent weakly coupled systems, the steady increase from 49.7mV for $[\text{Ni}_2\{(\text{Me}_2\text{NH}_2\text{mxy})_2[[16]\text{cyclidene}]_2\}]^{4+}$ to 105mV for $[\text{Ni}_2\{(\text{Me}_2\text{NH}_2\text{CH}_2\text{CH}_2)_2[[14]\text{cyclidene}]_2\}]^{4+}$ correlates well with the decreasing metal-metal separation. In terms of metal-metal distances, the double link $\text{N(CH}_2\text{CH}_2)_2\text{N}$ in $[\text{Ni}_2\{(\text{Me}_2\text{pip})_2[[16]\text{cyclidene}]_2\}]^{4+}$ is expected to bring two metal sites closer together than the stretched lid-on link $\text{NH-CH}_2\text{-CH}_2\text{-NH}$ in $[\text{Ni}_2\{(\text{Me}_2\text{NH}_2\text{CH}_2\text{CH}_2)_2[[16]\text{cyclidene}]_2\}]^{4+}$. The 16-membered macrocyclic units in the latter complex are known to have a saddle shape and therefore the 14-membered analogue $[\text{Ni}_2\{(\text{Me}_2\text{NH}_2\text{CH}_2\text{CH}_2)_2[[14]\text{cyclidene}]_2\}]^{4+}$ with the same dimethylene links but very flat macrocyclic units should also result in a considerable shortening in the metal-metal distance.

The apparent correlation between $\Delta E_{1/2}$ values and metal-metal distances is interpreted in terms of several contributions to the $\Delta E_{1/2}$ values. For electronically symmetric binuclear complexes, the non-zero values for $\Delta E_{1/2}$ can be attributed to four factors: 113

1. Statistical contributions—the $\text{M(II)}$-$\text{M(II)}$ species can be oxidized to give $\text{M(II)}$-$\text{M(III)}$ or $\text{M(III)}$-$\text{M(II)}$ and the $\text{M(III)}$-$\text{M(III)}$ complex reduced to give either $\text{M(III)}$-$\text{M(II)}$ or $\text{M(II)}$-$\text{M(III)}$. The statistical value for the comproportionation constant is 4 and the corresponding $\Delta E_{1/2}$ value is 36mV. (2) Electrostatics—the second oxidation occurs adjacent to a greater positive charge than the first oxidation, it will occur at a higher potential. (3) Solvation energies—the solvation energies will be different for the $\text{M(II)}$-$\text{M(II)}$, $\text{M(II)}$-$\text{M(III)}$ and $\text{M(III)}$-$\text{M(III)}$ species. Finally, (4) electron delocalization or resonance—the extra
electron of the divalent atom in M(II)-M(III) species is partially delocalized onto the M(III) site, shifting the second potential higher than that of totally localized electron.

In the present case, the last factor should be negligibly small due to the absence of possible delocalization pathways. In addition, the electrochemistry of these dinickel(II) complexes is expected to be insensitive to the solvation of the nickel(III) site, as mentioned above. Therefore the $\Delta E_{1/2}$ values which are greater than 36mV are primarily due to the electrostatic interaction within the binuclear molecules. (The last two entries are mononuclear complexes and these represent a hypothetical binuclear system in which two metals are infinitely separated and should yield $\Delta E_{1/2} = 36\text{mV}$. The slightly higher number obtained for $\text{[Ru(NH}_3)_5(\text{py})]^2^+}$, (approximated as a spherical charged particle in the theory) could be due to the slight difference between the present and Richardson and Taube’s experimental setups). It is noted that the $m$-xylylene bridged species behaves in much the same way as the unbridged mononuclear cyclidene complex and this is expected.

The cyclic voltammetric behavior of the paramagnetic dicobalt(II) complexes turned out to be very irreversible and difficult to analyze. Cobalt(II) lacunar complexes having $R^2 = H$ yield similarly irreversible electrochemistry.\textsuperscript{11}\textsuperscript{13} The CV traces for three dicobalt(II) complexes are given in Figures 20–22. The peak potentials for the major oxidation waves in these cyclic voltammograms fall within the range found for cobalt(II) lacunar complexes.\textsuperscript{107,111}

Electrochemistry of dicopper(II) derivatives (Figure 23) proved to be extremely irreversible for the reductive scan due to the instability
Figure 20. Cyclic Voltammogram of

\[ [\text{Co}_2(\text{Me}_2\text{NH}_2\text{mxy})_2([16]\text{cyclidene})_2)]^{\text{II}^+}. \]

(In acetonitrile containing 0.1M TBAB, at room temperature, scan rate 100 mV/sec.)
Figure 21. Cyclic Voltammograms of

\[ \text{[Co}_2\text{((Me}_2\text{NH})_2\text{CH}(_2)\text{CH}_2)_2([16\text{cyclidene}]_2)]^{4+} \]

(In acetonitrile containing 0.1M TBAB, at room temperature,
scan rate 20, 50, 100, 200 mV/sec.)
Figure 22. Cyclic Voltammogram of

\[ \text{[Co}_2\text{((Me}_2\text{NMe})_2\text{CH}_2\text{CH}_2)_2([16]cycloidene)_2)}\]^{4+}.

(In acetonitrile containing 0.1M TBAB, at room temperature, scan rate 100 mV/sec.)
Figure 23. Cyclic Voltammogram of

\[ \text{[Q} \text{]_2\{(Me}_2\text{NH}_2\text{)(CH}_2\text{)}_3\text{][[16]cyclidene}_2]^{4+}. \]

(In acetonitrile containing 0.1M TBAB, at room temperature,
scan rate 100 mV/sec.)
of copper(I) species, which disproportionates to copper(II) species and copper metal. The Cu(II)→Cu(III) oxidation, however, behaved nicely and reversible potential was obtained. Only one of the dicopper(II) complexes has been electrochemically characterized to date; the CV trace of \([Cu_2((Me_2(NH)_2(CH_2)_3)_2[[16]cyclophane])]^{4+}\) is given in Figure 23.

2.2.6 EPR Spectral Characterization of Magnetic Interaction in Dicobalt(II) and Dicopper(II) Complexes.

The previous two sections on NMR spectroscopic and electrochemical studies on the diamagnetic dinickel(II) compartmental complexes illustrated the overall molecular geometry and the dimensions of the cavity that separates the two metal atoms in the structure. At room temperature these complexes can be approximated as roughly cofacial with two symmetry elements. The precise molecular geometry, however, appears to be intrinsically of lower symmetry and fluctuation behavior is observed.

With these features in mind, an EPR spectroscopic study of the paramagnetic dicobalt(II) and dicopper(II) derivatives will be described in this section. Attention will be focused on the magnetic interaction between the two paramagnetic metal centers.

In order to assess the magnetic properties of these complexes, magnetic moments were determined in solution by Evans' method. The results are given in Table 11. The magnetic moments at room temperature calculated for the dicobalt(II) complexes are consistent with two low spin cobalt(II) ions per molecule. The values for the dicopper(II) complexes are also consistent with one unpaired electron for each of the two copper(II) ions. All the numbers in Table 11 have been corrected for diamagnetic contribution from the ligands and anions and also for
Table 11. Magnetic Moments of Paramagnetic Bis(cyclidene) Complexes

\[ [M_2\{(Me_2((NR^2)_2)R^1)_2([16]cyclidene)\}_2]^n_+ \] in Acetonitrile Solution.\(^a\)

<table>
<thead>
<tr>
<th>( \mathbf{M} )</th>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>( T/K )</th>
<th>( \mu_{\text{eff}}/\text{B.M.} ) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/CoCl</td>
<td>((\text{CH}_2)_2)</td>
<td>H</td>
<td>237</td>
<td>2.09</td>
</tr>
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<td></td>
<td></td>
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<td>252</td>
<td>1.98</td>
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<td>\text{CH}_3</td>
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\(^a\) Determined by Evans' method. Concentration 9 - 15 mM.

\(^b\) Calculated per metal atom. \(\pm 0.04\) B.M.
the changes in concentration of the complex at low temperatures due to volume contraction of the solvent. The paramagnetism arising from the metal centers thus obtained for the dicobalt(II) and dicopper(II) complexes appears slightly greater than spin-only values (1.73 B.M. per metal atom) at room temperature and does not vary appreciably at temperatures down to -40°C. This can be taken as an indication of a very small magnetic interaction between the two paramagnetic metal centers. It is not possible to describe the interaction in any quantitative terms without extensive magnetic susceptibility data, but the subtle nature of the metal-metal magnetic interaction is reflected in the EPR spectra of these complexes, which is discussed below.

$\gamma$-Band EPR spectra were recorded for frozen solutions at 77K. Figure 24 shows the EPR spectra of $[\text{Co}_2\{\text{Me}_2\text{NH}_2\text{CH}_2\text{CH}_2\}_2([16]\text{cyclidine})_2]^4+$ in acetonitrile with and without 1-methylimidazole (1-MeIm) added. The dimethylene linked species is representative of the dicobalt(II) systems with relatively short metal-metal distances. For comparison, the EPR spectrum of the $m$-xyylene linked complex is given in Figure 25. The EPR parameters obtained in different media are summarized in Table 12.

The EPR spectra of these dicobalt(II) complexes in the presence of nitrogenous axial base are consistent with axial symmetry with the $g_{//}}$ region split into eight lines due to the nuclear hyperfine coupling to the cobalt nucleus ($I=7/2$). This spectral pattern resembles that of the mononuclear lacunar$^{107}$ and vaulted$^{108}$ cobalt(II) complexes, except that the superhyperfine structure due to the nitrogen nucleus ($I=1$) of the axial base is hardly resolved in the binuclear species. The fact that
Figure 24. EPR Spectra of [Co₂((Me₂(NH)₂CH₂CH₂)₂([16]cyclidene)₂)]⁴⁺.
(a) In Acetonitrile Alone and (b) with Excess 1-Methylimidazole Added. (EPR recorded at 77K)
Figure 25. EPR Spectra of \([\text{Co}_2(\text{Me}_2(\text{NH})_2\text{mxy})_2(\text{[16]cycloidene})_2]^4+\).

(a) In Acetonitrile Alone and (b) with Excess 1-Methylimidazole Added. (EPR recorded at 77K)
Table 12. EPR Parameters for Dicobalt(II) Bis(cyclidene) Complexes.

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<th>R^1</th>
<th>R^2</th>
<th>Solvent/Base</th>
<th>g_\perp</th>
<th>g_∥</th>
<th>A^CO/G</th>
<th>A^N/G</th>
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<tr>
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<td>(CH_3)_2</td>
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<td>acetonitrile</td>
<td>2.27</td>
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<td>acetone/pyridine</td>
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<td>1.99</td>
<td>100.0</td>
<td>14.</td>
</tr>
<tr>
<td>Co</td>
<td>mxyl</td>
<td>H^G</td>
<td>acetone/pyridine</td>
<td>2.31</td>
<td>2.02</td>
<td>101.0</td>
<td>13.</td>
</tr>
</tbody>
</table>

---


b. Mononuclear unbridged complex, [Co{Me_2(NMe_2)_2[16]cyclidene}]^{2+}.

c. Mononuclear lacunar complex, [Co{Me_2(NH)_2mxyl[16]cyclidene}]^{2+}. 
monomeric species with similar ligand systems display well-resolved EPR signals under the same conditions supports the view that the apparent poor resolution for the binuclear complexes is not an experimental artifact, due, for instance, to the quality of the glass, but rather an indication of some metal-metal interaction.

In the absence of strongly coordinating base, the short dimethyleine linked complex displays EPR spectra with ill-resolved cobalt hyperfine structure. The EPR signals obtained in acetone and dichloromethane are essentially isotropic, with little structure.

If two paramagnetic metal centers (S=1/2) are located close enough to display significant interaction, a "triplet" spectrum would be expected. If the rate of electron exchange is fast compared to the EPR resonance frequency ($10^{10}$ sec$^{-1}$), then each electron experiences a nuclear spin equal to the total nuclear spin of the two metals. The resulting hyperfine splitting, $A$, is half that for a related mononuclear S=1/2 system.$^{35,116}$ Such hyperfine structure is not observed with the dicobalt(II) compartmental complexes coordinated by a strong base. The EPR signals obtained for acetone and dichloromethane glasses may represent an exchange coupled system with a hyperfine structure having $A_{//} = 50-60$ gauss (mononuclear counterparts typically exhibit $A_{//} = 100-120$ gauss) but with the hyperfine structure not resolved. It should be recalled that the dimethylene linked complex contains one chloride ion per molecule; this anion may assist the electronic coupling. In any event the magnitude of such an exchange interaction should be no greater than the X-band microwave quantum, which is about 0.3 cm$^{-1}$.

The EPR transition could be further split by zero-field splitting, D. As mentioned in the Introduction, this parameter D is used to
estimate the metal-metal distance. $D$ is composed of two terms, $D_{\text{pseudo}}$ (from spin-orbit coupling) and $D_{\text{dd}}$ (from the dipolar coupling), which is related to the metal-metal separation, $r$, by the equation $r = (0.65g//^2/D_{\text{dd}})^{1/3}$ in which $r$ is in Å and $D_{\text{dd}}$ in cm$^{-1}$.\textsuperscript{13,35} When exchange interaction is small, $D_{\text{pseudo}}$ can be ignored. On the basis of this equation, the magnitude of the zero-field splitting for systems with large metal-metal separation ($r > 10\AA$), as in the present binuclear complexes, is estimated to be smaller than 28 gauss ($2.6 \times 10^{-3}$ cm$^{-1}$), with $g//\approx$ approximated at about 2. The corresponding splitting in $g\perp$ region ($g\perp = 2.3$) is 37 gauss or smaller. Splitting of these magnitudes would be detectable in a reasonably resolved spectrum.

Perhaps the best phrase that describes the EPR spectral characteristics of the dicobalt(II) bis(cyclidene) complexes is dipolar broadening. This effect appears to be intramolecular because the signal shape does not change appreciably upon dilution. Another experiment illustrates this point further. The dicobalt(II) species can be electrochemically oxidized to dicobalt(II/III) and dicobalt(III) states despite their generally irreversible electrochemistry. When one of the two cobalt centers is oxidized, the resulting mixed-valence species exhibits an EPR spectrum typical of mononuclear lacunar complexes in acetonitrile solvent with well-resolved nitrogen superhyperfine structure. This also indicates that the unpaired electron in the mixed-valence species is localized on one metal center at 77K. This is shown in Figure 26 for the dimethylene linked dicobalt species.

Collman et al. have reported seemingly similar spectra for some of their dicobalt porphyrin complexes. Particularly the diporphyrin with the shortest three-atom linkages, Co$_2$(PTF3)$_4$ (denoted in the
Figure 26. EPR Spectral Changes upon Electrolysis of

$[\text{Co}_2(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2)_2(\text{[16]cyclohexadiene})_2]^{4+}$.

(a) Starting Material, (b) Oxidized by One Equivalent at 0.0V (vs. Ag/AgNO$_3$), and (c) Oxidized by Two Equivalents at the Same Potential as (b). (In acetonitrile containing 0.1M TBAB, at room temperature)
Introduction as Co$_2$(L9;R$^1$=CONHCH$_2$), exhibits "one broad transition signal with an isotropic g factor of 2.33" in 1:1 toluene-dichloromethane (frozen solution) with or without added 1-methylimidazol. In addition, Co$_2$(FTF4) (or Co$_2$(L9;R$^2$ = CONH(CH$_2$)$_2$)) is reported to exhibit "a single broad transition signal with g = 2.33". The parallel transition shows "a poorly resolved triplet due to the interaction of the nitrogenous axial base (1-methylimidazole)". These features are somewhat reminiscent of those mentioned above for the dicobalt(II) cyclidene complexes. On the other hand, a series of Co$_2$(FTF4), Co$_2$(FTF5), and Co$_2$(FTF6) show EPR spectra more characteristic of exchange-coupled systems according to the same authors. The extracted zero-field splitting parameters, however, have yielded values for M-M distances that are larger than those determined for analogous dicopper(II) porphyrins by more than 2 Å. The same problem has been encountered with another series of meso-linked diporphyrins, Co$_2$(L10). Obviously a complete description of metal-metal interaction in face-to-face macrocyclic complexes of cobalt(II) requires a more sophisticated analysis. Especially when Co-Co distances are evaluated, the contribution from exchange interaction should not be underestimated. In fact, Collman et al. have tentatively interpreted the isotropic signal and the apparent absence of Co-Co zero-field splitting for Co$_2$(FTF3) system as due to "some orbital interaction enforced by the short distance, giving rise to singlet and triplet states", suggesting significant spin pairing. This interpretation does not apply to the present dicobalt(II) cyclidene complexes where Co-Co distances are as large as 10 Å. A more important factor to consider might be the
deviation from cofaciality which would result in the M-M axis not being coincident with the magnetic vector. Delocalization of each unpaired electron onto the ligand would also make the simple picture of dipolar coupling less applicable. At any rate it is a curious coincidence that the reported cobalt diporphyrins with short Co-Co distances display either monomer-like or ill-defined isotropic EPR signals not unlike those observed with the present nonporphyrin analogues with Co-Co separations that are at least twice as large.

The EPR spectra of dicopper(II) bis(cyclidene) compartmental complexes in acetonitrile solution at 77K are more typically isotropic, as shown in Figure 27. The addition of a coordinating base results in a change of the spectral pattern toward a more axial signal with the hyperfine splitting due to the copper (I=3/2) barely resolved. Super-hyperfine structure due to in-plane nitrogen nuclei, which is readily observed in the $g_{||}$ region for the mononuclear lacunar complex of copper(II), is not resolved, however. These features are similar to those of the dicobalt(II) analogues.

Most notable is the fact that, even in the case of the m-xyylene linked species, the half-field transition ($\Delta M_g = 2$) is detected at around $g = 4$. This signal is normally taken as an indication of exchange coupling in dicopper(II) systems, along with a seven-line pattern in the full-field transition with $A^{Cu}$ being half of that for the mononuclear counterpart. The latter feature is not well-defined here. Zero-field splitting is also not observed. It is surprising that the half-field transition can be detected for a system with a Cu-Cu distance of some 13Å. EPR parameters for the dicopper(II) complexes are given in Table 13.
Figure 27. EPR Spectra of $[\text{Cu}_2\{\text{Me}_2\text{NH})_2\text{mxy1}\}_2\{16\text{cyclidene}\}_2]^{4+}$.

(a) In Acetonitrile Alone and (b) Excess Pyridine Added.

(EPR recorded at 77K)
Table 13. EPR Parameters for Dicopper(II) Bis(cyclidene) Complexes.

| $R^1$   | $R^2$ | Solvent/Base     | $g(\Delta m_s=2)$ | $g_{||}$ | $g_{\perp}$ | $A_{Cu}/G$ | $A_{V}/G$ |
|---------|-------|------------------|-------------------|---------|------------|-----------|-----------|
| $(CH_2)_2$ | H     | acetonitrile     | 3.98$^b$          | 2.03$^c$| -          |           |           |
| $(CH_2)_3$ | H     | acetonitrile     | 4.00$^b$          | 2.04$^c$| -          |           |           |
| mxyl     | H     | acetonitrile     | 3.98$^b$          | 2.04$^c$| -          |           |           |
|          |       | pyridine         | -                 | 2.17    | 2.03       | 188.      |           |
| $(CH_3)$ | $^d$H | acetone          | -                 | 2.14    | 2.02       | 206.      |           |
|          |       | acetone/pyridine | 2.16              | 2.02    | 191.       | 16.8      |           |
| mxyl     | $^e$H | acetone          | -                 | 2.20    | 2.07       | 199.      | 18.       |

a. Estimated from the spectra recorded at 77K.
b. Weak.
c. Nearly isotropic.
d. Unbridged monomeric complex, $[Cu(Me_2(NHMe)_2[16]cycloidene)]^{2+}$ (Ref. 141).
e. Unbridged lacunar complex, $[Cu(Me_2(NH)_{2mxyl}[16]cycloidene)]^{2+}$. 
In summary the magnetic properties of the dicobalt(II) and dicopper(II) bis(cyclidene) complexes qualitatively indicate a weak interaction between the two paramagnetic ions. It is difficult to factor the exchange and dipolar contributions. In the case of cofacial diporphyrins with short M-M distances it is more safely assumed that the dipolar interaction dominates. As the M-M distance becomes larger, the relative contribution from dipolar coupling may decrease rapidly. The mechanism of the very small but detectable exchange interaction is not at all clear.

2.3 Reaction of Dicobalt(II) Compartmental Cyclidene Complexes with Dioxygen.

The work described in this section concerns the reactivity toward dioxygen of the dicobalt(II) compartmental cyclidene complexes, particularly those of the relatively short dimethylene linked species, [Co₂((Me₂(NH)₂CH₂CH₂)₂[16]cyclidene)₂]⁴⁺, and the one with long m-xylylene linking groups, [Co₂((Me₂(NH)₂mxy)₂[16]cyclidene)₂]⁴⁺. It is clear from the discussion in the previous section that the binuclear dicobalt(II) complexes of interest here are characterized as bimetallic systems having flexible molecular cavities, which are large enough to preclude strong metal-metal interaction and which, in turn, eliminates the possibility that the binuclear complex might undergo a simultaneous two-electron redox process. In addition, Chang has claimed that metal-metal separations of 5.4Å or greater, in similar compartmental complexes, favor the binding of two dioxygen molecules, one to each metal ion. Therefore, these compartmental cyclidene complexes are expected to undergo oxygenation reaction with a 1:1 (Co:O₂) stoichiome-
try, unlike some of the diporphyrin systems mentioned in the Introduction.

2.3.1 Formation and Decomposition of Dioxygen Adducts of Dicobalt(II) Complexes.

Reversible oxidation potentials are not observed; however, the values for the peak potentials suggest that the cobalt(II) centers in the compartmental cyclidene complexes should have dioxygen affinities similar to those of the lacunar complexes of cobalt(II). Therefore the oxygenation reaction was first studied in the presence of 1-methylimidazole in order to facilitate comparison. When an acetone/1-MeIm solution of the dicobalt(II) complex is exposed to air at room temperature, the cobalt(II) is rapidly oxidized to cobalt(III). This occurs for the four complexes having as bridge groups, dimethylene (both \( R^2 = H \) and \( CH_3 \)), trimethylene, and \( m \)-xyylene. Figure 28 illustrates this process, showing EPR spectral changes for the \( m \)-xyylene-linked complex upon oxygenation. The axial signal due to cobalt(II) completely disappears after exposure to air for 60 seconds. The resulting small signal at \( g \approx 2 \) indicates that only a small amount of paramagnetic species remains. This rapid autooxidation is in marked contrast to the lacunar family of cobalt(II) dioxygen carriers. For instance, \([Co(1-MeIm)\{Me_2(NR^2)_2(CH_2)_6[16]cyciidene\}]^{2+}\) complexes form 1:1 Co:O_2 adducts, that autooxidize with halflives of 4100 seconds \( (R^2 = H) \) and 6300 seconds \( (R^2 = CH_3) \), respectively, at 20°C. The dinuclear cobalt(II) complexes are also believed to bind dioxygen but the resulting dinuclear dioxygen adducts seem to undergo a further, very rapid, irreversible reaction.
Figure 28. Changes in EPR Spectra that Accompany the Reaction of

\[
\text{[(Co(1-MeIm))}_2(\text{Me}_2\text{NH}_2\text{mxyyl})_2(\text{[16]cyclidene}_2)_2]}^{4+}
\]

with Air at Room Temperature.

(In acetone containing 1-MeIm, EPR recorded at 77K)
Evidence for the formation of dioxygen adducts by the dicobalt(II) species was obtained at low temperatures. Figure 29 shows the use of EPR to show the time course of formation and decomposition of the dioxygen adduct of \([(\text{Co}(1-\text{MeIm}))_2(\text{Me}_2(\text{NH})_2\text{mxy1})_2(\text{[16]cyclidene})_2)]^{3+}\) at 

\[-40^\circ\text{C}\]

in the presence of 0.1 torr of dioxygen. The axial signal at \(g^e = 2, g^\perp = 1.98, g^\parallel = 2.05\) and \(A^\perp = 16.7 \text{ Gauss}\) is characteristic of 1:1 \(\text{Co}:\text{O}_2\) adducts.\(^{117}\) It is noted that, after only 20 seconds of exposure, the intensity of this signal does not account for all of the cobalt that is present. As a rule of thumb, the EPR signals for 1:1 \(\text{Co}:\text{O}_2\) adducts are about ten times more intense than the corresponding low spin cobalt(II) signal. On this basis the above signal corresponds to, at most, roughly 20\% of the starting cobalt(II). This signal disappears with time, and exposure to pure oxygen does not restore its intensity. Therefore this complex must have an enormous affinity toward dioxygen and, further, the resulting \((\text{Co}:\text{O}_2)_2\) complex must decay to a diamagnetic species very rapidly even at 

\[-40^\circ\text{C}\].

In contrast, the dimethylene linked complex \((R^2 = \text{H})\) of dicobalt(II) exhibited a different behavior at low temperature. The reaction of this complex with 0.1 torr of oxygen at 

\[-45.3^\circ\text{C}\]

was monitored by EPR spectra and the results are shown in Figure 30. First of all, most of the cobalt(II) forms the 1:1 \(\text{Co}:\text{O}_2\) adduct and this \(\text{O}_2\) complex persists. Initially nitrogen superhyperfine coupling is not resolved in the signal due to cobalt(II). However exposure to 0.1 torr of oxygen for 20 seconds results in improved resolution. When all of the low spin cobalt(II) signal disappears (400 seconds exposure), the height of the signal from the cobalt-dioxygen adduct is about 3.7 times that of the
Figure 29. EPR Spectral Changes that Accompany the Reaction of

\[ [(\text{Co}(1-\text{MeIm}))_2((\text{Me}_2\text{NH})_2\text{mxy})_2([16\text{cycloidene}])_2)]^{4+} \]

with \( O_2/N_2 \) at \(-40^\circ\text{C}\).

(In acetone containing 1-MeIm, EPR recorded at 77K)
Figure 30. EPR Spectral Changes that Accompany the Reaction of

\[
[(\text{Co}(1\text{-MeIm}))_2((\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2([16]\text{cyclidene})_2)]^{4+}
\]

with \(O_2/N_2\) at \(-45.3^\circ C\).

(In acetone containing 1-MeIm, EPR recorded at 77K)
initial cobalt(II) signal. At this point, the addition of pure oxygen leads only to a slight change in the intensity and shape of the signal. The EPR signal of this fully oxygenated species is unusual in shape. It displays a small component at $g = 1.84$, which causes the $g_\perp$ region to appear somewhat different from that typical of Co:O$_2$ adducts. This may indicate a considerably distorted geometry for the Co-O$_2$ moiety in this species.

The unusual behavior described above can be rationalized adequately by assuming that the O$_2$ adduct has Structure XI. One of the cobalt centers has been oxidized to cobalt(III) and the other site forms the 1:1 Co:O$_2$ adduct. Since the cobalt(III) center is almost certain to be 6-coordinate with two axial base (1-MeIm) molecules, one of them can fill much of the space in the molecular cavity, thereby creating a lacuna into which dioxygen can enter and bind to the remaining cobalt(II) center. It is assumed here that the first cobalt(II) center has an oxygen affinity as high as the two independent cobalt(II) sites in the m-xylylene bridged complex and that it is also as highly susceptible to oxidation. The second cobalt(II) site also must have a high oxygen binding constant ($P_{1/2} < 0.1$ torr) but the stability of the bound dioxygen seems to be greatly enhanced. The possible interaction
of this bound oxygen with either the 1-MeIm or the cobalt(III) center may explain the unusual shape of the EPR signal.

Without a quantitative evaluation of the EPR signals the Co/O₂ composition is presently somewhat speculative. However, an experiment carried out in the absence of such a strong axial base as 1-MeIm demonstrates the generation of an intense EPR signal ascribed to (CoO₂)₂ species. Figure 31 compares the EPR spectra of the unoxygenated dimethylene derivative in acetone and its oxygen adduct (760 torr O₂, bubbling for 200 seconds, at -45.5°C). The latter spectrum is not well resolved, perhaps due to dipolar broadening interaction between the two CoO₂ moieties. However, the peak-to-peak height amounts to about twelve times that of initial cobalt(II) signal.

Similar behavior was observed for the same dimethylene linked complex in dichloromethane. It is not clear whether some species serves as an axial ligand for the cobalt(II) complex and its dioxygen adduct in this medium. At -46.0°C the fully oxygenated solution exhibits roughly isotropic signal centered at g = 2.00. The intensity of this signal is about ten times that of the initial cobalt(II) signal. This signal has absolutely no hyperfine structure but the peak-to-peak separation of 80 gauss is not consistent with the presence of an organic radical species. Therefore a (CoO₂)₂ species is assumed to be present and the broadening is attributed to the spin-spin relaxation.

The oxygenation behavior of the dimethylene-bridged complex in acetonitrile and pyridine solvents at low temperatures is intermediate between the two extreme cases (with strongly coordinating base and in weakly coordinating solvents) mentioned above. The EPR parameters for
Figure 31. EPR Spectral Changes upon Oxygenation of

\[ \text{[Co}_2\{\text{Me}_2\text{(NH)}_2\text{CH}_2\text{CH}_2\}_2\{\text{[16]cyclidene}_2\}_2\}^{4+} \]

in Acetone at -45.5°C. (EPR recorded at 77K)
the cobalt-dioxygen adducts observed in various media are summarized in Table 14.

A question arises as to whether, or to what extent, the formation of these dioxygen adducts is reversible. The reversibility and equilibrium of dioxygen binding are better studied by monitoring electronic absorption spectra. Figure 32 exemplifies absorption spectral changes for the dimethylene linked dicobalt(II) complex, dissolved in acetone alone, upon repetitive alternate bubbling of full atmospheric pressures of oxygen and nitrogen. The visible spectrum of the unoxygenated material is featureless. Upon bubbling pure oxygen for 120 seconds at -44.1°C, a distinct band grows in at 522 nm, which disappears completely upon purging with nitrogen. Thus the process is reversible at this temperature. Figure 33 shows the absorption spectral changes that accompany the introduction of various partial pressures of oxygen to the same system. The spectra appear to go through two isosbestic points, 479 nm at low pressures of oxygen and 475 nm at higher pressures. This may or may not represent stepwise dioxygen binding. Even a slow irreversible side reaction could displace the initial isosbestic point. However, the behavior is consistent with the expectation that both a (CoO₂/Co) adduct and a (CoO₂)_2 adduct form, if the two complexes have similar absorption spectra in this region (apparent P_{1/2} = 10 torr). If 1-MeIm is coordinated to the cobalt atoms, the corresponding band appears as a shoulder at around 500 nm upon full oxygenation and extensive flushing with nitrogen leads only to a slight decrease in absorbance, suggesting the progress of an irreversible process that follows the formation of (CoO₂)_2 adduct.
Table 14. EPR Parameters for Dioxygen Adducts of Dicobalt(II) Bis(cyclidene) Complexes.

| $R^1$ | $R^2$ | Solvent/Base            | $g_{||}$ | $A_{CO}^G$ | $g_J$ | $\Delta_{P,P}$ |
|-------|-------|-------------------------|----------|------------|-------|---------------|
| mxy1  | H     | acetonitrile/1-MeIm     | 2.05     | 16.7       | 1.98  | -             |
|       |       | pyridine                | 2.00     | -          | -     | 100           |
|       |       | acetonitrile            | 2.02     | -          | -     | 130           |
| (CH$_2$)$_3$ | H     | acetonitrile/1-MeIm     | 2.11     | 17.2       | 2.03  | -             |
| (CH$_2$)$_2$ | CH$_3$ | acetonitrile           | 2.00     | -          | -     | 125           |
| (CH$_2$)$_2$ | H     | acetonitrile/1-MeIm     | 2.06     | 17.2       | 1.99$^b$ | -             |
|       |       | acetonitrile/1-MeIm     | 2.00     | -          | -     | 140           |
|       |       | pyridine                | 2.01     | -          | -     | 160           |
|       |       | acetonitrile            | 2.03     | -          | -     | 130           |
|       |       | acetone                 | 2.03     | -          | -     | 132           |
|       |       | dichloromethane         | 2.00     | -          | -     | 80            |

a. Peak to peak separation for unresolved signal.
b. Partial oxygenation at $P_{O_2} = 0.1$ torr.
c. Full oxygenation at $P_{O_2} = 740$ torr.
Figure 32. Visible Absorption Spectral Changes Showing Reversible Oxygenation of $[\text{Co}_2((\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2)(\text{[16]cyclopenta})(2)]^{4+}$ in Acetone at $-44.1^\circ\text{C}$.
Figure 33. Visible Absorption Spectral Changes upon Exposure of 
\[ \text{Co}_2\{(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2\}_2\{\text{[16}\text{cyclidene}\}_2\}]^{2+} \text{ in Acetone} 
\text{to Various Pressures of Dioxygen at -43.4°C.}
The reaction scheme shown below is based on the observations described above and seems to apply to all the dicobalt(II) compartmental cyclidine complexes.

\[
\text{BCo} \quad \text{CoB} + O_2 \xrightarrow{K_1} \text{BCoO}_2 \quad \text{CoB} \quad (1)
\]

\[
\text{BCoO}_2 \quad \text{CoB} + O_2 \xrightarrow{K_2} \text{BCoO}_2 \quad \text{O}_2\text{CoB} \quad (2)
\]

\[
\text{BCoO}_2 \quad \text{CoB} \xrightarrow{B} \text{BCo}^{\text{III}} \quad \text{CoB} + O_2^- \quad (3)
\]

\[
\text{BCoO}_2 \quad \text{O}_2\text{CoB} \xrightarrow{B} \text{BCo}^{\text{III}} \quad \text{O}_2\text{CoB} + O_2^- \quad (4)
\]

\[
\text{BCo}^{\text{III}} \quad \text{O}_2\text{CoB} \xrightarrow{B} \text{BCo}^{\text{III}} \quad \text{BCo}^{\text{III}} + O_2^- \quad (5)
\]

\[
\text{BCo}^{\text{III}} \quad \text{CoB} + O_2 \xrightarrow{K_3} \text{BCo}^{\text{III}} \quad \text{O}_2\text{CoB} \quad (6)
\]

Reactions (1) and (2) represent the reversible binding of two dioxygen molecules. Either or both of the dioxygen adducts (formed in reactions (1) and (2)) can undergo irreversible oxidation. This process seems to
be strongly promoted when $B$ is a strong base. This produces a unique lacunar complex in which the bridging group contains a trivalent metal ion, and this novel species forms a dioxygen adduct. The bridging group $R^1$ seems to have a pronounced effect on the stability of the latter species.

The above scheme was constructed in order to account for the results obtained at low temperatures ($-40^\circ\text{C}$ to $-45^\circ\text{C}$). The reaction of the binuclear cobalt(II) complex with dioxygen compares to those of unbridged and/or lacunar families of cyclidene complexes. The identified reaction products included in the above scheme find precedents among mononuclear cyclidene complexes of cobalt(II). It is noted, however, that no evidence is available on the identity of the EPR silent species, which is generally designated as Co(III)B$_2$. For instance, it is plausible that the superoxide in the partially oxygenated species ($\text{CoO}_2/\text{Co}$), formed in the reaction (1) can oxidize the second cobalt(II) ion as indicated in Equation (7) instead of dissociating from the cobalt(III) as assumed in reaction (3).

\[
\begin{align*}
\text{BCo}_2 & \quad \text{Co}^{II}B \quad B \to \quad \text{BCo}^{III}B \quad \text{O}_2^{2-} \quad \text{Co}^{III}R \\
\end{align*}
\]

The resulting peroxo complex ($\text{Co(III)/O}_2^{2-}\text{Co(III)}$) would also be EPR silent. This reaction constitutes a two-electron process that may provide the basis for the distinction in behaviors between the binuclear complexes and their mononuclear counterparts. This may be important
particularly at low pressures of dioxygen. If the peroxide is dissociated from the cobalt, the reaction leads to the same result as though two one-electron processes had occurred, since the superoxide ions rapidly disproportionate to peroxide and dioxygen in the presence of protons (HA),\textsuperscript{118} which in the present case could well come from the \( R^2 \) groups of the ligand.

\[
O_2^- + HA \rightleftharpoons H_2O_2 + A^- \quad (8)
\]

\[
2H_2O_2 \rightarrow O_2 + H_2O_2 \quad \text{fast} \quad (9)
\]

\[
O_2^- + H_2O_2 \rightarrow O_2 + HO_2^- \quad \text{fast} \quad (10)
\]

It is noted that free superoxide, which is easily detectable by EPR if stabilized in certain media (an axial signal with \( g_{xx} = 2.083 \) and \( g = 2.008 \) in acetonitrile at 77K),\textsuperscript{118a} has not been observed in any dioxygen reaction of the present dicobalt(II) complexes. Thus the reactions (3)-(5) are most likely to be followed by the rapid reactions (9) and (10). The unfavorable dissociation of a peroxide ion in an aprotic medium may result from the deprotonation of the cyclidene ligand. Therefore a distinction between the two-electron and two one-electron pathways remain ambiguous in the absence of direct evidence for the peroxo-bound dicobalt(III) species.

Since the rate of disproportionation of the superoxide ions depends on the acidity of HA (reaction (8)), it is also possible (but less likely) that the superoxide acts as an outer-sphere reductant to the
cobalt(III) species. If the products in the reactions (3) - (5) are reduced back to cobalt(II) species in this manner, the equilibria (1) and (2) would be reestablished. This pathway is no faster than the rate of disappearance of cobalt(II) and cobalt-dioxygen complexes.

Another possibility for the formulation of the EPR silent component(s) cannot be entirely ruled out. An intermolecular \(\mu\)-peroxo complex, as shown below, may be formed if one base molecule can occupy the cavity.

\[
2\text{BCo}^{\text{II}} + \text{O}_2 \rightleftharpoons \text{BCo}^{\text{II}} - \text{O}_2^{\text{2-}} - \text{Co}^{\text{III}} \text{B} \text{Co}^{\text{II}} \quad (11)
\]

It has been shown that these binuclear compartmental cyclidene molecules are asymmetric, particularly at low temperatures. Therefore an asymmetric base adduct in which one of the base molecules is located inside the molecular cavity cannot be ruled out. The \(\mu\)-peroxo complex derived from such a base adduct could by itself account for 50% of the EPR silence at low pressures of oxygen. This model does not account for the fact that, in the EPR spectral studies shown in Figures 29 and 30, the introduction of excess dioxygen to the sample solution after treatment by 0.1 torr of dioxygen did not effect further spectral change. That result suggests that the species formed at the 0.1 torr level are mostly no longer reactive towards dioxygen. On the other hand, the \(\mu\)-peroxo complex of cobalt(III) should be converted back to 1:1 Co:O\(_2\) adducts when more dioxygen is introduced and this should
result in the growth of the characteristic EPR signal, if the formation equilibrium constant for the μ-peroxo complex is sufficiently small.

2.3.2 Kinetic Investigation of Autoxidation of Dicobalt(II) Complexes at Room Temperature.

The reaction of the dicobalt(II) complexes with dioxygen is difficult to delineate due to many possible reaction pathways following binding of dioxygen. A kinetic study was undertaken in an attempt to distinguish further between the possibilities.

The kinetics of the autoxidation reaction of these binuclear species were studied at room temperature and compared to those of their mononuclear counterparts. The autoxidation process at 25°C was studied by spectrophotometric means in the ultraviolet region for all four dicobalt(II) complexes having dimethylene (for both \( R^2 = H \) and \( CH_3 \)), trimethylene and \( m \)-xylylene links. An intense charge transfer absorption at around 340 nm allows the use of dilute solutions of the cobalt(II) complexes (3 x 10^{-5} M) and, in turn, pseudo-first order condition for the reaction since the concentration of dioxygen is estimated to be at least 2.5 x 10^{-4} M in organic solvents. The solvent system was 1.24 M pyridine in acetone; it was chosen since the moderately strong base pyridine is expected to yield a measurable autoxidation rate and also because the axial base binding equilibrium can still be saturated at available concentrations. The reaction was initiated by injecting a small aliquot of an anaerobically prepared acetone/pyridine solution of the dicobalt(II) complex into the same solvent system saturated with dioxygen. The absorbance at 340 nm was monitored for three to four apparent halflives and the data were fitted
to the first order rate law using the Kezdy-Swinbourne method (τ = 500-1000 seconds). A typical first order plot is given in Figure 34 for [(Co(py))₂{(Me₂(NH)₂mxyl)₂[[16]Cyclidene]₂}]⁴⁺. As can be seen, the kinetic behavior is biphasic and both phases appear to be first order in the dicobalt(II) complex in the presence of excess dioxygen. This was true for all four complexes studied. The observed rate constants, \( k_{\text{obs}}^{(1)} \) and \( k_{\text{obs}}^{(2)} \) are given in Table 15.

\[
-d[\text{O}_2]/dt = k_{\text{obs}}^{(1)}[\text{Co}_2][\text{O}_2]^{X[B]Y} + k_{\text{obs}}^{(2)}[\text{Co}_2][\text{O}_2]^{X'[B]Y'}
\]  

(12)

The \( k_{\text{obs}}^{(1)} \) values are less accurate owing to the data manipulation, including extrapolation from the second phase. The last entry applies to an unbridged mononuclear complex of cobalt(II), which yielded a similar overall kinetic profile. The observed rate constant for autoxidation of this complex is comparable to that determined by Evans⁴ for a lacunar complex \([\text{Co}(\text{Me}_2(\text{NMe})_2(\text{CH}_2)_5[[16]\text{Cyclidene}])^2⁺\), which also displayed biphasic kinetics. A marked contrast that the present binuclear complexes shows is that the magnitude of the observed rate constants is five to ten times greater than those of their mononuclear counterparts. In other words, the presence of an additional cobalt(II) center accelerates the rate at which the complexes are oxidized.

Extrapolation from the results obtained at low temperatures suggests that the dioxygen does bind to the cobalt(II) centers and that the subsequent irreversible reaction depletes the cobalt-dioxygen adducts.
Figure 34. First-Order Plot for the Reaction Between

\[ [\text{Co}_2((\text{MeNH}_2)_2\text{mxy})_2(\text{F}16]\text{cyclidene})_2]^\text{II}^+ \text{ and Dioxogen in}

Acetone/Pyridine at 25.0°C. ([Co\(_2\)] = 2.65 \times 10^{-5} \text{ M},

[py] = 1.24 \text{ M}, P_{O_2} = 744 \text{ torr, absorbance monitored at 350 nm}]\]
### Table 15. Rate Data for the Reaction of 

\[ [(\text{Co(py)})_2(\text{Me}_2(\text{NR}^2)_{2\text{R}_1})_2([16]\text{cyclidene})_2)]^4+ \text{ with Dioxygen in Acetone/Pyridine. } ([\text{py}] = 1.24 \text{M}) \]

<table>
<thead>
<tr>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>T/°C&lt;sup&gt;d&lt;/sup&gt;</th>
<th>k&lt;sub&gt;obs&lt;/sub&gt;&lt;sup&gt;(1)&lt;/sup&gt;x10&lt;sup&gt;3&lt;/sup&gt;/sec&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;(1)a&lt;/sup&gt;</th>
<th>k&lt;sub&gt;obs&lt;/sub&gt;&lt;sup&gt;(2)&lt;/sup&gt;x10&lt;sup&gt;4&lt;/sup&gt;/sec&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;(2)a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>mxyl</td>
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<tr>
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<tr>
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<td>2.36</td>
<td>0.9994</td>
</tr>
<tr>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>13.</td>
<td>0.9993</td>
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<tr>
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<td>-</td>
<td>1.67</td>
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<tr>
<td></td>
<td></td>
<td>25.0</td>
<td>-</td>
<td>-</td>
<td>1.28</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

- **a.** Correlation coefficient for the first-order linear plot.  
- **b.** Unbridged monomeric complex.  
- **c.** Determined by using a bubbling cell; the kinetics is biphasic, but the rate constant is not available for the first phase.  
- **d.** ±0.1°C.
There is a fundamental difference in the absorption spectral change between the dicobalt(II) and mononuclear cobalt(II) complexes with cyclidene ligands. The two absorption bands in the ultraviolet region of the mononuclear cobalt(II) complex change only slightly, forming one band of comparable or slightly higher extinction coefficient when the complex is converted completely to 1:1 Co:O₂ adduct. The band gradually diminishes with time. In contrast, the absorbance of the dicobalt(II) complex shows a large decrease immediately after oxygenation before measurement begins. These behaviors are compared in Figure 35. The absorbance change with time (after bubbling pure oxygen for 100 seconds, acetone/pyridine solution) is compared for mononuclear and binuclear cyclidene complexes of cobalt(II). The absorbance at t = 0 represents the unoxygenated complex. It is suggested that nearly half of the cobalt(II) centers in the binuclear species have already been oxidized within the first 50 seconds. The rate data obtained at low temperatures for the m-xylylene linked complex show that the observed rate constants decrease both in the first and the second phases as the temperature is lowered (Table 15). The absorbance change upon oxygenation at lower temperatures is closer to that associated with decay of the mononuclear 1:1 Co:O₂ adduct. Although two forms of dioxygen adducts are possible for the binuclear cobalt(II) complexes, (CoO₂/Co) and (CoO₂)₂ (reactions (1) and (2)), the relative amounts can not be estimated. The results obtained at -40° to -45°C suggested very large oxygen binding constants and it seems reasonable to assume that the binding constants are sufficiently high to form mainly a binuclear (CoO₂)₂ adduct even at room temperature. Therefore the fully oxygenated species, (CoO₂)₂, is considered first.
Figure 35. Change in Absorbance with Time After Exposure of
Cobalt(II) Cyclidene Complexes to Dioxygen at 25.0°C.

(a) \([\text{Co(py)}(\text{Me}_2\text{NMe}_2)_2[16]\text{cyclidene}]^{2+}\),

(b) \([(\text{Co(py)})_2(\text{Me}_2\text{N}(\text{H})\text{mxy})_2[[16]\text{cyclidene}_2]]^{4+}\).
The biphasic autoxidation has been commonly observed among mono­
nuclear lacunar complexes. The two phases have been fitted to first­
order kinetics involving the 1:1 Co:O₂ adduct. Thus, if the Co:O₂
moieties in the binuclear (CoO₂)₂ adduct in the present case decay inde­
dependently of each other at room temperature, the autoxidation mechanism
for the lacunar complexes may apply to the compartmental cyclidene
complexes as well. The biphasic decay of (CoO₂)₂ may or may not repre­
sent the stepwise dissociation of superoxide anions as in reactions (4)
and (5). The biphasic kinetics do not require of the first cobalt site
reaction to be slow enough to be measurable because the product of such
a first reaction, which is a lacunar complex, could well go through
biphasic reactions by itself as do other lacunar complexes.¹²⁰

Such a biphasic kinetics may be accounted for by parallel reactions
involving, for instance, two types of dioxygen adducts as shown below.

\[
\text{Co(II)}L'B + O_2 \overset{K'}{\underset{K''}{\rightleftharpoons}} \text{Col'B0₂} \quad (13)
\]

\[
\text{Col'B0₂} + B \rightarrow \text{Col'B'O₂} + BH^+ \quad (14)
\]

\[
\text{Co(II)L'B} + O_2 \overset{K''}{\underset{K'\prime}{\rightleftharpoons}} \text{Col'B0₂} \quad (15)
\]

\[
\text{Col'B0₂} \overset{B}{\rightarrow} \text{Co(III)L'B₂} + O_2^- \quad (16)
\]

\[
\text{Col'B0₂} \overset{B}{\rightarrow} \text{Co(III)L'B₂} + O_2^- \quad (17)
\]
The dioxygen adduct of the starting cobalt(II) complex becomes deprotonated to generate CoL*BO₂ in the reaction (14), and the two dioxygen adducts, CoLBO₂ and CoL'BO₂, decompose separately. For the dicobalt(II/III) lacunar complexes, such a deprotonation of the ligand should provide a facile pathway because the \( R^2 = H \) protons on the ligands are expected to be quite acidic. However, the fact that the N-methylated analogue of the dimethylene linked dicobalt(II) complex autoxidizes at comparable rate, or even more rapidly, than the \( R^2 = H \) analogue argues against a deprotonation of this type being the rate limiting step.

The rate of oxidation of the second cobalt center in the (Co(III)B₂/CoBO₂) species is expected to vary depending on the stability of the CoO₂ adduct. However, despite of the observed longevity at −45°C of an (CoO₂/Co(III)) adduct derived from \( \left[(\text{Co(NMim)})_2\left(\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2\right)_2\right]^{-} \left([\text{16} \text{cyclidene}]_2\right)^{4+} \) compared to that involving the \( m \)-xylylene linked complex, the autoxidation kinetics at room temperature are virtually insensitive to the difference in the \( R^1 \) groups. Therefore, a mechanism involving an intermediate, the stability of which is not so much affected by the cavity size, may be more plausible.

Kumar and Endicott have reported that a 1:1 Co:O₂ adduct, \( \text{Co}([\text{14} \text{aneN}_4\text{(H}_2\text{O})]\text{O}_2^{2+}) \) \( ([\text{14} \text{aneN}_4=1,4,8,11\text{-tetraazaacyclotetradecane}) \), autoxidizes more rapidly in the presence of added reducing agents than in its absence, in aqueous media. Among various reducing agents they investigated were the mildly reducing precursor, \( \text{Co}([\text{14} \text{aneN}_4\text{(H}_2\text{O})]_2^{2+}) \) and its 15-membered analogue, \( \text{Co}([\text{15} \text{aneN}_4\text{(H}_2\text{O})]_2^{2+}) \). Both led to formation of an inner sphere \( \mu \)-peroxo complex with the 1:1 Co:O₂
adduct. Strongly reducing agents, \([\text{Ru(NH}_3)_6]^{2+}\), \([\text{V(H}_2\text{O})_6]^{2+}\) and \([\text{Co(sep)}]^{2+}\), effected the decay of the cobalt-dioxygen adduct by the outer sphere reduction. The present dicobalt(II) cyclidene complexes can be pictured as having the additional reducing equivalents within the molecule when the \((\text{CoO}_2/\text{Co})\) adduct is formed. The formation of the intramolecular \(\mu\)-peroxo complex is not likely and therefore the oxidation of the second cobalt(II) center (reaction (7)) must occur either by an outer-sphere electron transfer from the cobalt(II) ion to the \(\text{CoO}_2\) moiety or by the transfer of the superoxide from one cobalt to the other along with concomitant oxidation of that cobalt ion. The former reaction may not be thermodynamically favored but could be driven by subsequent reaction(s). The latter may also involve substitution of the superoxide at the first cobalt site by a base or solvent molecule. Even a small amount of half-oxygenated species would be sufficient to drive the entire system along these pathways, if the half-oxygenated species exists in equilibrium with the fully-oxygenated complex. The reaction mode involving the half-oxygenated complex, \((\text{CoO}_2/\text{Co})\), invokes the transfer of superoxide (or an electron) through the molecular cavity whose size differs only slightly across the series \(\text{R}^1 = \text{dimethylene to m-xylylene}\). The observed biphasic kinetics may represent the dissociation of the superoxide from the first cobalt site followed by dissociation of peroxide from the second.

It is necessary to collect more kinetic data and mechanistically significant information in order to determine the mechanism of the autoxidation of these dicobalt(II) cyclidene complexes. Particularly, the possibility of the intramolecular electron transfer from cobalt(II)
ion to the superoxide bound to the other cobalt site cannot be evaluated without knowledge of the redox reactivity of such a cobalt-dioxygen adduct. Thus the reaction of the dicobalt(II) compartmental cyclidene complexes with dioxygen has not been fully elucidated. It is important to note, however, that the enhanced reactivity of these complexes towards dioxygen possibly stems from their binuclear nature despite the absence of a strong metal-metal interaction.

2.4 Guest-Host Chemistry Involving Binuclear Compartmental Cyclidene Complexes.

The previous sections have revealed that the relatively large and flexible molecular cavity in the compartmental cyclidene complexes is not suited to activate the dioxygen molecule toward 4-electron reduction in a manner similar to that realized in some of the binuclear cobalt(II) porphyrin complexes such as Co₂(FTF₄). It should be remembered that the remarkably accelerated autoxidation process seen among these dicobalt-(II) species suggests that two dioxygen molecules can be highly activated toward further reactions at each end of the binuclear molecules. Therefore another aspect of utilizing the intermetallic space was investigated, namely inclusion of organic molecules into the cavity.

The concept of guest-host association was originally developed for a large domain of organic host molecules, such as cyclodextrin and cyclophane,¹² which serve as hosts having the abilities to bind specific guest molecules without forming covalent bonds. When transition metal complexes are used as hosts, the association interaction can include coordination of the guest molecule to the metal atoms in the
host. In the following subsection, an example of such ligand inclusion complexes, derived from a dicobalt(II) bis(cyclidene) complex, is described. Emphasis is placed on enhanced metal-metal magnetic interaction and related reactivity of the dicobalt(II) complex towards dioxygen. The second subsection describes association of noncoordinating organic substrates to a binuclear cyclidene complex in aqueous media.

2.4.1 Inclusion Complex with a Coordinating Guest.

2.4.1.1 Isolation of a Base Inclusion Adduct of Dicobalt(II) Bis-(cyclidene) Complex, \([\text{Co}_2(4,4^{\prime}-\text{bipy})\{(\text{Me}_2\text{NH})_2\text{mxyl}\}_2([16]\text{cyclidene})_2\}^2\)Br\(_2\)(PF\(_6\))\(_2\). The title complex was prepared by reacting the host complex, \([\text{Co}_2((\text{Me}_2\text{NH})_2\text{mxyl})_2([16]\text{cyclidene})_2]\)^{2+}, with an excess of 4,4'-bipyridine dihydrate in a methanol/water mixture under reflux conditions. The isolated orange solid analyzed well as a 1:1 bis(cyclidene):base adduct.

The EPR spectrum of this material, isolated and redissolved in acetone (Figure 36) provides clear evidence for an exchange interaction between the two cobalt(II) centers. The cobalt hyperfine coupling, resolved in the \(g_{//}\) region (\(A_{//}^\text{Co} = 52.6\) gauss, \(g_1 = 2.29, g_{//} = 2.03\)), is consistent with an electron interacting with both cobalt nuclei. Zero-field splitting is not observed in either the \(g_{//}\) or \(g_1\) region. This is reasonable in the light of the intermetallic distance constrained by the bridging ligand (11.7\(\AA\), estimated from Ru-bipy-Ru\(^{123}\)). The exchange coupling must be mediated by the 4,4'-bipyridine ligand, perhaps primarily through \(\sigma\)-pathway. The \(d_{z^2}\) orbitals of the cobalt atoms may not overlap strongly with the \(\pi\) system of bipyridine. An attempt to
Figure 36. EPR Spectrum of

\[ \text{Co}_2(4,4'-\text{bipy})\{(\text{Me}_2(\text{NH})_2\text{mxyl})_2([16]\text{cyclidene})_2\}^{4+}. \]

(In acetone containing TBAB, EPR recorded at 77K)
prepare a similar base adduct with 4,4'-bipiperidine, a saturated analogue of 4,4'-bipyridine, in order to test this postulate was unsuccessful.

Magnetic moments were determined in solution by Evans' method and the results are given in Table 16. The values for effective magnetic moments are slightly, but significantly, larger than those for the host alone in acetonitrile solvent (Table 11, section 2.2.6) and virtually constant within the temperature range from room temperature down to -40°C. The change in electronic structure of the cobalt(II) center upon coordination of 4,4'-bipyridine may bring about the small increase in net magnetic moment of each cobalt(II) ion.

The enhanced intermetallic magnetic coupling and the formulation as a 1:1 Co₂:B adduct strongly suggest that the 4,4'-bipyridine is internally coordinated, thereby assisting the communication between the two cobalt(II) centers. The mode of reaction of this complex with dioxygen (vide infra) further supports the Structure XII, shown below.
Table 16. Magnetic Moments for [Co₂(4,4'-bipy){(Me₂(NH)₂mxyl)₂([16]cyclooctene)₂}]⁺ in Solution.

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<th>Solvent</th>
<th>T/K</th>
<th>(\mu_{\text{eff}}/\text{B.M.})</th>
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<tr>
<td>acetonitrile</td>
<td>233</td>
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<td>256</td>
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<tr>
<td></td>
<td>287</td>
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</table>

a. Determined by Evans' method. Concentration; 22.2 mM (acetonitrile), 17.5 mM (9:1 acetonitrile:acetone), 19.8 mM (1:2 acetonitrile:acetone), and 5.54 mM (acetone).

b. Calculated per metal atom. Corrected for ligand diamagnetism and solvent volume contraction at low temperatures, ± 0.05 B.M.
Since the axial base binding to cobalt(II) macrocyclic complexes is an equilibrium phenomenon, the inclusion complex forms in solution together with other types of base adduct:

\[ \text{Co} + \text{BB} \rightleftharpoons \text{Co-BB} \quad K_1 \quad (18) \]

\[ \text{Co-BB} \rightleftharpoons \text{Co-BB-Co} \quad K_2 \quad (19) \]

\[ \text{Co} + \text{BB} \rightleftharpoons \text{Co-Co-BB} \quad K'_1 \quad (20) \]

\[ \text{Co-BB} + \text{BB} \rightleftharpoons \text{BB-Co-Co-BB} \quad K'_2 \quad (21) \]

\[ \text{Co-Co-BB} + \text{Co} \rightleftharpoons \text{Co-Co-BB-Co} \quad K''_2 \quad (22) \]

Equation (22) represents formation of intermolecular polynuclear adducts but \( K''_2 \) can be assumed to be small in the presence of a large amount of base that is fairly strongly coordinating. Nevertheless, the equilibrium system is very complicated. In the particular case of 4,4'-bipyridine adduct of \( m \)-xylylene linked bis(cyclidene) complex of dicobalt(II), the equilibrium constant \( K_2 \) must be large enough to
facilitate isolation of the novel inclusion complex under the reaction conditions. In order to gain some insight into such a stabilization effect, a quantitative study of the axial base binding equilibria was carried out, using the mononuclear counterparts.

When a monodentate base is added to an acetone solution of the mononuclear unbridged complex, $[\text{Co}\{\text{Me}_2(\text{NMe}_2)_2[16]\text{cycloidene}\}]^{2+}$, the following single equilibrium is sufficient to describe the base binding.

$$\text{CoL} + B \rightleftharpoons \text{CoLB} \quad K_1 \quad (23)$$

The binding constants were determined by the method described by Stevens with some modifications for $B = \text{pyridine}$ and acetonitrile in acetone solvent. The absorption spectral change in the NIR region (Co(II) d-d transition) used in the determination is exemplified in Figure 37 and the results are given in Table 17. When 4,4'-hipyridine was used, the apparent spectral change was similar to that for $B = \text{pyridine}$ but isosbestic points were not as sharply defined. Accordingly the absorbance data did not fit to the above equilibrium. The two equilibria shown below yielded a better fit (Table 17).

$$\text{CoL} + BB \rightleftharpoons \text{CoL}(BB) \quad K_1 \quad (24)$$

$$\text{CoL} + \text{CoL}(BB) \rightleftharpoons \text{(CoL)}_2(BB) \quad K_2 \quad (25)$$
Figure 37. NIR Absorption Spectral Change of

$[\text{Co}(\text{Me}_2(\text{NMMe})_2[16]\text{cyclidene})]^2^+ \text{ in Acetone Upon Titration}$

With Pyridine. ([Co] = 1.01 x 10^-2 M throughout, 25.0°C)
Table 17. Axial Base Binding Constants$^a$ for 

$[\text{Co} \{\text{Me}_2(\text{NMe}_2)_2[16]\text{cyclidene}\}]^{2+}$ in Acetone (25.0°C).

<table>
<thead>
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<th>Base</th>
<th>$K_1^b$/M$^{-1}$</th>
<th>$K_2^c$/M$^{-1}$</th>
</tr>
</thead>
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<tr>
<td>acetonitrile</td>
<td>2.41±0.22</td>
<td>-</td>
</tr>
<tr>
<td>pyridine</td>
<td>288±21</td>
<td>-</td>
</tr>
<tr>
<td>4,4'-bipyridine</td>
<td>102.56±0.12</td>
<td>101.67±0.10</td>
</tr>
</tbody>
</table>

a. Determined at $\lambda_{\text{max}}$ of absorption band due to the base adduct; 790 nm
for $B$ = acetonitrile and 740 nm for $B$ = pyridine and 4,4'-bipyridine.

b. Equation (23) for $B$ = acetonitrile and pyridine and Equation (24) for $B$ = 4,4'-bipy.

c. Equation (25).

The greater value for $K_1$ (24) than $K_1$ (23) can be accounted for by the increased base strength of 4,4'-bipyridine. The value for $K_2$ (25) corresponds to the process (19) for the binuclear complex and provides an estimate of contribution to $K_2$ (19) based solely on the ligand strength. The ligand CoL(BB) does not retain the base strength of BB and therefore the large equilibrium constant $K_2$ expected for the process (19) should be attributed to an entropic factor (essentially a chelate effect) and perhaps a specific guest-host interaction of some sort (hydrophobic). Finally the binding constant for $B$ = acetonitrile indicates that acetonitrile will not compete well with pyridyl type ligands.

The dimeric adduct of 4,4'-bipyridine formed in the reaction (25), $[\text{Co} \{\text{Me}_2(\text{NMe}_2)_2[16]\text{cyclidene}\}]^{2+}(4,4'-\text{bipy})^{4+}$ was isolated previously by Dose$^{125}$ as a tetra(hexafluorophosphate) salt from methanol solution.
A concentrated solution of this material in acetone exhibits an EPR spectrum very similar to that of \([\text{Co}_2(4,4'-\text{bipy})\{(\text{Me}_2\text{NH})_2\text{mxyld})_2-([16]\text{cyclidene})_2]^4+\) (Figure 38(a), \(g_{//} = 2.00, g_\perp = 2.21, A_{CO}^0 = 49.7\) gauss), demonstrating the ability of 4,4'-bipyridine to bridge two cobalt(II) cyclidene units. However, the EPR spectrum changes drastically upon dilution to what appears to be a mixture of \((\text{CoL})_2(\text{BB})\) and \(\text{CoL}(\text{BB})\). The latter gives a typical monomeric spectrum (Figure 38(b)). Therefore the dimeric base adduct \((\text{CoL})_2(\text{BB})\) is not an equilibrium favored species and does not retain its integrity at concentrations about 0.4 mM or below. Such a concentration effect on the EPR spectrum is not observed with the inclusion adduct of dicobalt(II) bis(cyclidene) complex.

A strong base such as 1-MeIm does, however, displace the 4,4'-bipyridine. The EPR spectrum of the base inclusion adduct characteristic of a coupled metal pair reverts to the pattern for an uncoupled system upon addition of 1-MeIm.

Since the base inclusion adduct yields a characteristic EPR signal, the equilibrium mixture was examined by EPR. Figure 39 shows an EPR spectrum of \([\text{Co}_2\{\text{Me}_2\text{NH})_2\text{mxyld})_2([16]\text{cyclidene})_2]^4+\) in acetonitrile in the presence of excess 4,4'-bipyridine. The resolution in the \(g_{//}\) region is very poor but shows an indication of narrow cobalt hyperfine coupling along with a broad \(g_\perp\) lobe. When pyrazine, which has been more widely used as a good bridging ligand, is used instead of 4,4'-bipyridine, the EPR spectrum of the mixture is indicative more of the \((\text{CoB})_2\) adduct. Since pyrazine is not capable of bridging between the two cobalt atoms in the \(m\)-xyylene linked bis(cyclidene) complex, there
Figure 38. EPR Spectra of 

$[\text{Co}(\text{Me}_2\text{NMe}_2)_2(\text{16}\text{-cyclidene})_2(4,4'-\text{bipy})(\text{PF}_6)_4]$ Dissolved in Acetone. (a) 1.09 mM and (b) 0.351 mM.

(Solvent contained TBAB, EPR recorded at 77K)
Figure 39. EPR Spectrum of 

\[ \text{[Co}_2((\text{Me}_2\text{NH})_2\text{mxyl})_2([16]\text{cyclidene})_2)]^{4+} \] in the
Presence of Excess 4,4'-Bipyridine.

(In acetonitrile, EPR recorded at 77K)
appears to be little driving force for the base to reside inside the cavity. This demonstrates the necessity of appropriate matching of the size of the base and the cavity of the host molecule, although the steric requirements are probably not very stringent with compartmental bis(cyclidene) compounds having flexible linking groups. The EPR assessment of formation of desired base inclusion complexes for different combinations of dicobalt(II) bis(cyclidene) hosts and bridging ligands is summarized in Table 18. The dimethylene-linked complex (R² = H) generally displays axial signals attributable largely to species of the type (CoB)₂ in the presence of excess amino or pyridyl-type ligands, but the cobalt hyperfine structure is commonly broadened compared to the spectra of systems containing monofunctional bases, indicating that substantial amounts of magnetically coupled species are formed. This dicobalt(II) host (with base unbound) gives a very broad EPR signal by itself in acetonitrile or acetone solvent, but the generally sharper g₁ lobes of EPR signals for the base mixtures are taken to arise from base-bound species. The g' values (at the peak of g₁ lobe) in Table 18 are given to show this feature.

The title compound is thus the only example of a base inclusion adduct of a dicobalt(II) bis(cyclidene) complex proven to be isolable to date. When more quantitative equilibrium data become available for various systems, conditions can be found where the amount of desired base inclusion adduct is maximized.

The dicobalt(II) compartmental cyclidene complexes are most promising hosts for preparation of discrete binuclear guest-host complexes owing to the known preference of cobalt(II) macrocyclic
Table 18. Apparent EPR Parameters for Mixtures of 
$[\text{Me}_2\text{(Me}_2\text{NH})_2\text{R}^1][16\text{cyclidene}]^{4+}$
and Various Bridging Ligands.

<table>
<thead>
<tr>
<th>M</th>
<th>R$^1$</th>
<th>Solvent</th>
<th>Bridging Ligand</th>
<th>$g^a$</th>
<th>$g_\perp$</th>
<th>$g_{//}$</th>
<th>$A_{//}$/G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>mxyl</td>
<td>acetonitrile</td>
<td>4,4'-bipyridine$^b$</td>
<td>2.36</td>
<td>2.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acetonitrile</td>
<td>4,4'-bipyridine$^c$</td>
<td>2.39</td>
<td>2.29</td>
<td>2.22</td>
<td>1.98 105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acetonitrile</td>
<td>pyrazine</td>
<td>2.36</td>
<td>2.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acetone</td>
<td>4,4'-bipyridine</td>
<td>2.38</td>
<td>2.29</td>
<td>-</td>
<td>105</td>
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<td>(CH$_2$)$_3$</td>
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<td>1,4-diaminobenzene</td>
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<td>2.27</td>
<td>1.98</td>
<td>122.0</td>
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<td></td>
<td>acetone</td>
<td>1,4-dicyanobenzene</td>
<td>2.65</td>
<td>2.39</td>
<td>2.25</td>
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<td>(CH$_2$)$_2$</td>
<td>acetonitrile</td>
<td>1,4-diaminobenzene</td>
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<td>2.25</td>
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<td>122.0$^f$</td>
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<td>2.33</td>
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<td>101.4$^f$</td>
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<td></td>
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<td>4,4'-bipyridine$^b$</td>
<td>2.37</td>
<td>2.30</td>
<td>2.0</td>
<td>101.5$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acetone</td>
<td>pyrazine</td>
<td>2.37</td>
<td>2.39</td>
<td>2.29</td>
<td>2.03 106.8</td>
</tr>
<tr>
<td>Cu</td>
<td>mxyl</td>
<td>acetonitrile</td>
<td>4,4'-bipyridine$^b$</td>
<td>-</td>
<td>-</td>
<td>2.04</td>
<td>2.17$^g$ 186$^g$</td>
</tr>
<tr>
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<td>-</td>
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<td>2.15</td>
<td>202</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acetonitrile</td>
<td>4-cyanopyridine</td>
<td>-</td>
<td>2.03</td>
<td>2.16</td>
<td>196</td>
</tr>
</tbody>
</table>

a. At peak of $g_\perp$ lobe. $g' = 2.45-2.47$ in the absence of bridging ligands.
b. Dihydrate.
c. Dihydrochloride.
d. Apparently two sets of hfs both with $A_{//}^{Co} = 105$ gauss are observed.
e. Binding constant for 1,4-dicyanobenzene to $[\text{Co(Me}_2\text{(Me}_2\text{NH})_2][16\text{cyclidene}]]^{2+}$ is too small to measure. The EPR may represent base-unbound species.
f. Observed only on vertically expanded scale ($x 5 - x 8$).
g. Not well resolved.
compounds for a 5-coordinate structure. Diiron(II) analogues have been shown to assume low-spin 6-coordinate geometry around each iron center in solution by combining with added base.\textsuperscript{99} Therefore, the use of a bridging ligand would probably lead to formation of oligomeric materials. In an attempt to prepare the diiron(II) analogue of the title compound, \([\text{Fe}_2(4,4'-\text{bipy})\{(\text{Me}_2\text{NH})_2\text{mxylyl})_2([\text{16} \text{cyclidene}]_2)\}]^{4+}\), the starting diiron(II) complex was reacted with excess 4,4'-bipyridine in the same way as dicobalt(II) derivative (reflux condition). Preliminary electrochemical and NMR and IR spectral data for the isolated material suggest that the ligand may have rearranged, in the manner known for other lacunar ligands having \(R^2 = H\)\textsuperscript{145} (e.g., Structure XIII).

![Structure XIII](image)

Dicopper(II) bis(cyclidene) complexes were also examined for their potential to form base inclusion complexes by EPR spectroscopy. The data included in Table 18 show that the dicopper(II) complex having \(R^1 = \text{m-xylylene}\), in the presence of 4,4'-bipyridine, displays an EPR spectrum similar to that obtained with pyridine as the axial ligand. The
spectral pattern is typical of mononuclear copper(II) cyclidene complexes and no indication of enhanced intermetallic magnetic coupling is observed. This behavior is exactly the opposite to that of its dicobalt(II) analogue.

2.4.1.2 Reactivity of the Base Inclusion Complex, \([\text{Co}_2(4,4'\text{-bipy})(\text{Me}_2\text{NH})_2\text{methyl}_2[[\text{cyclidene}]]]^4+\). The electrochemistry of the title complex was investigated in the hope of obtaining information on the redox reactivity that goes along with the EPR evidence for the exchange interaction described above. Unfortunately the electrochemical behavior proved to be as irreversible as that of the starting dicobalt(II) complex and the studies provided no information on metal-metal interactions. Figure 40 shows the cyclic voltammogram of the base adduct in acetonitrile. The complex is almost electroinactive and an appreciable current flow is observed only by using electrodes with large surface (platinum disk or wire) and concentrated solutions. The small oxidation wave at around 0.0V (vs. Ag/AgNO\(_3\)) is assignable to the Co(II/III) oxidation since electrolysis at this potential leads to an EPR spectral change consistent with the oxidation of the cobalt centers. Somewhat surprising is the fact that the electrolysis can be carried out for two equivalents at this potential, as well as at the potential beyond the second oxidation wave, which is a major current flow. The EPR spectral change is shown in Figure 41.

The EPR spectrum in Figure 41(b) for the mixed-valence base adduct displays eight triplets in the \(g_\parallel\) region due to the cobalt hyperfine and nitrogen superhyperfine coupling, respectively, indicating that the unpaired electron is localized on one cobalt atom. However, a broad,
Figure 40. Cyclic Voltammograms of 

\[ \text{[Co}_2(4,4'-\text{bipy})\{(\text{Me}_2\text{NH})_2\text{mxy}1\}_2\{[16]\text{cyclidene}\}_2\}]^{4+}. \]

(In acetonitrile containing 0.1M TBAB, [Co2]~0.9mM of sample 
with low bromide content, platinum disk electrode, 
scan rate 100 and 200 mV/sec.)
Figure 41. EPR Spectral Change Upon Electrolysis of

\[ \text{[Co}_2(4,4'-\text{bipy})\text{(Me}_2\text{NH})_2\text{mxy)]}_{2}\text{[\text{16}cyclidene]}}_{2}^{4+}. \]

(a) Starting Material, (b) Oxidized by One Equivalent at 0.0V
(vs Ag/AgNO\textsubscript{3}), and (c) Oxidized by Two Equivalents at the Same
Potential as (b). (In acetonitrile containing 0.1M TBAB)
more nearly isotropic EPR signal recorded at room temperature is unlike those observed for mononuclear cyclidene complexes and suggests electron delocalization at elevated temperatures.

The cyclic voltammetric data suggest that the apparent peak potential for the cobalt oxidation process, particularly the second wave, may be shifted for kinetic reasons. However, one must be cautious in interpreting electrochemical results when halide is present. Figure 42 shows a cyclic voltammogram of tetra-n-butylammonium bromide in acetonitrile solvent. The bromide to bromine oxidation results in the oxidation current flow at about 0.35 V which is very close to the second oxidation wave mentioned above. The bromide content in several samples of this compound varies from 2 to 0.35 moles (per Co₂) depending on isolation conditions but pure tetra(hexafluorophosphate) salt has not been obtained. This does not mean that the observed electrochemistry is due entirely to anion oxidation but implies that the complex is essentially electrode inactive and chemical oxidation by bromine may be responsible for the results of controlled potential electrolysis.

\[
2 \text{Br}^- \rightarrow \text{Br}_2
\]  

(26)

\[
\text{Co-BB-Co} \rightarrow \text{Co-BB-Co}^{5+} + \text{Co-BB-Co}^{6+}
\]

(27)
Figure 42. Cyclic Voltammogram of \((n-Bu)_4NBBr\).
(In acetonitrile containing 0.1M TBAB, platinum disk electrode, scan rate 100 mV/sec.)
Thus the electrode process appears sluggish for this complex and yet the mixed-valence species was generated electrochemically and used to study the reaction with dioxygen. Since this complex of cobalt(II) is no longer a lacunar complex, one would expect to see a behavior common to a number of (unprotected) cobalt(II) dioxygen carriers such as Co(salen), namely formation of both 1:1 and 2:1 Co:O₂ adducts. Such a behavior was indeed observed, and actually served as supporting evidence for the formulation with the base molecule residing inside the cavity.

Figure 43 illustrates reversible dioxygen binding of \([\text{Co}_2(4,4'\text{-bipy})(\text{AN})((\text{Me}_2\text{NH})_2\text{mxyl})_2(\text{[16]cyclidene})_2)]^{5+}\) (AN=acetonitrile) at -40°C in acetonitrile (containing TBAB) by showing the absorption spectral changes that accompany repetitive alternate exposure to O₂ and N₂. There is no indication of irreversible autoxidation over a period of one hour at this temperature. Introduction of gradually increasing amounts of dioxygen yields the spectral change given in Figure 44. Close inspection of the region around 480 nm reveals the presence of two distinct isosbestic points, 482 nm for spectra at \(P_{O_2} = 0 - 37.1\) torr and 485 nm for the rest, \(P_{O_2} = 98.5 - 742.3\) torr. The two oxygen binding equilibria, shown below, suggested by these data find supporting evidence in the EPR spectral changes recorded on the same solutions that were used for the visible absorption spectral studies.

\[2 \text{Sc}^{III} \text{BB-Co}^{II} + O_2 \rightleftharpoons \text{Sc}^{III} \text{BB-Co}^{III} \text{O}_2^2- \text{Co}^{III} \text{BB-Co}^{III} \text{S} \]  \( (28) \)

\[\text{Sc}^{III} \text{BB-Co}^{III} \text{O}_2^2- \text{Co}^{III} \text{BB-Co}^{III} \text{S} + O_2 \rightleftharpoons 2 \text{Sc}^{III} \text{BB-Co}^{III} \text{O}_2 \]  \( (29) \)
**Figure 43.** Visible Absorption Spectral Change of

$$[\text{Co}_2(4,4'-\text{bipy})\{(\text{Me}_2\text{NH})_2\text{mxyl})_2([16]\text{cyclidene})_2\}]^{5+}$$

in Acetonitrile upon Alternate Flushing with O$_2$ and N$_2$ at $-40^\circ$C.

(Solvent contained TBAB, flushing period 200 sec.)
Figure 44. Visible Absorption Spectral Change of

\[ \{\text{Co}_2(\text{4,4'}\text{-bipy})\text{(Me}_2\text{NH})\text{pmyl})_2\text{[16]cyclidene}_2\}^5+ \]

in Acetonitrile upon Exposure to Various Pressure of Dioxygen

at \(-38^\circ\text{C}\). (Solvent contained TBAB)
The first set of EPR spectra in Figure 45 for the range $P_{o_2} = 0 - 19$ torr indicate that at these low pressures of oxygen the low-spin cobalt(II) species forms the diamagnetic 2:1 Co:O$_2$ adduct (reaction (28)). It is only beyond 37 torr that substantial amounts of the 1:1 Co:O$_2$ adduct begins to form (reaction (29)) as is evident from the second set of EPR spectra in Figure 45.

The behavior of the mixed-valence base adduct as a fairly stable oxygen carrier is in marked contrast to that of the corresponding binuclear host itself, $[Co_2\{(Me_2(NH)_{2}mxyl\}_2([16]cyclidene)_2)]^{5+}$. This species was also prepared electrochemically and the visible absorption was monitored after bubbling 760 torr of oxygen for 200 seconds at -40°C. A shoulder-like band at 505nm formed initially and then quickly diminished with time; little reversibility was observed. This is qualitatively in accord with the intermediacy of such a Co(II/III)$_2$ species during the rapid autoxidation of Co(II)$_2$ m-xylylene-linked cyclidine complex discussed in the Section 2.3. Since in the mixed-valence base adduct, Co(II/III)$_2$-bipy, the O$_2$ must bind outside the cavity, it is even less protected than that in the mixed-valence lacunar species, Co(II/III)$_2$. Consequently, the marked resistance to autoxidation of the former can be rationalized in terms of the low electron density at cobalt(II) due to electron withdrawal by the cobalt(III) center via the bridging base. That is, the effect is due to a very special axial base.

It is noted, however, that the completely reversible oxygen binding by the Co(II/III)$_2$-bipy complex is observed only at low temperatures. At -20°C the oxygen affinity is clearly lower (apparent $P_{1/2} = 160$ torr)
Figure 45. EPR Spectral Change of

$[\text{O}_2(4,4'-\text{bipy})\{\text{Me}_2\text{NH}_2\text{mxyl}\}_2([16]\text{cyclidene})_2)]^{5+}$

in Acetonitrile upon Exposure to Various Pressures of Dioxygen

at $-40^\circ\text{C}$. (Solvent contained TBAB)
and the isosbestic points are no longer defined as sharply as at -40°C, due to the progress of an irreversible process during the measurements. This species is still quite susceptible to autoxidation in comparison to normal mononuclear cobalt(II) lacunar complexes.

It has been demonstrated above that the internally coordinated bridging ligand does assist the intermetallic communication. The next logical step is to investigate the dioxygen reactivity of the original dicobalt(II)-bipy system. Table 19 summarizes the results of an EPR study of the interaction of this complex with dioxygen at -45°C in acetone and the sample EPR spectra indicated in this Table are given in Figure 46. When the Co(II)$_2$-bipy complex is exposed to a very small amount of oxygen (1.1 torr), the EPR spectral pattern of the starting material that is indicative of metal-metal coupling changes to one more typical of monomeric low spin cobalt(II) cyclidene complex. The intensity of this axial signal is some 70-80% of the original Co(II)$_2$-bipy signal (approximated by the peak-to-peak height). At this stage, full atmospheric pressure of dioxygen is introduced, whereupon all of the cobalt(II) signal disappears and, at the same time, an intense well-resolved signal characteristic of 1:1 Co:O$_2$ adduct is generated. Note that the intensity of this signal accounts for almost all of the cobalt(II) that is present prior to the full oxygenation and also about 80% of the starting Co(II)$_2$-bipy species.

The above results indicate that at very low concentrations of oxygen the complex is quickly converted to a species in which the Co-Co magnetic coupling is absent and the cobalt(II) site in this species binds dioxygen to form a common 1:1 Co:O$_2$ adduct. A question arises
Table 19. Summary of EPR Spectral Changes Associated with the Interaction of \([\text{Co}_2(4,4'-\text{bipy})\{\text{Me}_2\text{(NH)}_2\text{mxy}l\}_2([16]\text{cyclidene})_2\}]^{4+}\) in Acetone$^b$ and Dioxygen and $-45^\circ C$.

<table>
<thead>
<tr>
<th>$P_O_2$/torr</th>
<th>Exposure time/sec.</th>
<th>Spectral Pattern</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>Co(II)$_2$</td>
<td>100</td>
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<tr>
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<td>40</td>
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<td>Co(II)</td>
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<td>+200</td>
<td>Co(II)</td>
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<tr>
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<td>+200</td>
<td>Co(II)$_c$</td>
<td>76</td>
</tr>
<tr>
<td>740</td>
<td>+200</td>
<td>CoO$_2$ small</td>
<td>798</td>
</tr>
</tbody>
</table>

a. [Co$_2$] - 3.5 mM.
b. Figure 46(a). $g\_| = 2.28$, $g// = 2.02$, $A^{\text{Co}}// = 52.5$ gauss.
c. Figure 46(b). $g\_| = 2.28$, $A^{\text{Co}}// = 106$ gauss, $g// not determined.$
d. Figure 46(c). $g// = 2.07$, $g\_| = 2.00$, $A^{\text{Co}}// = 18.2$ gauss.
Figure 46. EPR Spectra Specified in Table 19.
concerning the nature of the first species. It is recalled that the mixed-valence species, Co(II/III)$_2$-bipy, produced by electrolysis in acetonitrile displays a similar EPR pattern and therefore the slightly oxygenated material must also be in the mixed-valence state. The question is then whether the cobalt(III) site is the same as electrochemical oxidation product (reaction (30), $S = \text{solvent}$).

$$\text{Co-BB-Co}^{4+} + \text{O}_2 \rightarrow \text{Co-BB-CoS}^{5+} + \text{O}_2^- \quad ? \quad (30)$$

This model requires an assumption that one of the cobalt(II) sites in the Co(II)$_2$-bipy complex has an unusually high susceptibility to autoxidation. This contrasts with the largely retarded reactivity of the second cobalt(II) site in the mixed-valence state. Collman et al.$^{97}$ reported that Co$_2$(FTF)$_4$ slowly forms an intramolecular μ-superoxo complex, Co(III)-O$_2^-$/Co(III), starting with Co(II)$_2$ and O$_2$. Separately prepared mixed-valence complex, Co(II/III)$_2$, on the other hand, reacts instantaneously with dioxygen and produces the same μ-superoxo complex. It is inferred that dioxygen can oxidize one of the cobalt(II) centers in the starting dicobalt(II) species. However, the reactivity pattern of Co$_2$(FTF)$_4$ hardly compares to the present system. Taube et al.$^{126}$ analyzed the autoxidation kinetics of binuclear ruthenium(II) ammines in terms of two one-electron oxidation steps, each of a ruthenium center. The rate constants for these two processes did not differ drastically. Therefore, this model (reaction (30)), which assumes a very rapid oxidation of the first cobalt(II) center
followed by dioxygen uptake by the resulting mixed-valence product does not find favorable precedents.

The alternative explanation assumes that dioxygen ligand remains in the mixed-valence species. The equations shown below describe formation of dioxygen adducts of Co(II)$_2$-bipy involving both 2:1 (intermolecular $\mu$-peroxo species) and 1:1 Co:O$_2$ components.

\[
\begin{align*}
\text{n} \quad \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{II}} + \text{(n-1)} \quad \text{O}_2 & \rightleftharpoons \quad \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}} - (\text{O}_2^{\text{2-}} - \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}})_{\text{n-1}} \quad (31) \\
\text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}} - (\text{O}_2^{\text{2-}} - \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}})_{\text{n-1}} + 2 \quad \text{O}_2 & \rightleftharpoons \quad (32) \\
\text{O}_2^{\text{2-}} - \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}} - (\text{O}_2^{\text{2-}} - \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}})_{\text{n-1}} - \text{O}_2 \\
\text{O}_2^{\text{2-}} - \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}} - (\text{O}_2^{\text{2-}} - \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}})_{\text{n-1}} - \text{O}_2 + \text{(n-1)} \quad \text{O}_2 & \rightleftharpoons \quad (33) \\
\text{n} \quad \text{O}_2^{\text{2-}} - \text{Co}^{\text{II}}_{\text{BB-Co}}^{\text{III}} - \text{O}_2 
\end{align*}
\]

The $\mu$-peroxo oligomers (or dimer for the simplest case, $n = 2$), which should show little or no exchange coupling between the terminal cobalt centers, would be formed predominantly at low oxygen concentration.
the (equation (31)). The conversion of this W-peroxo species to the 
(CoO₂)₂-bipy species upon full oxygenation explains the EPR spectral 
change. The CoO₂ moieties in this molecule must be sufficiently far 
from each other to result in little broadening of the signal. The novel 
mixed dioxygen adduct in which both 1:1 and 2:1 Co:O₂ moieties are 
present within the same molecule (reaction (32)) is presented as a 
likely intermediate formed at moderate pressures of dioxygen.

This model does not invoke an unusual reactivity of the cobalt(II) 
cyclidene species and only known chemistry of cobalt dioxygen carriers 
is included. It is noted that the dioxygen adduct complexes are not 
very stable even at -45°C and irreversible autooxidation does take place 
to some extent, judging from the change in the EPR intensity. Three 
pieces of data which seem to support this model are presented below.

1) When the same type of EPR experiment is carried out in 
acetonitrile solvent (-41°C), the EPR spectral change is qualitatively 
quite similar to that observed in acetone. However, if 38 torr of 
dioxygen is introduced to the solution after the spectral pattern has 
changed completely to what appears to be that of mixed-valence species 
(600 seconds or longer at 2.0 torr), an intense signal due to a 1:1 
Co:O₂ moiety is generated at the expense of all of the cobalt(II) 
signal. It is recalled that the genuine Co(II/III)₂-bipy complex 
prepared electrochemically in the same solvent barely forms a small 
amount of the 1:1 Co:O₂ complex at this pressure (Figure 45). This 
suggests that the dioxygen-induced mixed-valence species is different 
from the product of electrochemical oxidation.
ii) Bulk magnetic susceptibility is a property which should distinguish among the Co(II)$_2$, Co(II/III)$_2$, and Co(III)$_2$ states. When the Co(II)$_2$-bipy complex is dissolved in various mixtures of acetone/acetonitrile, and exposed to the bubbling through of pure O$_2$ for 200 seconds followed by N$_2$ for 600 seconds at -40$^\circ$C, the molecular magnetic moment (determined by the Evans' method) decreases by only 9 - 24%. Prolonged manipulation and repeated O$_2$/N$_2$ flush results in some variation of the results. This is more consistent with the second model involving reversible dioxygen uptake followed by slow irreversible autoxidation since the rapid oxidation of one of the cobalt(II) centers would yield a smooth decrease of the magnetic moment by 50% or more under these experimental conditions.

iii) The first model predicts formation of superoxide radical, and the trapping of this reaction component would serve as a positive evidence for the model. Therefore a spin trapping experiment was conducted in an attempt to convert the superoxide radical to a more stable spin adduct with 5,5'-dimethyl-1-pyrroline-1-oxide (DMPO) (reaction (34)).

\[
\text{DMPO} + \text{O}_2^- \rightarrow \text{DMPO-O}_2^-
\]

(34)
Figure 47 shows the results of such an experiment in which the Co(II)$_2$-bipy complex in acetone was exposed to 0.1 torr of O$_2$ at -40°C in the presence of about ten-fold excess DMPO for 400 seconds. The signal generated in this manner and immediately recorded at room temperature is a triplet ($A^N = 14.6$ gauss, $g = 2.00$). When KO$_2$ is solubilized in acetone by 18-crown-6 and DMPO is added, the resulting EPR doublet of triplets ($A^N = 14.5$ gauss, $A^H = 21.5$ gauss, and $g = 2.00$) appears to be an acetone based radical trapped by DMPO, judging from the hyperfine coupling constants.$^{127}$ In acetonitrile, however, KO$_2$/18-crown-6 yields a triplet as a major signal ($A^N = 14.8$ gauss). When the various components (Co(II)$_2$-bipy, Co(II/III)$_2$-bipy, KO$_2$/18-crown-6 and DMPO) are combined, the resulting EPR spectra are complicated but interpretable as a mixture of the above mentioned triplet and a doublet of triplets with varied intensities.

As to the identity of the species giving rise to the triplet signal, the oxidation product of DMPO, Structure XIV (DMPOX), seems to be consistent with the triplet pattern. Floyd and Soong$^{128}$ reported the

![XIV](image)

generation of DMPOX in an aqueous hematin-cumene hydroperoxide system, but the reported values for the hyperfine coupling constants are
Figure 47. EPR Spectrum of a Spin Adduct Generated by the Reaction of $[\text{Co}_2(4,4'\text{-bipy})\{\text{Me}_2(\text{NH})\text{mxyyl}\}_2\{[16]\text{cyclidene})_2\}]^{4+}$ and Dioxygen in the Presence of DMPO. (Reaction conditions; solvent=acetone, $P_{O_2} = 0.1$ torr, exposure period = 400 sec., temperature = $-40^\circ C$, EPR recorded at room temperature)
considerably different from the present case. However, Drago et al. have recently reported their work with a cobalt(II) Schiff base complex, Co(SMDPT) (SMDPT = bis(salicylidene-γ-iminopropylmethylamine), in which they have observed a triplet EPR signal due to DMPOX ($A_N = 13$ gauss, $g = 2.009$) in toluene. They have also been able to trap a 1:1 Co:O$_2$ adduct of Co(SMDPT), Co(SMDPT)O$_2$, by DMPO. The spin adduct, Co(SMDPT)O$_2$-DMPO, displays a characteristic doublet of triplet ($A_N = 12.8$ gauss, $A_{HB} = 7.68$ gauss, $g = 2.008$) but a triplet signal is generated upon prolonged exposure of the CoSMDPT/DMPO solution to oxygen, showing the formation of DMPOX. The analogy can be drawn that, in the present system, the cobalt-dioxygen adducts postulated in reactions (32) and (33) were present but the oxidation of DMPO had progressed before the EPR spectrum was recorded so that only a triplet was observed.

Lastly, autoxidation kinetics at room temperature were studied for the Co(II)$_2$-bipy adduct in the same manner as described in Section 2.3.2. The complex shows only 5% decrease in absorbance over a period of 1400 seconds after exposure to dioxygen (760 torr) in acetone alone, even at 25°C, but the addition of pyridine (1.24 M) effects a rapid pseudo first-order autoxidation of Co(II)$_2$-bipy species. The overall kinetics appears to be biphasic as is the case with the binuclear host alone but the first phase is markedly accelerated and $k_{obs}^{(1)}$ cannot be evaluated. The rate constant for the second phase ($k_{obs}^{(2)} = 9.29 \pm 0.12 \times 10^{-4}$ sec$^{-1}$) is nearly identical to that obtained for the host in the same solvent. The acceleration of a certain reaction as reflected in the first phase kinetics must be related to a difference in
structure, possibly involving Co-Co interaction. Clarification of such a relationship has to await a full determination of kinetic parameters.

2.4.2 Interaction of Noncoordinating Guest with Binuclear Bis-(cyclidene) Host, [CuNi{(Me$_2$(NH)$_2$mxy)$_2$([16]cyclidene)$_2$}]Cl$_4$.

The title heterobinuclear complex was synthesized for the purpose of incorporating one copper(II) center in the binuclear molecule. When association of noncoordinating guest molecules takes place, the relaxation enhancement, due to the paramagnetic copper(II) ion, of the nuclear spins of the various protons on the guest can be studied by NMR spectroscopy. In favorable cases, the paramagnetic contribution to the relaxation rate, $T_{1p}^{-1}$, is determined by NMR measurements of the spin-lattice relaxation time $T_1$ and then used to estimate the distance between the copper center and the particular protons. The technique has been applied to several other copper(II) vaulted cyclidene complexes, and the experimental background has been reviewed elsewhere.$^{57,130}$

Table 20 summarizes the results of $T_1$ measurements for $[CuNi{(Me}_2$(NH)$_2$mxy)$_2$([16]cyclidene)$_2$]$^{4+}$ in D$_2$O and two different guests, n-butanol and 2,6-dimethylphenol at 306 K. $T_{10}$ and $T_1$ designate the spin-lattice relaxation time in the absence and presence of CuNi host, respectively. First, in the case of the n-butanol guest the rate constant for copper-enhanced relaxation, $T_{1p}^{-1} (= T_1^{-1} - T_{10}^{-1})$, decreases in the order of methyl $>$ $\gamma$ $>$ $\beta$ $>$ $\alpha$, indicating that the average distances of these protons from the copper ion increase in this order. It should be noted that the hydroxyl end of n-butanol is farther from the copper atom than the methyl group. This is interpreted to mean that the molecular cavity of the binuclear host is sufficiently
Table 20. $T_1$ Data for n-Butanol and 2,6-Dimethylphenol in the Presence of $[\text{CuNi}((\text{Me}_2\text{NH})_2\text{mxyt})_2]\{[16]\text{cyclidenen}_2\}]^{4+}$
(Solvent $D_2O$, Temperature 304K)

<table>
<thead>
<tr>
<th>Guest</th>
<th>n-Butanol</th>
<th>$P^b = 4.33 \times 10^{-4}$</th>
<th>2,6-Dimethylphenol</th>
<th>$P = 5.62 \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Protons</td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>$T_{10}(s)$</td>
<td>5.48$\pm$1.1</td>
<td>4.82$\pm$0.05</td>
<td>5.26$\pm$0.01</td>
<td>6.06$\pm$2.0</td>
</tr>
<tr>
<td>$T_1(s)$</td>
<td>5.24$\pm$0.05</td>
<td>4.55$\pm$1.00</td>
<td>4.76$\pm$0.01</td>
<td>5.27$\pm$0.01</td>
</tr>
<tr>
<td>$T_1p^{-1}$</td>
<td>0.0083</td>
<td>0.0123</td>
<td>0.0201</td>
<td>0.0248</td>
</tr>
<tr>
<td>$r(\tilde{R})^c$</td>
<td>8.4$\pm$1.0</td>
<td>7.9$\pm$1.15</td>
<td>7.3$\pm$1.1</td>
<td>7.0$\pm$1.1</td>
</tr>
</tbody>
</table>

a. Proven to be a mixture of CuNi and Ni$_2$ binuclear species. The concentration of CuNi host was calculated based on analyzed copper content.

b. $[\text{host}]/[\text{guest}]$ ratio.

c. Assumptions made: $\frac{1}{T_1p} = \frac{\chi q}{T_{1M} + T_{1M}} + \frac{1}{T_{1(p)}} = \frac{\chi q}{T_{1M}} = \frac{P}{T_{1M}}$, where $\chi$ = mole fraction of binary guest-host complex $T_{1M}$ ($=PT_{1p}$) appears in the Solomon-Bloembergen equation.
hydrophobic that the n-butanol is accommodated in the pocket with the hydrophobic end inside, on time average. The aromatic guest 2,6-dimethylphenol also yielded $T_1^{-1}$ values for three different protons, which suggest that the hydroxyl end points away from the copper.

The important molecular parameter $r$, the distances between the guest protons and the host copper atom in a guest-host association complex, were calculated from these data using Solomon-Bloembergen equation. Several assumptions were made including those that the association is binary ([CuNi]:Guest=1:1) and that the equilibrium is saturated under the experimental conditions. When these assumptions are verified in future studies, the calculated values for $r$ will be compared with those obtained for mononuclear vaulted cyclidene complexes.

These results demonstrate that the binuclear compartmental cyclidene complexes can accommodate organic substrates via hydrophobic interaction in the same manner as the vaulted complexes, which have been shown to catalyze some oxidation reactions. The dicobalt(II) or diiron(II) bis(cyclidene) complexes may, therefore, perform such catalysis, and they may be particularly suitable for oxidation reaction of bifunctional substrates, utilizing both of the metal sites.

Preliminary qualitative GC work has indicated that a dicobalt(II) complex having $R^1 = \text{dimethylene}$ catalyzes the autoxidation of 3,5-di-$\text{t}$-butylcatechol almost exclusively to corresponding $\alpha$-quinone.

$$\begin{align*}
\text{O}_2 & \quad \text{(C}_2\text{H}_5)_3\text{N} \\
\text{in acetonitrile ambient temperature} & \quad \rightarrow \\
\text{in acetonitrile ambient temperature} & \quad (35)
\end{align*}$$
The product, 3,5-di-t-butyl-o-benzoquinone, was actually isolated from the extract of the reaction in 54% yield. This represents at least 16 catalytic turnovers (reactant:catalyst = 29:1) for the 30 minute reaction period. When its mononuclear counterparts, [Co{Me₂(NMe₂)₂[16]-cyclidene}]²⁺, are used, the reaction was not so clean and several more products were detected by GC. It is encouraging that the binuclear catalyst shows no sign of degradation.

For a monophenol substrate, 3,5-di-t-butylphenol, catalytic oxidation using the same binuclear dicobalt(II) complex having dimethylene links led to formation of corresponding \( \beta \)-benzoquinone. This catalysis itself is not so impressive since the reaction can be catalyzed by mononuclear cobalt(II) complexes just as well but the reaction appears to be very clean with the binuclear catalyst.

Although the oxidation work is only preliminary, it is clear that binuclear catalysts are superior to mononuclear species for bifunctional substrates. The particular reaction mentioned above does not utilize the hydrophobic incorporation of the substrate into the pocket. More work needs to be done in order to combine the two aspects of the desired catalysis, that is, substrate inclusion and activation of two dioxygen molecules, all within the cavity of the binuclear catalyst.
Chapter 3
EXPERIMENTAL

3.1 General Procedures.

Bench top syntheses of dinickel(II) and dicopper(II) complexes were generally conducted open to room atmosphere and, when necessary, under a blanket of dry nitrogen. The oxygen sensitive complexes of dicobalt(II) and diiron(II) were prepared and handled in a vacuum atmospheres glove box containing dry, oxygen-free nitrogen. Synthesis of chromium(III) complexes, involving chromium(II) starting materials, was also performed in the glove box.

All chemicals used in this work were of reagent grade or higher. Chromous chloride used in synthesis of chromium(III) complexes was purchased from Pfaltz and Bauer, Inc. Solvents used in cobalt(II), iron(II), and chromium(II) reactions and physical measurements were purified by conventional means and purged with nitrogen.

3.2 Physical Measurements.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Laser DI FT mass spectra were obtained by Dr. C. Cody on a Nicolet FTMS-1000 instrument, equipped with a Tachisco Model 215G pulsed CO$_2$ laser, at Nicolet Analytical Instruments, Madison, Wisconsin. FAB mass
spectrum was recorded on a Kratos MS-30 mass spectrometer, using xenon bombardment gas: an Ion-Tek gun operating at 6 kV was used to produce and accelerate the bombarding gas. The samples were made up by dissolving the compound in water and adding this to a glycerol matrix.

IR spectra were obtained in the solid state as nujol mulls pressed between potassium bromide plates or as potassium bromide pellets with a Perkin-Elmer Model 283B Infrared Spectrometer (4000-200 cm⁻¹).

Electronic spectra were measured on either a Cary 17D recording spectrophotometer or Varian 2300 spectrophotometer using 1 cm quartz cells. Spectrophotometric studies of interaction of dicobalt(II) complexes with dioxygen were conducted using a 1 cm gastight quartz cell, fitted with a gas inlet and bubbling tube, from Precision Cells, Inc., Hicksville, New York. Solutions were exposed to a given partial pressure of dioxygen by bubbling through the solution of a gas mixture of nitrogen and oxygen accurately mixed using a series of calibrated rotameters (Matheson, Inc.). Axial base binding equilibria of cobalt(II) complexes was studied with absorption spectra as a probe with a 1 cm quartz cell equipped with a 1 ml gastight syringe. The procedure was previously described by Stevens. Temperature was maintained within ±0.2°C throughout the spectral measurements with either a Neslab or FTS constant-temperature circulation system with methanol passing through a Varian variable-temperature cell holder and was measured with a calibrated copper-constantan thermocouple attached to the cell holder itself.

Calculation of the axial base binding constants mentioned above were performed using the computer programs NONLINFIT and
Routine proton NMR spectral measurements were carried out with a Varian Associates 390L spectrometer at 90 MHz, while carbon-13 NMR spectra were recorded on a Bruker WP-80 spectrometer operating in the Fourier transform mode at 20 MHz. High resolution proton spectra were recorded on a Bruker WP200 or a Bruker WM300 spectrometer. The DEPT spectrum and $T_1$ data were obtained by Mr. T. Meade using Bruker WP200, WM300, and Nicolet 500 spectrometers. Deuterated solvents were used throughout, and all chemical shifts are reported relative to TMS. Solution magnetic susceptibility was measured by Evans' method on a Bruker WM300 spectrometer at 300 MHz operated by Mr. T. Meade. A Wilmad Coaxial Innercell WGS-5BL was assembled with a regular proton NMR tube for this measurement. All the tubes used for magnetic susceptibility measurements were thoroughly cleaned with sulfuric acid and then an aqueous 1 M EDTA solution to remove paramagnetic contaminants. The effective magnetic moment was calculated as follows.

The shifts of the proton resonance lines of inert indicator molecules (either acetone or acetonitrile solvent was used as an indicator in this work) in solution caused by paramagnetic substances, measured by an NMR spectrometer with a superconducting magnet, are given by the following expression:

$$\Delta f/f = (4\pi/3)\Delta X_v$$

where $\Delta f$ = resonance frequency for the indicator signal in sample solution - resonance frequency of reference indicator signal (Hz), $f =$
operating frequency of the NMR instrument (Hz), and $\Delta X_v = \text{volume susceptibility of the solution} - \text{volume susceptibility of the solvent}$. (Note that the corresponding expression for a permanent magnet is $\Delta f/f = -(2\pi/3)\Delta X_v$, according to these definitions). The molar susceptibility of the paramagnetic complex, $\chi_M$, is approximated by the equation:

$$\chi_M = \frac{3\Delta \gamma M}{4\pi fm}$$

where $m =$ mass of the complex contained in 1 ml of solution (g/ml$^{-1}$) and $M =$ molecular weight of the complex ($M/2$ is used when the susceptibility is calculated per metal atom of binuclear molecule). An assumption has been made that the mass susceptibility arising from a difference in densities of the solution and the solvent alone can be neglected.$^{115a,b}$ A correction is applied to the gram concentration, $m$, for volume contraction of the solvent in determinations at low temperatures; $^{115d}$

$$m_T = m_{RT}(d_T/d_{RT})$$

where $d_T$ and $d_{RT}$ are the solvent densities at temperature $T$ and room temperature,$^{134}$ respectively. The molar susceptibility thus obtained is referenced to the solvent and includes a diamagnetic contribution from the ligand, $\chi^L$, which is corrected for using Pascal constants.$^{135}$

$$\chi^P_M = \chi_M - \chi^L$$
The effective magnetic moment due to the paramagnetic metal ion is then calculated by the equation:

$$
\mu_{\text{eff}} = \frac{3kT_X^M}{2N\mu_B^2} \longrightarrow 2.83 \left(T_X^M\right)^{1/2} \text{ (in B.M.)}
$$

where the symbols have their usual meanings.

Electrochemical measurements were made by Dr. K. Goldsby and Dr. M. Chavan with a Princeton Applied Research Corporation potentiostat-galvanostat, Model 173, equipped with a Model 175 linear programmer and a Model 179 digital coulometer and also with a PAR Model 174A polarographic analyzer. Cyclic voltammetric and polarographic curves were recorded on a Houston Instruments Model 2000 X-Y recorder. The cell design was described by Chavan elsewhere. The working electrode for cyclic voltammetry was a platinum disk, unless otherwise noted, with potentials measured vs. a silver wire immersed in 0.1M silver nitrate in acetonitrile as reference. Differential pulse polarographic data were taken using a platinum bead electrode and also referenced to Ag/0.1M AgNO$_3$. All measurements were carried out in acetonitrile solutions containing 0.1M tetra-n-butylammonium tetrafluoroborate (TBAB) as supporting electrolyte in a glove box in which the temperature was 25°-30°C under an atmosphere of dry, oxygen-free nitrogen.

EPR measurements were performed on a Varian E-112 spectrometer in the X-band at 9.3 GHz; $g$ values are quoted relative to DPPH ($g = 2.0036$) and solution samples were run either frozen at 77K in quartz tubes.
fitted with a Taperlok stopper or at ambient temperatures in a Wilmad commercial flat cell. Solutions of dicobalt(II) complexes were oxygenated by a known mixture of nitrogen and oxygen (prepared in the same way as mentioned for electronic spectral measurements) directly in an EPR tube fitted with a bubbling tube (Figure 48), which was immersed in a temperature controlled FTS methanol bath, and then frozen with the bubbling tube pulled out of the solution.

Gas chromatography was performed on a Carlo Erba 4160 series GC equipped with a flame ionization detector, a Carlo Erba Model 200 cryogenic unit, and a Houston Instruments B-5000 strip chart recorder. A J and W 30M x 0.32 mm, 1.0 m thickness, DB-5 capillary column was employed using a splitless injection at 20°C and programming 20° to 260°C at 10°/min.
Figure 48. EPR Apparatus Used For Controlled Oxygenation of Dicobalt(II) Complexes.
3.3 Synthesis.

3.3.1 Mononuclear Nickel(II) Unbridged Complexes.

\((3,11\text{-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2-)-K^NN}\)nickel(II), \([\text{Ni}\{\text{Ac}_2\text{Me}_2[16]\text{tetraenatoN}\}]\).\) This complex was prepared according to the published procedure.\(^{136}\)

\((3,10\text{-Diacetyl-4,9-dimethyl-1,5,8,12-tetraazacyclotetradeca-1,3,8,10-tetraenato(2-)-K^NN}\)nickel(II), \([\text{Ni}\{\text{Ac}_2\text{Me}_2[14]\text{tetraenatoN}\}]\).\) This complex was donated by Mr. R. Shaw.

\[(2,12\text{-Dimethyl-3,11-bis[1-methoxyethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-K^NN}\)nickel(II)] Hexafluorophosphate, \([\text{Ni}\{\text{Me}_2(\text{OME})_2[16]\text{cyclidene}]\right\)(PF\(_6\))\(_2\). This complex was prepared according to the published procedure.\(^{137}\)

\[(2,11\text{-Dimethyl-3,10-bis[1-methoxyethylidene]-1,5,8,12-tetraazacyclohexadeca-1,4,8,11-tetraene-K^NN}\)nickel(II)] Hexafluorophosphate, \([\text{Ni}\{\text{Me}_2(\text{OME})_2[14]\text{cyclidene}]\right\)(PF\(_6\))\(_2\). This complex was synthesized according to Schammel's procedure.\(^{137}\) In a separate preparation, ethylfluorosulfonate was used in place of methylfluorosulfonate in the published procedure expecting the ethylated analogue, \([\text{Ni}\{\text{Me}_2(\text{OEt})_2[14]\text{cyclidene}]\right\)(PF\(_6\))\(_2\). The product, however, appears to be \([\text{Ni}\{\text{Me}_2(\text{OME})_2-[14]\text{cyclidene}]\right\)(PF\(_6\))\(_2\). (Anal. Found: Ni, 8.37; C, 31.51; H, 4.61; N, 8.28. Calcd. for NiC\(_\text{18}^\text{H}_{28}^\text{N}_4^\text{O}_2^\text{P}_2^\text{F}_1_2\cdot0.5\text{CH}_3\text{OH}:}\) Ni, 8.42; C, 31.88; H, 4.34; N, 8.04. Probably the ethoxy groups in the initially formed complex, \([\text{Ni}\{\text{Me}_2(\text{OEt})_2[14]\text{Cyclidene}]\right\)^{2+}, were replaced by methoxy group of methanol which was used in the work up procedure. Such a reaction has been observed in the case of 15-membered cyclidene analogue.\(^{138}\)
(4,10-Dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato-
(2-)K^4W)nickel(II), [Ni(Me_2[16]tetraenatoW)]. This complex was
prepared according to the published procedure.\textsuperscript{139}

[\((2,12-\text{Dimethyl}-3,11-\text{bis}[1-(\text{dimethylamino})\text{ethyldiene}]-1,5,9,13-
tetraazacyclohexadeca-1,4,9,12-tetraene-K^4W)\text{nickel(II)}\)] Hexafluorophosphate, [Ni(Me_2(NMe_2)_2[16]cycloidene)](PF_6)_2. This complex was prepared
according to the procedures of Schammel.\textsuperscript{137}

[\((2,12-\text{Dimethyl}-3,11-\text{bis}[1-(\text{ethylenediamino})\text{ethyldiene}]-1,5,9,13-
tetraazacyclohexadeca-1,4,9,12-tetraene-K^4W)\text{nickel(II)}\)] Hexafluorophosphate, [Ni(Me_2(NHCH_2CH_2NH_2)_2[16]cycloidene)](PF_6)_2. This complex was
prepared according to the published procedure\textsuperscript{100a} with slight
modifications. A solution of 3.54 g (4.99 mmoles) of [Ni(Me_2(OMe)_2-
[16]cycloidene)](PF_6)_2 in 50 ml of acetonitrile was added dropwise to 100
ml of acetonitrile containing 6.2 g (0.10 moles) of ethylenediamine
under a blanket of nitrogen. The resulting deep red solution was
stirred 30 minutes longer and then rotovapped to half its volume before
a 2g quantity of NH_4PF_6 in 80 ml of 1:1 methanol:water mixture was
added. Further rotary evaporation caused precipitation of a yellow
solid, which was collected by filtration, washed extensively with 1:1
methanol:water, and dried in vacuo. Yield: 2.5 g (63\%). Anal. calcd.
for NiC_{22}H_{40}N_8P_2F_12·0.5CH_3OH: Ni, 7.44; C, 34.24; H, 5.36; N, 14.20.
Found: Ni, 7.44; C, 34.22; H, 5.42; N, 14.73.

[\((2,11-\text{Dimethyl}-3,10-\text{bis}[1-(\text{ethylenediamino})\text{ethyldiene}]-1,5,8,12-
tetraazacyclohexadeca-1,4,8,11-tetraene-K^4W)\text{nickel(II)}\)] Hexafluorophosphate, [Ni(Me_2(NHCH_2CH_2NH_2)_2[14]cycloidene)](PF_6)_2. The solvents used
for this synthesis were purged with nitrogen prior to use and the
solutions were kept under a blanket of nitrogen. A solution of 1.93 g (2.77 mmoles) of \([\text{Ni}{\text{Me}_2(\text{OMe})_2}[14]\text{cyclidene}](\text{PF}_6)_2\cdot0.5\text{CH}_3\text{OH}\) was dissolved in 100 ml of acetonitrile and dripped into a solution of 0.68 g (11 mmoles) of ethylenediamine in 100 ml of acetonitrile. After stirring for two hours, the solvent was slowly replaced by repeated rotary evaporation with ethanol added. As the solvent became rich in ethanol, an orange solid started to precipitate and at the same time some of the material turned oily. Overnight stirring resulted in formation of orange solid, which was filtered, washed with ethanol and then ether, and dried in vacuo. Yield: 1.7 g. Anal. calcd. for \(\text{NiC}_2\text{H}_{36}\text{N}_8\text{P}_2\text{F}_{12}\): Ni, 7.96; C, 32.59; H, 4.92; N, 15.20. Found: Ni, 8.16; C, 33.07; H, 4.92; N, 14.55; \(\text{N}/\text{Ni}=7.5\).

\([2,12-\text{Dimethyl-3,11-bis[1-(butanediamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^N}\text{Ni}(\text{II})]\) Hexafluorophosphate, \([\text{Ni}{\text{Me}_2(N\text{H}(\text{CH}_2)_4\text{NH}_2)_2}[16]\text{cyclidene}](\text{PF}_6)_2\). This complex was synthesized in a similar manner to \([\text{Ni}{\text{Me}_2(N\text{HCH}_2\text{CH}_2\text{NH}_2)_2}[16]\text{cyclidene}](\text{PF}_6)_2\) except that ethylenediamine was replaced by 4.4 g (50 mmoles) of 1,4-butanediamine. In this case, addition of methanol/water mixture was sufficient to induce precipitation. Yield: 4.0 g. Chemical analysis (Ni, 7.61; C, 37.86; H, 5.72; N, 12.96) is consistent with a composition \(\text{NiC}_{24.3}\text{H}_{43.8}\text{N}_{7.1}\) rather than the expected formulation \(\text{NiC}_{26}\text{H}_{48}\text{N}_8\text{P}_2\text{F}_{12}\), suggesting the presence of bridged cyclidene complexes of a composition \(\text{NiC}_{22}\text{H}_{36}\text{N}_6\text{P}_2\text{F}_{12}\).

\([2,12-\text{Dimethyl-3,11-bis[1-(pentanediamino)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^N}\text{Ni}(\text{II})]\) Hexafluorophosphate,
phate, \([\text{Ni}\{\text{Me}_2(\text{NH}(\text{CH}_2)_5\text{NH}_2)_2[16]\text{cyclo}	ext{dene}]\}(\text{PF}_6)_2\). This preparation was performed following published procedures.\(^{103}\)

\([(2,12-\text{Dimethyl}-3,11-\text{bis}[1-(\text{m-xylylendiamino})\text{ethyldene}]-1,5,9,13-\text{tetraazacyclobexadeca}-1,4,9,12-\text{tetraene-κ}^4\text{N}\text{nickel(II)}])\ \text{Hexafluorophosphophate}, \ [\text{Ni}\{\text{Me}_2(\text{m-xylylNH}_2)_2[16]\text{cyclo}	ext{dene}]\}(\text{PF}_6)_2\]. Preparation of this compound was first carried out in a similar manner to \([\text{Ni}\{\text{Me}(\text{NHCH}_2\text{CH}_2\text{NH}_2)_2[16]\text{cyclo}	ext{dene}]\}(\text{PF}_6)_2\). However, the product turned oily upon removal of acetonitrile. Therefore the reaction was run at the stoichiometric ratio of the two reactants using 7.00 g (10.0 mmoles) of \([\text{Ni}\{\text{Me}_2(\text{OMe})_2[16]\text{cyclo}	ext{dene}]\}(\text{PF}_6)_2\) in 100 ml of deaerated acetonitrile and 3.0 g (22 mmoles) of \(\text{m-xylylendiamine}\) in 100 ml of the same solvent. The resulting red solution was reduced in volume via rotary evaporation to about 10 ml and loaded on an alumina column. A yellow moving band, containing predominantly the monomeric lacunar complex \([\text{Ni}\{\text{Me}_2(\text{NH})_2\text{mxyl}[16]\text{cyclo}	ext{dene}]\}(\text{PF}_6)_2\) (1.86 g), was eluted with acetonitrile. The desired product was then eluted with 3% ethanol/acetonitrile and the volume was reduced to 10 ml and 200 ml of 1:1 methanol:water was added. Rotary evaporation induced precipitation of a yellow powder, which was collected by filtration, washed by ethanol and then ether, and dried in vacuo. Yield: 4.21 g. Anal. calcd. for \(\text{NiC}_{34}\text{H}_{48}\text{N}_8\text{P}_2\text{F}_{12}\): Ni, 6.40; C, 44.51; H, 5.27; N, 12.21. Found: Ni, 6.55; C, 43.61; H, 5.25; N, 11.14. (It corresponds to a composition \(\text{NiC}_{32.5}\text{H}_{46.7}\text{N}_7.1\). The particularly low nitrogen content may suggest the presence of bridged material, but carbon and hydrogen contents are not very low).
[(2,12-Dimethyl-3,11-bis[1-(piperazine)ethylidene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^N]nickel(II)] Hexafluorophosphate, [Ni{Me_2(pip)_2[16]cyclidene}](PF_6)_2. This complex was synthesized by the method of Takeuchi.\textsuperscript{100a}

3.3.2 Dinickel(II) Complexes of Compartmental Bis(cyclidene).

Some of the complexes were synthesized in two ways as mentioned in Section 2.1.1 and the route is specified by either Scheme 1 or 2 accordingly.

[(2,7,9,15,17,22,24,30-Octamethyl-3,6,10,14,18,21,25,29,32,36,39,43-dodecemazatricyclo[21.7.7.1^7,16]tetraconta-1,7,9,14,16,22,24,29,31,36,38,43-dodecaene-κ^N]dinickel(II)] Hexafluorophosphate, [Ni_2{(Me_2(NH)_2CH_2CH_2)_2-[16]cyclidene}_2](PF_6)_4. Scheme 1. The published procedures\textsuperscript{103} were slightly modified. Two solutions, one containing 10.0 g (14.1 mmoles) of [Ni{Me_2(OMe)_2[16]cyclidene}](PF_6)_2 in 500 ml of acetonitrile and the other containing 0.88 g (15 mmoles) of ethylenediamine in 500 ml of acetonitrile, were simultaneously added dropwise to a vigorously stirred reservoir of 500 ml of solvent. The volume of the resulting red solution was reduced via rotary evaporation to 20 ml and applied to a neutral alumina column. Elution with acetonitrile yielded a yellow band moving down the column. The volume of the collected orange solution was reduced to 30 ml and ethanol was slowly added, whereupon a yellow precipitate formed. Yield: 5.09 g.

To a solution of the above solid in 200 ml of acetone was added a solution of 4.5 g (14 mmoles) of (n-Bu)_4NCl (purity 85\%) in 250 ml of acetone. The resulting yellow powder was collected, dissolved in 150 ml of water, and filtered again. The brown filtrate was loaded onto CM-
Sephadex by passing through a small column (1.8 cm x 20 cm). The loaded resin was transferred to the top of a larger column (3.5 cm x 30 cm) and elution was begun with 0.2M aqueous Na$_2$SO$_4$. The column showed two small pale yellow bands which appeared to be due to dipositive impurities. The concentration of the eluant was then raised to 0.4M and three bands developed in the column. The fast moving predominant yellow band was collected. Addition of 5g quantity of NH$_4$PF$_6$ in water resulted in immediate precipitation of a yellow powder, which was filtered, washed with water and then ethanol, and dried in vacuo. This material was recrystallized from an acetonitrile/ethanol mixture, forming a yellow microcrystalline solid. Yield: 3.41 g (31.7%). Anal. calcd. for Ni$_2$C$_4$H$_6$N$_2$P$_4$F$_2$·$^{2}$C$_2$H$_5$OH·$^{2}$H$_2$O: Ni, 7.65; C, 34.35; H, 5.24; N, 10.93. Found: Ni, 7.50; C, 34.36; H, 5.10; N, 11.31.

Crystals for x-ray structural determination were grown from acetonitrile with a small amount of ethanol added. Anal. calcd. for Ni$_2$C$_4$H$_6$N$_2$P$_4$F$_2$·CH$_3$CN·H$_2$O: Ni, 7.99; C, 34.31; H, 4.80; N, 12.38. Found: Ni, 7.90; C, 34.39; H, 4.69; N, 12.01.

The other two bands eluted from Sephadex with 0.4M Na$_2$SO$_4$ were worked up in the same way. About 0.2 g of solid was isolated from each band. The product from the first of these two fractions gave a proton-NMR spectrum much simpler and sharper than that of the predominant species. Although these minor fractions were not fully characterized, the chromatographically separable species could be different configurational isomers.

Scheme 2. A solution of 1.96 g (2.56 mmole) of [Ni(Me$_2$(NHCH$_2$CH$_2$-NH$_2$)$_2$[16]cyclidene)](PF$_6$)$_2$ in 200 ml of acetonitrile and a solution of
1.81 g (2.55 mmoles) of [Ni{Me₂(OMe)₂[16]cyclo]dene}(PF₆)₂ in 200 ml of acetonitrile were dripped simultaneously into a reservoir of 300 ml of acetonitrile over two hours. The volume was reduced to 10 ml via rotary evaporation and passed through a neutral alumina column with acetonitrile as the eluent. The fast moving yellow band was collected and the volume was reduced to 10 ml, to which ethanol was added to induce crystallization. The product was filtered, washed with ethanol, and dried in vacuo. Yield: 2.1 g (53% for this step). The carbon-13 NMR spectrum of this product was identical to that of the product of Scheme 1.

\[(2,7,9,15,17,22,24,30-\text{Octamethyl}-3,6,10,14,18,21,25,29,32,36,39,\] 43-dodecaazatricyclo[21.7.7.7\textsuperscript{®}]tetraconta-1,7,9,14,16,22,24,\] 29,31,36,38,43-dodecaene-K\textsuperscript{8}N)dinickel(II) \] Chloride, \[\text{[Ni}_2\{\text{Me}_2(\text{NH})_2-\] \text{CH}_2\text{CH}_2\}_2\{[16]cyclo]dene\}_2\}]\text{Cl}_4.\] To a solution of 0.28 g (0.20 mmoles) of \[\text{[Ni}_2\{\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2\}_2\{[16]cyclo]dene\}_2\}]\text{Cl}_4 in 50 ml of acetone was added another acetone solution of (n-Bu)_₄NCl (1.0 g, 3.1 mmoles) in 20 ml. The resulting yellow voluminous solid was collected by filtration and washed with acetone. After drying under vacuum, the powdery solid was recrystallized from methanol/acetone. Yield: 0.05 g (26%).

\[(2,7,9,14,16,21,23,28-\text{Octamethyl}-3,6,10,13,17,20,24,27,29,33,35,\] 39-dodecaazatricyclo[20.6.6.6\textsuperscript{®}]tetraconta-1,7,9,13,15,21,23,27,29,\] 33,35,39-dodecaene-K\textsuperscript{8}N)dinickel(II) \] Hexafluorophosphate, \[\text{[Ni}_2\{\text{Me}_2(\text{NH})_2-\] \text{CH}_2\text{CH}_2\}_2\{[14]cyclo]dene\}_2\}\text{PF}_6\}_4.\] Scheme 1. The reaction was carried out in the same way as the [16]cyclo]dene analogue, using 2.51 g (3.60 mmoles) of \[\text{[Ni}_2\{\text{Me}_2(\text{OMe})_2[14]cyclo]dene\}]\text{PF}_6\}_2 \cdot 0.5\text{CH}_3\text{OH} and 0.22 g (3.66 mmoles) of ethylenediamine. The alumina chromatography, however,
was unsuccessful; no band separation was observed. Therefore, the initial product was directly subjected to Sephadex chromatography. The elution with 0.4M Na$_2$SO$_4$ was not clean and three bands developed, leaving a pale green color on the resin as they descended. The first two yellow bands yielded no solid upon addition of aqueous NH$_4$PF$_6$ (excess), whereas the third red band led to formation of an orange powder. This material was filtered, washed with water and ethanol, and dried in vacuo. Yield: 0.18 g. Anal. calcd. for Ni$_2$C$_{36}$H$_{56}$N$_{12}$P$_4$F$_{24}$·C$_2$H$_5$OH·2Na$_2$SO$_4$: Ni, 7.04; C, 27.35; H, 3.74; N, 10.07. Found: Ni, 7.24; C, 28.09; H, 3.78; N, 9.95.

Scheme 2. The reaction was carried out in the same way as for the [16]cyclidene analogue, using 1.49 g (2.02 mmoles) of [Ni(Me$_2$(NHCH$_2$CH$_2$-NH$_2$)$_2$[14]cyclidene)](PF$_6$)$_2$ and 1.36 g (1.95 mmoles) of [Ni(Me$_2$(OMe)$_2$-[14]cyclidene)](PF$_6$)$_2$·0.5CH$_3$OH. Yield: 0.20 g.

[(2,3,6,7,9,15,17,18,21,22,24,30-Dodecamethyl-3,6,10,14,18,21,25,-29,32,36,39,43-dodecaazatricyclo[21.7.7.7$^{16}$]tetratetraconta-1,7,9,-14,16,22,24,29,31,36,38,43-dodeacaen-κ$^8$N)dinickel(II)] Hexafluorophosphate, [Ni$_2$((Me$_2$(NMe)$_2$CH$_2$CH$_2$)$_2$(((16)cyclidene)$_2$)](PF$_6$)$_4$. To a 100 ml of acetonitrile solution of [Ni$_2$((Me$_2$(NH)$_2$CH$_2$CH$_2$)$_2$((16)cyclidene)$_2$)](PF$_6$)$_4$ (1.63 g, 1.09 mmoles) was added a methanolic solution of sodium metal (0.10 g, 4.4 mmoles, in 7 ml), upon which the color of the solution turned immediately from yellow-orange to deep red. After stirring for one hour, the solvent was evaporated to dryness and the residue was extracted with 50 ml of dichloromethane and filtered through Celite. Solvent was added to the filtrate to produce a volume of 100 ml and 3.2 ml (51.4 mmoles) of methyl iodide was added under nitrogen. After
stirring overnight under nitrogen, the volume of the solution was concentrated on a rotovap and 1.63 g (>9.5 mmol) of NH₄PF₆ in 100 ml of methanol was added. The resulting dark yellow-orange precipitate was collected by filtration. This solid was redissolved in acetonitrile and passed down through neutral alumina column, eluting with acetonitrile. A yellow solution was collected, leaving a brown band on the top of the column. Rotary evaporation followed by addition of ethanol resulted in formation of a yellow solid.

The above product was metathesized to the chloride with (n-Bu)₄NCl and its aqueous solution was loaded on a Sephadex column. Only one orange band resulted from elution with 0.4M aqueous Na₂SO₄. The complex hexafluorophosphate was recovered from this effluent by adding excess NH₄PF₆. The solid thus obtained was recrystallized from acetonitrile/ethanol. Yield: 0.92 g (58%). Anal. calcd. for Ni₂C₄H₇₂N₁₂F₄P₂: Ni, 8.01; C, 36.04; H, 4.95; N, 11.46. Found: Ni, 7.94; C, 35.96; H, 4.90; N, 11.68.

[(2,8,10,16,18,24,26,32-Octamethyl-3,7,11,15,19,23,27,31,34,38,41,-
45-dodecaazatricyclo[23.7.7.7^9,17]hexatetraconta-1,8,10,15,17,24,26,31,-
33,38,40,45-dodecaene-κ₈N)dinickel(II)] Hexafluorophosphate, [Ni₂{(Me₂-(NH)₂(CH₂)₃}_2([16]cyclidene)₂}(PF₆)₄. This complex was synthesized in a similar manner to [Ni₂{(Me₂(NH)₂CH₂CH₂)₂([16]cyclidene)₂}(PF₆)₄, (Scheme 1), replacing the ethylenediamine by 1,3-diaminopropane (1.05 g, 14.2 mmol). Yield: 4.5 g (41%). Anal. calcd. for Ni₂C₂H₆₈N₁₂F₄-
F₂₄.H₂O.2.5CH₃CN: Ni, 7.53; C, 36.21; H, 4.99; N, 13.03. Found: Ni,
7.40; C, 36.13; H, 5.01; N, 12.94.
The complex was prepared according to the published procedure\textsuperscript{103} (Scheme 2). The product was purified using CM-Sephadex resin as described above for the dimethylene (R\textsuperscript{1}) analogue. Yield: 17%. The synthetic procedures for this complex, modified from the published method,\textsuperscript{101} were essentially identical to those described for [Ni\{Me\textsubscript{2}(NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}[16]cyclidene\}_2]\textsubscript{4}(PF\textsubscript{6})\textsubscript{4}, except that 1.92 g (14.1 mmoles) of \textsubscript{m}-xylylenediamine replaced the ethylenediamine in Scheme 1 and that 5.30 g of [Ni\{Me\textsubscript{2}(NH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}[16]cyclidene\}_2]\textsubscript{4}(PF\textsubscript{6})\textsubscript{2} and 4.10 g (5.78 mmoles) of [Ni\{Me\textsubscript{2}(OMe\textsubscript{2})[16]cyclidene\}_2]\textsubscript{4}(PF\textsubscript{6})\textsubscript{2} were used in Scheme 2. Purification by means of CM-Sephadex chromatography was applied in both routes. In the Scheme 1, elution of a large yellow band due to monomeric lacunar complex preceded the collection of the desired tetrapositive species, unlike the case of the dimethylene (R\textsuperscript{1}) bridged analogue. In the Scheme 2, a small red band was separated on the column when eluted with 0.2M aqueous Na\textsubscript{2}SO\textsubscript{4} before the desired yellow band came down with 0.4M aqueous Na\textsubscript{2}SO\textsubscript{4}. (This minor dipositive impurity must have been a byproduct in the first step in the Scheme 2 and displayed no
NMR signals due to aromatic carbons). Yield, Scheme 1: 1.8 g (16%); Scheme 2: 3.8 g (42% for the second step).

\[[\{2,12,14,20,22,32,34,40-\text{Octamethyl-3,11,15,19,23,31,35,39,42,46-,50,54-}\text{dodecaza}\text{pentacyclo}[31.7.7.13,21.15.9.125,29]\text{hexapentacta}-1,5,7,9(56),12,14,19,21,25,27,29(48),32,34,39,41,46,49,54-\text{octadecane-}^\text{\(\kappa^8\text{N}\)}\text{dinickel(II)}\]] \text{Chloride, [Ni}_2]\{(\text{Me}_2(\text{NH})_2\text{methyl})_2\{[16]\text{cyclidene}\}_2\}\text{Cl}_4.\]  This complex was prepared in the same manner as for \([\text{Ni}_2\{(\text{Me}_2(\text{NH})_2-\text{CH}_2\text{CH}_2)_2\{[16]\text{cyclidene}\}_2\}\text{Cl}_4,\] starting with 0.32 g (0.21 mmole) of appropriate hexafluorophosphatate salt and 0.27 g (0.84 mmole) of (n-Bu)_4NCl. Yield: 0.15 g (65%), orange powder.

\[[\{2,7,9,15,17,22,24,29-\text{Octamethyl-3,6,10,14,18,21,25,29,32,36,41-,45-}\text{dodecaaza}\text{pentacyclo}[21.7.7.8.16.23,6.2^{18},21]\text{octatetraconta-1,7-,9,14,16,22,24,29,31,36,40,45-}\text{dodecaene-}^\text{\(\kappa^8\text{N}\)}\text{dinickel(II)}\]] \text{Hexafluoro-}\text{phosphate, [Ni}_2\{(\text{Me}_2(\text{pip})_2\{[16]\text{cyclidene}\}_2\}](\text{PF}_6)_4.\] Scheme 2. Two solutions, one containing 3.65 g (4.47 mmole) of \([\text{Ni}\{(\text{Me}_2(\text{pip})_2-\{[16]\text{cyclidene}\}\}(\text{PF}_6)_2\] in 200 ml of acetonitrile and the other containing 3.17 g (4.47 mmole) of \([\text{Ni}\{(\text{Me}_2(\text{OMe})_2\{[16]\text{cyclidene}\}\}(\text{PF}_6)_2\] in 200 ml of acetonitrile, were simultaneously dripped into a reservoir of 300 ml of continuously stirred acetonitrile over a period of three hours. After stirring further for three hours, the volume of the resulting deep red solution was reduced via rotary evaporation, upon which some yellow precipitate started to form. The solid was redissolved by adding 200 ml of acetone and the solution was diluted to about 2 liters with water. This solution was loaded onto a small amount of CM-Sephadex resin placed in a funnel with a coarse frit by passing the solution through it. The loaded resin was transferred to the top of another Sephadex column (3.5
cm x 30 cm). The first brown band which developed by eluting with 0.2M aqueous Na$_2$SO$_4$ was not well separated from the subsequently moving broad band and therefore elution was continued until the more concentrated eluent (0.3M in Na$_2$SO$_4$) came through almost colorless. The concentration of the eluent was then raised to 0.4M and a broad brown band was collected. A 6g quantity of NH$_4$PF$_6$ in water was added to this solution to precipitate the complex hexafluorophosphate. The resulting dark orange powder was filtered and quickly washed with some 50 ml of acetonitrile, leaving a bright yellow solid. This material was dissolved in minimum amount of 1:1 acetonitrile:nitromethane and ethanol was added to induce crystallization. Yield: 0.51 g (7.6%).

Anal. calcd. for Ni$_2$Cu$_{12}$H$_{68}$N$_{12}$P$_{14}$F$_{24}$: Ni, 8.03; C, 36.14; H, 4.69; N, 11.49. Found: Ni, 7.91; C, 36.17; H, 4.92; N, 11.65.

(2,8,17,23-Tetramethyl-10,15,25,30-tetraoxo-3,7,18,22,32,36,39,43-octaaazatricyclo[21.7.7.16,28]tetraconta-1,7,9(38),16,22,24(31),-36,43-octaenato(4-){N}dinickel(II), [Ni$_2${(adip)$_2$(Me$_2$[16]tetraenato-N$_4$)$_2$}]. Published procedures$^{140}$ for similar reactions were followed. Two solutions, one containing 3.1 g (10. mmoles) of [Ni(Me$_2$[16]-tetraenatoN$_4$)] and 6.0 ml (20. mmoles) of triethylamine in 500 ml of ether and the other containing 1.87 g (10.2 mmoles) of adipoyl chloride (COCl(CH$_2$)$_4$COCl) in 500 ml of ether, were simultaneously added dropwise to a stirred volume of 300 ml of ether. The resulting pale orange precipitate was collected by filtration and washed extensively with water. The solid, dried under vacuum, was then dissolved in 100 ml of chloroform and passed through a neutral alumina column. After a dark red solution was allowed to pass through, the loaded material was
chromatographed by eluting with 3% ethanol in chloroform. A red band was collected and the volume of the solution was reduced by rotary evaporation to 10 ml. Addition of ethanol induced precipitation of dark orange solid, which was filtered and washed quickly with methanol. The remaining bright orange solid was recrystallized from chloroform/ethanol. Yield: 0.29 g (6.8%). Anal. calcd. for Ni₂C₄₀H₅₀N₈O₄·H₂O: Ni, 13.85; C, 56.61; H, 6.89; N, 13.21. Found: Ni, 13.84; C, 56.49; H, 6.57; N, 13.02.

The above methanol wash yielded purple microcrystalline solid on standing. A clean 17-peak carbon-13 NMR spectrum of this material is consistent with the singly bridged structure presented in Section 2.1.1. Vapor pressure osmometry yielded a molecular weight of 573 in chloroform (720 expected for Ni₂C₃₄H₅₀N₈O₂). Yield: 0.18 g.

[((10,15,25,30-Tetramethoxy-2,8,17,23-tetramethyl-3,7,18,22,32,36,-39,43-octaazatricyclo[21.7.7.7^16,24]tetratetraconta-1(30),2,7,9,15,17,-22,24,31,36,38,43-dodecaene-K¹N)dinickel(II)] Hexafluorophosphate, [Ni₂-((OMe)₂(CH₂)₂{[16]cyclidene}₂)](PF₆)₄. To a solution of 0.74 g (0.89 mmoles) of [Ni₂{(adip)₄(Me₂[16]tetraenatoN₄)₂}] in 60 ml of dry dichloromethane was added 1.30 ml (16.1 mmoles) of methylfluorosulfonate. During a six hour period of stirring, the orange solution turned to a yellow slurry. About 20 ml of methanol was added before the solvent was removed to dryness via rotary evaporation. A saturated methanolic solution of NH₄PF₆ was added to the oily residue with continuous stirring, inducing formation of a greenish yellow powder. This solid was collected and recrystallized from acetonitrile/methanol. Yield: 0.93 g (71%). Anal. calcd. for
$\text{Ni}_2\text{C}_4\text{H}_{68}\text{N}_8\text{O}_4\text{P}_4\text{F}_{24}\cdot\text{CH}_3\text{CN} \cdot \text{SH}_2\text{O}$: N, 7.33; C, 34.50; H, 5.10; N, 7.87.

Found: N, 7.33; C, 34.37; H, 5.11; N, 7.67.

$[(10,15,25,30\text{-Tetrakis(dimethylamino)}\text{-2,8,17,23\text{-tetramethyl-3,7,18,22,32,36,39,43\text{-octaaza}}\text{atri}cyclo[21.7.7.7^{16,24}]\text{tetraconta-1(30)},2,7,9,15,17,22,24,31,36,38,43\text{-dodecaene-κ}^8\text{N}^2\text{dinickel(II)}\text{]}]} \text{Hexafluorophosphate, } [\text{Ni}_2\{(\text{Me}_2\text{N})_2\text{(CH}_2\text{)}_4\}_2\{(16\text{cyclidene})_2\}](\text{PF}_6)_4$. Dimethylamine gas was bubbled through a solution of 0.93 g of $[\text{Ni}_2\{(\text{OMe})_2\text{(CH}_2\text{)}_4\}_2\{(16\text{cyclidene})_2\}](\text{PF}_6)_4$ in 50 ml of acetonitrile for ten minutes, during which time the color of the solution turned from yellow-orange to deep red. After further stirring for ten minutes, the solvent was removed on a rotovap and 50 ml of methanol was added. Overnight refrigeration resulted in formation of yellow solid, which was collected by filtration, washed with cooled methanol, and dried in vacuo. Yield: 0.30 g (32%).

Small scale Sephadex chromatography was carried out on this material; only one yellow band was eluted with 0.4M aqueous Na$_2$SO$_4$, leaving a small dark brown band on the top of the column.

$[(2,10,12,18,20,28,30,36\text{-Octamethyl-6,24\text{-dithia-3,9,13,17,21,27,31,35,38,42,45,49\text{-dodecaaza}}\text{atri}cyclo[27.7.7.7^{11,19}]\text{pentaconta-1,10,12,-17,19,28,30,35,37,42,44,49\text{-dodecaene-κ}^8\text{N}^2\text{dinickel(II)}\text{]}]} \text{Hexafluorophosphate, } [\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\}_2\{(16\text{cyclidene})_2\}](\text{PF}_6)_4$. This complex was donated by Dr. C. Cairns.

3.3.3 Ligand Salts.

$(2,12\text{-Dimethyl}-3,11\text{-bis[1-(dimethylamino)ethylidene]-1,5,9,13\text{-tetraaza}}\text{cyclohexadeca-1,4,9,12\text{-tetraenesN}_4} \text{)} \text{Hexafluorophosphate, } [\text{N}_4\text{(Me}_2$
This monomeric ligand salt was synthesized according to the method of Wilkins.\(^{142}\)

\[(\text{NMMe}_2)_2[16\text{cyclidene}](\text{PF}_6)_4\].

\[(2,7,9,15,17,22,24,30-\text{Octamethyl}-3,6,10,14,18,21,25,29,32,36,39,43-\text{dodecaazatricyclo}[21.7.7.7^{8,16}]\text{tetratetraconta}-1,7,9,14,16,22,24,29,31,-36,38,43-\text{dodecaeneNg}) \text{Chloro/hexafluorophosphate.} \quad [\text{Hg}-\{(\text{Me}_2(\text{NH})_2\text{CH}_2-\text{CH}_2)_2[[16\text{cyclidene}]]\}(\text{PF}_6)_4] \]

Two grams (1.3 mmoles) of \([\text{Ni}_2((\text{Me}_2(\text{NH})_2\text{CH}_2-\text{CH}_2)_2[[16\text{cyclidene}]])(\text{PF}_6)_4\), was dissolved in 200 ml of acetonitrile and HCl gas was bubbled through it for 20 minutes, during which time the amber solution turned bluish green. The volume of the solution was reduced to a minimum on a rotovap and the oily residue was dissolved in 100 ml of water. Addition of 2.0 g (12 mmoles) of NH\(_4\)PF\(_6\) in water at 0°C resulted in formation of a white precipitate, which was quickly collected by filtration, washed with cold water, isopropanol, and then ether, and dried in vacuo. Yield: 1.2 g.

\[(2,3,6,7,9,15,17,18,21,22,24,30-\text{Dodecamethyl}-3,6,10,14,18,21,25,-29,32,36,39,43-\text{dodecaazatricyclo}[21.7.7.7^{8,16}]\text{tetratetraconta}-1,7,9,14,-16,22,24,29,31,36,38,43-\text{dodecaeneNg}) \text{Chloro/hexafluorophosphate,} \quad [\text{Hg}-\{(\text{Me}_2(\text{NMMe})_2\text{CH}_2\text{CH}_2)_2[[16\text{cyclidene}]]\}(\text{PF}_6)_4] \]

This reaction was carried out in the same way as the previous example, using 0.92 g (0.63 mmoles) of \([\text{Ni}_2((\text{Me}_2(\text{NMMe})_2\text{CH}_2\text{CH}_2)_2[[16\text{cyclidene}]])(\text{PF}_6)_4\), except that a large excess of NH\(_4\)PF\(_6\) was added at the end. Yield 0.63 g.

\[(2,8,10,16,18,24,26,32-\text{Octamethyl}-3,7,11,15,19,23,27,31,34,38,41,-45-\text{dodecaazatricyclo}[23.7.7.9^{17}]\text{hexatetraconta}-1,8,10,15,17,24,26,31,-33,38,40,45-\text{dodecaeneNg}) \text{Chloro/hexafluorophosphate.} \quad [\text{Hg}-\{(\text{Me}_2(\text{NH})_2-(\text{CH}_2)_3)_2[[16\text{cyclidene}]]\}(\text{PF}_6)_4] \]

Hydrogen chloride gas was bubbled through a solution containing 1.0 g (0.70 mmoles) of
[[Ni₂{(Me₂(NH)₂(CH₂)₃₂([16]cyclidene)₂)](PF₆)₄} in 100 ml of acetonitrile, turning its color from amber to blue. An acetonitrile solution containing tetrachlorozincate ions (prepared from 0.20 g, 3.0 mmoles, of zinc metal) was slowly dripped into this solution. The resulting voluminous white precipitate was collected by filtration and washed extensively with acetonitrile. The tetrachlorozincate salt of the ligand obtained in this way was metathesized to hexafluorophosphate salt by dissolving it in 30 ml of water and adding an excess amount of NH₄PF₆ in water. Yield: 0.80 g.

(2,8,10,16,18,24,26,32-Octamethyl-3,7,11,15,19,23,27,31,38,41,-45-dodecaazatricyclo[23.7.7.7¹]hexatetraconta-1,8,10,15,17,24,26,31,-33,38,40,45-dodecaeneN₈) Bromo/hexafluorophosphate, [Hg{(Me₂(NH)₂-(CH₂)₃₂([16]cyclidene)₂)]Brₓ(PF₆)₈₋ₓ. Two grams (1.4 mmoles) of [Ni₂{(Me₂(NH)₂(CH₂)₃₂([16]cyclidene)₂)](PF₆)₄ was slurried in 40 ml of methanol and HBr gas was vigorously bubbled through it until a white precipitate formed. After allowing the mixture to cool to room temperature, the solid was collected by filtration, washed with a small amount of methanol and then ether, and dried in vacuo. The IR spectrum of this product exhibited intense peaks arising from the hexafluorophosphate anions. Yield: 1.81 g.

(2,12,14,20,22,32,38,40-Octamethyl-3,11,15,19,23,31,35,39,42,46,-50,54-dodecaazapentacyclo[31.7.7.7⁵.7¹]hexapentaconta-1,5,7,9(56),12,14,19,21,25,27,29(48),32,3₄,3₉,4₁,4₆,4₉,5₄-octadecaeneN₈) Chloro/hexafluorophosphate, [Hg{(Me₂(NH)₂-xyl)₂([16]cyclidene)₂]}Clₓ-(PF₆)₈₋ₓ. The ligand tetrachlorozincate salt was prepared in the same manner as described for the trimethylene (=R¹) analogue, starting with
1.3 g (0.83 mmole) of \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{mxyl}\}_2[[16]\text{cyclidene}}\)](\text{PF}_6)_4. The solid was dissolved in 30 ml of water and an aqueous solution of 1.5 g (9.2 mmole) of \(\text{NH}_4\text{PF}_6\) was dripped into it at 0°C. A white precipitate formed immediately and gradually turned viscous. The green aqueous solution was decanted and 50 ml of isopropanol was added to the residue. Overnight stirring resulted in formation of off-white solid. Yield: 0.68 g.

\((2,12,14,20,22,32,34,40\text{-Octamethyl-3,11,15,19,23,31,35,39,42,46}-\)
\(50,54\text{-dodecaazapentacyclo}\{31.7.7.7^{13},21.15,9.125,29\}\text{hexapentaconta-1,5,7,9(56),12,14,19,21,25,27,29(48),32,34,39,41,46,49,54-octadecaneN}_8\)
Bromide, \([\text{H}_8\{(\text{Me}_2\text{NH})_2\text{mxyl}\}_2[[16]\text{cyclidene}}\)]\text{Br}_8. Hydrogen bromide gas was vigorously bubbled through a methanolic slurry (20 ml) of 1.0 g (0.64 mmole) of \([\text{Ni}_2\{(\text{Me}_2\text{NH})_2\text{mxyl}\}_2[[16]\text{cyclidene}}\)](\text{PF}_6)_4 for 20 minutes. The resulting white precipitate was filtered, washed with methanol, and air dried. The IR spectrum of this material indicated the absence of hexafluorophosphate ions. Yield: 0.84 g (87%).

\((2,7,9,15,17,22,24,29\text{-Octamethyl-3,6,10,14,18,21,25,29,32,36,41,45}-\)
\(dodecaazapentacyclo\{21.7.7.7^{18},16.23,6.2^{18,21}\}\text{octatetraconta-1,7,9,14}-\)
\(16,22,28,29,31,36,40,45\text{-dodecaeneN}_8\) Chloro/hexafluorophosphate,
\([\text{H}_8\{(\text{Me}_2\text{pip})_2\}_2[[16]\text{cyclidene}}\)]\text{Cl}_x(\text{PF}_6)_8-x. This ligand salt was prepared in the same manner as described for \([\text{H}_8\{(\text{Me}_2\text{NMMe})_2\text{CH}_2\text{CH}_2\}_2-\)
\([[[16]\text{cyclidene}}\)](\text{PF}_6)_8, using 0.80 g (0.55 mmole) of \([\text{Ni}_2\{(\text{Me}_2\text{pip})_2\}_2[[16]\text{cyclidene}}\)](\text{PF}_6)_4. Yield: 0.82 g.

### 3.3.4 Dicobalt(II) Complexes.

\([(2,7,9,15,17,22,24,30\text{-Octamethyl-3,6,10,14,18,21,25,29,32,36,39}-\)]
43-dodecaazatricyclo[21.7.7.8.16]tetraconta-1,7,9,14,16,22,24,29,-31,36,38,43-dodecaene-κ®N)dicobalt(II) Chloro-tris(hexafluorophosphate), [Co2((Me2(NH)2CH2CH2)2([16]cyclidene)2)]Cl(PF6)₃. The ligand salt, [H₈((Me2(NH)2CH2CH2)2([16]cyclidene)2)]Clₓ(PF₆)₈-x (0.94 g) was slurred in 30 ml of methanol and warmed. A mixture of 0.33 g (1.3 mmoles) of Co(CH₃COO)₂·4H₂O and 0.30 g (3.7 mmoles) of Na(CH₃COO) in 20 ml of methanol was added to the ligand slurry. The resulting orange-red solution was mildly refluxed for one hour, during which time an orange microcrystalline solid precipitated. After the solution was allowed to cool to room temperature, the product was collected by filtration and recrystallized from acetonitrile/ethanol. Yield: 0.54 g (71% based on x = 2). Anal. calcd. for Co₂C₄₀H₆₄N₁₂Cl₃F₁₈·CH₃OH·H₂O: Co, 8.72; C, 36.44; H, 5.22; N, 12.44; Cl, 2.62. Found: Co, 8.71; C, 36.48; H, 5.25; N, 12.20; Cl, 2.56.

[(2,3,6,7,9,15,17,18,21,22,24,30-Dodecamethyl-3,6,10,14,18,21,25,-29,32,36,39,43-dodecaazatricyclo[21.7.7.8.16]tetraconta-1,7,9,14,-16,22,24,29,31,36,38,43-dodecaene-κ®N)dicobalt(II)] Hexafluorophosphate, [Co₂((Me2(NMe)₂CH₂CH₂)₂([16]cyclidene)₂)](PF₆)₄. This reaction was performed in a similar manner as the previous example, using 0.63 g of [H₈((Me₂(NMe₂)CH₂CH₂)₂([16]cyclidene)₂)]Clₓ(PF₆)₈-x, 0.22 g (0.88 mmoles) of Co(CH₃COO)₂·4H₂O and 0.36 g (2.6 mmoles) of Na(CH₃COO)·3H₂O. The product, however, did not precipitate from the reaction mixture. Therefore, the solvent was evaporated to dryness under vacuum and the dark red residue was extracted with 50 ml of acetonitrile. After passing through a neutral alumina column (1.8 cm x 15 cm), eluting with acetonitrile, the volume of the solution was reduced to 10 ml and
ethanol was added until the solution turned cloudy. Orange solid formed on standing. Yield: 0.23 g (43% based on x = 2). Anal. calcd. for Co$_2$C$_{4}H_{72}N_{12}P_{4}F_{24}$: Co, 8.04; C, 36.03; H, 4.95; N, 11.46. Found: Co, 7.83; C, 35.83; H, 4.98; N, 11.56.

[(2,8,10,16,18,24,26,32-Octamethyl-3,7,11,15,19,23,27,31,34,38,41,-45-dodecaazatricyclo[23.7.7.9,17]hexatetraconta-1,8,10,15,17,24,26,31,-33,38,40,45-dodecane-κ^8N)dicobalt(II)] Hexafluorophosphate, [Co$_2$((Me$_2$-(NH)$_2$(CH$_2$)$_3$)$_2$((16)cyclidene)$_2$)](PF$_6$)$_4$. This complex was prepared in the same manner as for the above example, using 0.80 g of [H$_8$((Me$_2$(NH)$_2$-(CH$_2$)$_3$)$_2$((16)cyclidene)$_2$)]Cl$_x$(PF$_6$)$_{8-x}$. Yield: 0.36 g. Anal. calcd. for Co$_2$C$_{4}H_{72}N_{12}P_{4}F_{24}$: Co, 8.19; C, 35.06; H, 4.76; N, 11.68. Found: Co, 7.64; C, 33.74; H, 4.76; N, 11.70.

[(2,12,14,20,22,32,34,38-Octamethyl-3,11,15,19,23,31,35,39,42,46,-50,54-dodecaazapentacyclo[31.7.7.7.13,21.15,9.125,29]hexapentaconta-1,5,7,9(56),12,14,19,21,25,27,29(48),32,34,39,41,46,49,54-octadecaene-κ^8N)dicobalt(II)] Hexafluorophosphate, [Co$_2$((Me$_2$(NH)$_2$methyl)$_2$((16)cyclidene)$_2$)](PF$_6$)$_4$. The ligand bromide salt, [H$_8$((Me$_2$(NH)$_2$methyl)$_2$((16)cyclidene)$_2$)]Br$_8$ (0.77 g, 0.51 mmoles), was slurred in 40 ml of warm methanol and to this was added a methanolic solution of 0.36 g (1.4 mmoles) of Co(CH$_3$COO)$_4$H$_2$O and 0.74 g (5.4 mmoles) of Na(CH$_3$COO)$_3$H$_2$O. After the resulting deep red solution was refluxed for 20 minutes, orange microcrystals started to precipitate. This complex bromide (or a bromide/acetate mixture) was isolated by filtration, washed with ethanol, and dried under vacuum. Yield: 0.67 g.

The above solid was dissolved in 30 ml of a 5:1 methanol:water mixture and to this was added a saturated methanolic solution of NH$_4$PF$_6$,
precipitating a pale orange microcrystalline product. Yield: 0.59 g (69%). Anal. calcd. for Co₂C₆₂H₇₂N₁₂P₄F₂₄·6H₂O: Co, 7.05; C, 37.38; H, 5.07; Br, 10.06. Found: Co, 7.05; C, 37.58; H, 5.26; N, 9.82; Br, 0.14.

$$[(4,4'-\text{bipyridine})(2,12,14,20,22,32,34,40-\text{Octamethyl}-3,11,15,19,23,27,29,31,35,39,42,46,50,54-\text{dodecaazapentacyclo}[31.7.7.7^{13}.21.15.9.1^{25}.29]-\text{hexapentaconta}-1,5,7,9(56),12,14,19,21,25,27,29(48),32,34,39,41,46,49,54-\text{octadecaene}-K^{8}N)\text{dicobalt(II)}] \text{Dibromo-bis(hexafluorophosphate)}$$, [Co₂-(4,4'-bipy)(Me₂(NH)₂)mxyl)₂[[16]cyclidine)₂]Br₂(PF₆)₂. Half a gram of the bromide salt of the m-xylylene linked bis(cyclidine) complex prepared according to the preceding synthesis was slurried in 20 ml of 1:1 methanol:water mixture and 0.45 g (2.3 mmoles) of 4,4'-bipyridine dihydrate was added. The resulting dark red solution was refluxed for 30 minutes and stirred further for 60 minutes. Then the solution was filtered and a 1g quantity of NH₄PF₆ in 8 ml of 1:1 methanol:water mixture was slowly dripped into it. A yellow powdery product was collected by filtration, washed extensively with methanol, and dried in vacuo. Yield: 0.59 g (90% based on bromide formulation for the starting material). Anal. calcd. for Co₂C₆₂H₈₀N₁₄Br₂P₂F₁₂·CH₃OH·6H₂O: Co, 6.82; C, 43.76; H, 5.60; N, 11.34. Found: Co, 6.85; C, 43.70; H, 5.61; N, 11.22.

3.3.5 Dicopper(II) Complexes.

$$[(2,8,10,16,18,24,26,32-\text{Octamethyl}-3,7,11,15,19,23,27,31,34,38,41,45-\text{dodecaazatricyclo}[23.7.7.7^{9}.1^{7}]{\text{hexatetraconta}-1,8,10,15,17,24,26,31,33,38,40,45-\text{dodecaene}-K^{8}N)\text{dicopper(II)}}] \text{Hexafluorophosphate}, [\text{Cu}_2(\text{Me}_2-$$
A mixture of 0.40 g of 
$[\text{Hg}((\text{Me}_2\text{NH})_2(\text{CH}_2)_3)_2([16]\text{cyclidene})_2])\text{Br}_x(\text{PF}_6)_{8-x}$, 0.12 g (0.60 mmoles) of 
Cu(CH$_3$COO)$_2$·H$_2$O and 0.31 g (2.3 mmoles) of Na(CH$_3$COO)·3H$_2$O in 100 ml of methanol was brought to reflux and stirred for two hours. The dark red solution was then reduced in volume to 10 ml via rotary evaporation and to this was added a methanolic solution of 2.0 g (12 mmoles) of 
NH$_4$PF$_6$. At the end of addition, the solution turned cloudy. A brick red solid formed upon refrigeration; the solid was collected by filtration and recrystallized from an acetonitrile/ethanol mixture. 
Yield: 0.36 g. Anal. calcd. for Cu$_2$C$_2$H$_{68}$N$_{12}$P$_4$F$_{24}$: Cu, 8.78; C, 34.84; H, 4.73; N, 11.61. Found: Cu, 7.56; C, 34.75; H, 5.09; N, 11.11.

$[\text{Cu}_2((\text{Me}_2\text{NH})_2\text{axyl})_2([16]\text{cyclidene})_2])\text{(PF}_6)_4$. This complex was synthesized following the procedures described for the previous case. One gram of the ligand salt, 
$[\text{Hg}((\text{Me}_2\text{NH})_2\text{axyl})_2([16]\text{cyclidene})_2])\text{Cl}_x(\text{PF}_6)_{8-x}$, reacted with 0.22 g (1.1 mmoles) of Cu(CH$_3$COO)·H$_2$O and 0.71 g (5.2 mmoles) of Na(CH$_3$COO)·3H$_2$O, yielded 0.55 g of product. Yield: 62% based on x = 2. Anal. calcd. for Cu$_2$C$_2$H$_{72}$N$_{12}$P$_4$F$_{24}$·C$_2$H$_5$OH: Cu, 7.85; C, 40.08; H, 4.86; N, 10.39. Found: Cu, 7.99; C, 40.03; H, 4.85; N, 10.65.

$[\text{Cu}_2((\text{Me}_2\text{NH})_2\text{axyl})_2([16]\text{cyclidene})_2])\text{(PF}_6)_4$. This complex was synthesized following the procedures described for the previous case. One gram of the ligand salt, 
$[\text{Hg}((\text{Me}_2\text{NH})_2\text{axyl})_2([16]\text{cyclidene})_2])\text{Cl}_x(\text{PF}_6)_{8-x}$, reacted with 0.22 g (1.1 mmoles) of Cu(CH$_3$COO)·H$_2$O and 0.71 g (5.2 mmoles) of Na(CH$_3$COO)·3H$_2$O, yielded 0.55 g of product. Yield: 62% based on x = 2. Anal. calcd. for Cu$_2$C$_2$H$_{72}$N$_{12}$P$_4$F$_{24}$·C$_2$H$_5$OH: Cu, 7.85; C, 40.08; H, 4.86; N, 10.39. Found: Cu, 7.99; C, 40.03; H, 4.85; N, 10.65.

$[\text{Cu}_2((\text{Me}_2\text{NH})_2\text{axyl})_2([16]\text{cyclidene})_2])\text{(PF}_6)_4$. This complex was synthesized following the procedures described for the previous case. One gram of the ligand salt, 
$[\text{Hg}((\text{Me}_2\text{NH})_2\text{axyl})_2([16]\text{cyclidene})_2])\text{Cl}_x(\text{PF}_6)_{8-x}$, reacted with 0.22 g (1.1 mmoles) of Cu(CH$_3$COO)·H$_2$O and 0.71 g (5.2 mmoles) of Na(CH$_3$COO)·3H$_2$O, yielded 0.55 g of product. Yield: 62% based on x = 2. Anal. calcd. for Cu$_2$C$_2$H$_{72}$N$_{12}$P$_4$F$_{24}$·C$_2$H$_5$OH: Cu, 7.85; C, 40.08; H, 4.86; N, 10.39. Found: Cu, 7.99; C, 40.03; H, 4.85; N, 10.65.
dioopper(II) Chloride, \([\text{Cu}_2(\text{Me}_2(\text{NH})_2\text{axyl})_2(\text{[16]cyclidene})_2])\text{Cl}_4\). This complex was prepared by metathesizing 0.10 g (0.062 mmoles) of the complex hexafluorophosphate salt, described above, with 0.27 g (0.83 mmoles) of \((\text{n-Bu})_4\text{NCl}\) in 15 ml of acetone. The crude purple product was recrystallized from methanol/acetone. Yield: 0.065 g (79%). Anal. calcd. for \(\text{Cu}_2\text{C}_5\text{H}_{12}\text{N}_2\text{Cl}_4\cdot2\text{CH}_3\text{OH}\cdot5\text{H}_2\text{O}\): Cu, 9.86; C, 50.35; H, 7.04; N, 13.05. Found: Cu, 9.80; C, 50.32; H, 6.99; N, 13.14.

3.3.6 Mixed-Metal Complexes.

\([(2,7,9,15,17,22,24,30-\text{Octamethyl}-3,6,10,14,18,21,25,29,32,36,39,\text{-H}_3-\text{dodecaazatricyclo[21.7.7.8°°]}\text{tetratetraconta-1,7,9,14,16,22,24,29,\text{-31,36,38,43-dodecaene-κŋN})opper(II)nickel(II)]}\text{Cl}\text{[CuNi}(\text{Me}_2-(\text{NH})_2\text{CH}_2\text{CH}_2)_2(\text{[16]cyclidene})_2])\text{Cl}_4\). A mixture of 0.14 g (0.70 mmoles) of \(\text{Cu(CH}_3\text{COO})_2\cdot\text{H}_2\text{O}\), 0.12 g (0.68 mmoles) of \(\text{Ni(CH}_3\text{COO})_2\cdot4\text{H}_2\text{O}\), and 0.78 g (5.7 mmoles) of \(\text{Na(CH}_3\text{COO})_2\cdot\text{H}_2\text{O}\) dissolved in 20 ml of methanol was added to 80 ml of acetonitrile containing 1.17 g of \([\text{H}_8((\text{Me}_2(\text{NH})_2\text{CH}_2\text{CH}_2)_2(\text{[16]cyclidene})_2])\text{Cl}_x(\text{PF}_6)_8-x\]). The resulting dark red cloudy solution was refluxed for two hours and then the solvent was removed on an rotovap. The residue was extracted with acetonitrile and filtered. The addition of a saturated ethanolic solution of \(\text{NH}_4\text{PF}_6\) to the filtrate, after reducing its volume to 5 ml, resulted in precipitation of a brick red powder. This material was filtered, washed well with ethanol, and air dried. Yield: 0.45 g.

Two tenths of a gram of the above product was dissolved in 10 ml of acetonitrile and diluted to 200 ml with water. The solution was loaded on a column (1.8 cm x 25 cm) packed with CM-Sephadex resin by passing
the solution through it. Elution of the absorbed complexes was begun with 0.2M aqueous Na₂SO₄, which effected only slow movement of the deep red band. When 0.3M aqueous Na₂SO₄ was passed down the column, a small yellow band was separated. Finally a more concentrated eluent (0.4M) effected development of the second orange band, leaving the deep red band behind. The addition of an excess amount of NH₄PF₆ in water to each eluted fraction led to isolation of \(0.03\) g (dark yellow), \(0.14\) g (orange), and \(0.06\) g (brick red) of powdery crude products from the first, second, and the third band, respectively. (No colored material remained on the column). The second, predominant band proved to contain a CuNi species on the basis of EPR evidences.

The above orange solid (0.14 g) was dissolved in 3 ml of acetone and filtered to remove white solid and 0.13 g (0.39 mmoles) of \((n\text{-Bu})₄\text{NiCl}\) in 2 ml of acetone was added to the filtrate. The resulting voluminous pale brown solid was collected by filtration and recrystallized from methanol/acetone, yielding 0.036 g of maroon microcrystals. Anal. found: Cu, 4.74; Ni, 4.55; Cu/Ni = 0.963 (copper-nickel complex chloride).

The brick red product from the slowest moving band was recrystallized from acetonitrile/ethanol. Yield: 0.041 g (dicopper complex hexafluorophosphate). Anal. calcd. for \(\text{Cu}_2\text{C}_4\text{H}_{6}\text{H}_4\text{N}_2\text{PF}_{28}\cdot\text{H}_2\text{O}\): Cu, 8.33; C, 33.41; H, 4.63; N, 11.69. Found: Cu, 8.73; C, 33.60; H, 4.46; N, 11.60.

The first minor fraction was not worked up since its EPR spectrum indicated the presence of copper species. It appears that the separation of the first two bands was incomplete.
Attempted synthesis and separation of [[(2,12,14,20,22,32,34,40-
Octamethyl-3,11,15,19,23,31,35,39,42,46,50,54-dodecaazapentacyclo-
[31.7.7.7.13.21.15.9.125.29]hexapentaconta-1,5,7,9(56),12,14,19,21,25,-
27,29(48),32,34,39,41,46,49,54-octadecaene-K^8N)copper(II)nickel(II)]
Chloride, [CuNi(Me_2(NH)_2mxyl)([16]cycloidene)_2]Cl_4. To a slurry of
1.30 g (0.859 mmole) of [H_8((Me_2(NH)_2mxyl)([16]cycloidene)_2)]Br_8 in 100
ml of methanol was added a methanolic solution (100 ml) containing 0.17
g (0.85 mmole) of Cu(CH_3COO)_2·H_2O, 0.15 g (0.85 mmole) of
Ni(CH_3COO)_2·4H_2O and 0.47 g (3.5 mmole) of Na(CH_3COO)·3H_2O. The
resulting deep red solution was refluxed for two hours and worked up in
the same manner as the preceding case. Yield: 1.29 g (brick red
powder).

The above solid was dissolved in 4 liters of 20% acetonitrile in
water and the solution was loaded on CM-Sephadex resin by the usual
means. Elution of the absorbed material with 0.2M aqueous Na_2SO_4
resulted in the development of two small bands, one yellow and the other
purple. An increase in the eluent concentration led to the separation
of a dark red band, which started to "tail" and leave yellow color on
the column as it came down. Finally, 0.4M aqueous Na_2SO_4 effected
separation of a large dark red band, which was collected. Apparently
one more brown, slow moving band came off afterwards, leaving green
material on the top of the column, although at this stage the band
separation became unclear.

The hexafluorophosphate salt of the species in the collected band
was recovered by adding a 3g quantity of NH_4PF_6. Recrystallization of
the isolated, powdery product from acetonitrile/ethanol led to formation
of 0.23 g of microcrystals. Methathesis of 0.15 g of this material using 0.80 g (2.7 mmoles) of (n-Bu)$_4$NCl in 30 ml of acetone yielded a greenish yellow powder, which was filtered and recrystallized from methanol/acetone. Yield: 0.04 g. Anal. found: Cu, 2.07; Ni, 6.98; C, 49.65; H, 6.71; N, 10.86. The separation was clearly not satisfactory in this preparation.

**Attempted synthesis and separation of trans-[Bis(acetonitrile)(2-,7,9,15,17,22,24,30-octamethyl-3,6,10,14,18,21,25,29,32,36,39,43-dodecaazatricyclo[21.7.7.7,1®]tetratetraconta-1,7,9,14,16,22,24,29,31,36,-38,43-dodecaene-κ$^8$N)chromium(III)nickel(II)] Hexafluorophosphate, **[Cr(AN)$_2$N1((Me$_2$(NH)$_2$CH$_2$CH$_2$)$_2$([16]cyclidene)$_2$)}(PF$_6$)$_5$. The starting chromous compound, CrCl$_2$(AN)$_2$, was prepared according to the procedures of Sperati,$^{143}$ except that anhydrous chromous chloride was used. A 1.86 g sample of [H$_8$((Me$_2$(NH)$_2$CH$_2$CH$_2$)$_2$([16]cyclidene)$_2$)}Cl$_x$(PF$_6$)$_{8-x}$ (1.12 mmoles if $x = 2$) was dissolved in 50 ml of warm acetonitrile and to this was added 0.21 g (1.0 mmole) of CrCl$_2$(AN)$_2$ dissolved in 10 ml of ethanol. Upon addition of 0.91 g (9.0 mmoles) of triethylamine, the solution turned dark red and some precipitate formed. Further addition of 0.30 g (1.3 mmoles) of NiCl$_2$·6H$_2$O caused deepening of the color of the solution. After refluxing for 30 minutes, the solvent was removed under vacuum and the residue was extracted with acetonitrile and filtered. The filtrate was passed through a neutral alumina column (1.8 x 18 cm) but no clear band separation was observed with acetonitrile as the eluent and the initially loaded brown band merely broadened. Therefore, all of the deep red solution that came through the column was collected and crude products were precipitated by evaporation of the
solvent followed by addition of excess amount of NH$_4$PF$_6$ in ethanol. Yield: 0.41 g.

The above solid was converted to a water-soluble form by metathesis in acetone with 0.70 g (2.1 mmoles) of (n-Bu)$_4$NCl and loaded on a CM-Sephadex column (1.8 cm x 16 cm). The 0.2M aqueous Na$_2$SO$_4$ eluent did not effect band separation, whereas elution with 0.4M Na$_2$SO$_4$ resulted in development of a yellow band, which yielded a yellow solid upon addition of excess NH$_4$PF$_6$ in water. (This product is most likely a Ni$_2$ component, judging from its IR spectrum and EPR silence.) The remaining dark red material was so strongly absorbed that the 0.5M Na$_2$SO$_4$/H$_2$O eluent did not affect the elution at all. However, almost all of the material descended smoothly when 1.0M aqueous NaCl was used as an eluent. This fraction yielded a small amount of brown product, which is presumably a Cr$_2$ component since its EPR spectrum shows a very broad, featureless signal around g = 3.4.

3.3.7. Chromium(III) Complexes.

**trans-**[(2,12-Dimethyl-3,11-bis[1-(dimethylamino)ethyldene]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-K$^+$N)bis(pyridine)chromium-(III)] Hexafluorophosphate, [Cr(py)$_2$[Me$_2$(NM$_2$)$_2$]$_2$[16]cyclidene)](PF$_6$)$_3$. The starting chromous compound, CrCl$_2$(py)$_2$, was prepared following the procedures previously described by Edwards, except that anhydrous chromous chloride was used.

A 0.90 g (0.93 mmoles) sample of [H$_4$(Me$_2$(NM$_2$)$_2$]$_2$[16]cyclidene]- (PF$_6$)$_4$ was dissolved in 30 ml of acetonitrile and slowly added to a heated slurry of 0.30 g (1.1 mmoles) of CrCl$_2$(py)$_2$ in 30 ml of
acetonitrile and 10 ml of pyridine. The resulting brown slurry turned to a deep red solution upon addition of 0.43 g (4.2 mmoles) of triethylamine. After refluxing for an additional hour, the solvent was evaporated to dryness and the residue was extracted with a small amount of acetonitrile and passed through a neutral alumina column (1.8 x 15 cm). A greenish yellow moving band was collected and its volume was reduced to a minimum under vacuum. Addition of 2 ml of pyridine followed by about 30 ml of ethanol resulted in precipitation of dark yellow microcrystals. Yield: 0.68 g.

The above product was redissolved in 10 ml of pyridine and heated for 30 minutes. After filtering hot, the volume was reduced to half and a saturated ethanolic solution of NH₄PF₆ was slowly added to induce precipitation of a yellow solid, which was collected by filtration, washed with ethanol, and dried in vacuo. Yield: 0.45 g (47%). Anal. calcd. for CrC₃₂H₆₈N₈P₁₈F₁₈: Cr, 5.04; C, 37.26; H, 4.69; N, 10.86. Found: Cr, 4.98; C, 37.39; H, 4.87; N, 10.88.

This complex was characterized through IR, EPR, and electronic spectra and electrochemical measurements, and the data are summarized in Table 22 (Appendix B).

**trans-[Bis(acetonitrile)(2,12-Dimethyl-3,11-bis[1-(dimethylamino)-ethyldiene]-1,5,9,13-tetraazacycloclohexadeca-1,4,9,12-tetraene-K⁺N)chromium(III)] Chloro/hexafluorophosphate, [Cr(AN)₂(Me₂(NMe₂)₂[16]-cyclidene)]ClO₆(PF₆)₂.** This complex was synthesized in a manner similar to the above bis(pyridine) analogue except that CrCl₂(py)₂ was replaced by 0.22 g (1.1 mmoles) of CrCl₂(AN)₂ and pyridine by acetonitrile. Yield: 0.40 g (48%). Anal. calcd. for CrC₂₆H₄₄N₈ClO₆-
P_{2.4}F_{14.4}:  Cr, 5.84; C, 35.09; H, 4.98; N, 12.59; Cl, 2.30. Found:  
Cr, 5.95; C, 35.12; H, 5.18; N, 11.91; Cl, 2.26.

Characterization data for this complex are also summarized in Table 22.

trans-\{(2,8,10,16,18,24,26,32-Octamethyl-3,7,11,15,19,23,27,31,34,- 
38,41,45-dodecaazatricyclo[23.7.7.7^{17}17]heptatriaconta-1,8,10,15,17,24,- 
26,31,33,38,40,45-dodecaene-x^6\}tetrakis(pyridine)dichromium(III) Hexa-
fluorophosphate, [(Cr(py)$_2$)$_2$\{(Me$_2$(NH)$_2$(CH$_2$)$_3$/2[[16]cyclidene)$_2$\}]PF$_6$].

This complex was isolated from an attempted reaction to prepare a half-
metallated complex, [Cr(py)$_2$H$_4$\{(Me$_2$(NH)$_2$(CH$_2$)$_3$/2[[16]cyclidene)$_2$\}]X$_7$.

To a slurry of 0.31 g (0.45 mmoles) of CrBr$_2$(py)$_6$ in 5 ml of 
pyridine was added a ligand solution containing 0.74 g of [H$_8$\{(Me$_2$(NH)$_2$(CH$_2$)$_3$/2[[16]cyclidene)$_2$\}]Br$_x$(PF$_6$)$_{8-x}$ (0.45 mmoles if $x = 4$) in 30 ml of 
acetonitrile and 10 ml of methanol. The green slurry gradually turned 
through a green solution to a deep red solution upon heating. Addition 
of 0.18 g (1.8 mmoles) of triethylamine caused little change. After 
refluxing for an additional hour, the volume of the solution was reduced 
to 10 ml and about 40 ml of a saturated ethanolic solution of NH$_4$PF$_6$ was 
added. The resulting yellow powder was filtered and redissolved in 15 
ml of acetonitrile. Upon addition of 0.23 g (0.91 mmoles) of AgPF$_6$ in 5 
ml of acetonitrile, this solution turned slightly cloudy. The solvent 
was evaporated to 5 ml under vacuum and the cloudy mixture was 
chromatographed with neutral alumina. Elution of a yellow moving band 
with acetonitrile followed by reduction of the volume and slow addition 
of a saturated ethanolic solution of NH$_4$PF$_6$ led to formation of a yellow 
powder, which was collected by filtration and recrystallized from
pyridine/ethanol. Yield: 0.090 g (9.8% based on x = 4). Anal. calc. for Cr₂C₆₂H₈₈N₁₆P₆F₃₆: Cr, 5.12; C, 36.66; H, 4.37; N, 11.03. Found: Cr, 5.31; C, 36.68; H, 4.68; N, 11.16.

The EPR spectrum of this complex (dissolved in acetonitrile and recorded at 77K) displays a very broad signal centered at g = 3.32. The magnetic moment of this complex in acetonitrile solution proved to be unusually large, 4.36 B.M. (at 236 K) --- 4.63 B.M. (at 295 K) per Cr atom.
APPENDIX A

Crystallographic Data for

\[ \text{[Co}_2\{\text{Me}_2\text{(NH)}_2\text{mxyl}\}_2\{\text{[16]cyclidene}\}_2\}\text{]}\text{Cl}_4 \cdot 2\text{CH}_3\text{OH} \]
<table>
<thead>
<tr>
<th>Atom</th>
<th>Z</th>
<th>X</th>
<th>X</th>
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</thead>
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<td>( {\text{(1) 0.7712}} )</td>
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<td>( {\text{(1) 0.0500}} )</td>
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</table>

Table 21: Atomic Positions for \( {\text{C(phenyl)CH}_2} \)
Figure 49. Stereoscopic Figure of

\[ \text{[Co}_2(\text{Me}_2\text{NH}_2\text{mxyl})_2([16\text{cyclidene}_2])\text{Cl}_n\cdot2\text{CH}_3\text{OH}]. \]
APPENDIX B

Characterization of Mononuclear Unbridged Complexes of Chromium(III)
Table 22. Summary of Characterization Data for Mononuclear Chromium(III) Unbridged Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>IR (^{a})</th>
<th>EPR (^{b})</th>
<th>UV-VIS (^{c})</th>
<th>CV (^{d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr(py)}_2\text{Me(NMe}_2)_2{\text{16}\text{cyclidene}}]\text{(PF}_6\text{)}_3)</td>
<td>(\nu(\text{C=N}), \nu(\text{C=C}); 1605\text{sh}, 1575, 1562\text{sh})</td>
<td>(g_1 = 3.39, g_2 = 1.89) (nearly axial, four lines are weakly resolved in (g_1) region)</td>
<td>In pyridine: 355(15900), 390(sh,12840), 455(sh,2700), 600(sh,36) In acetonitrile: 379(13850)</td>
<td>Oxidation: 0.625(0.110), 0.840(0.140) Reduction: -1.46((\text{E}_p, \text{irrev.})) -1.66((\text{E}_p, \text{irrev.}))</td>
</tr>
<tr>
<td>([\text{Cr(AN)}_2\text{Me}_2\text{(NMe}_2)<em>2{\text{16}\text{cyclidene}}]\text{Cl}</em>{0.6}\text{(PF}<em>6\text{)}</em>{2.4})</td>
<td>(\nu(\text{C==N}), 2296\text{w})</td>
<td>(g_1 = 4.35, g_2 = 3.04, g_3 = 1.83) (rhombic)</td>
<td></td>
<td>Oxidation: 0.635(0.080), 0.915(0.090) Reduction: -1.44((\text{E}_p, \text{irrev.}))</td>
</tr>
</tbody>
</table>

\(^{a}\text{Selected frequencies/cm}^{-1}.

\(^{b}\text{In acetonitrile, EPR recorded at 77K.}

\(^{c}\lambda_{\text{max}}/\text{nm (c).}

\(^{d}\text{E}_{1/2}/\text{V (vs Ag/AgNO}_3\text{) (\Delta E}_p/\text{V), in acetonitrile.}
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(c) Reference 64, especially Bulkowski, J.E.; Summers, W.E., III, p. 445-457.


(b) Agnus, Y.L. In Reference 64, p. 371-393.


71. (a) Nelson, S.M. In reference 64, p. 331-369, and references therein.


(b) Reference 6.


   (c) Reference 84.


   (d) Reference 77.


(c) Takeuchi, K.J.; Busch, D.H. Ibid. 1983, 105, 6812-6816.


(b) Reference 14.


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