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INVESTIGATIONS OF OXYGEN REACTIVITY WITH SYNTHETIC COPPER(I), IRON(II), COBALT(II), AND COBALT(I) COMPLEXES DERIVED FROM NITROGENOUS PENTADENTATE LIGANDS

Rice University

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by

JUDITH ANNE MARTIN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

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HOUSTON, TEXAS

APRIL 1982
ABSTRACT

INVESTIGATIONS OF O$_2$ REACTIVITY WITH SYNTHETIC COPPER(I), IRON(II), COBALT(II), AND COBALT(I) COMPLEXES DERIVED FROM NITROGENOUS PENTADENTATE LIGANDS

by

Judith Anne Martin

The {bis-2,6-[1-(2-imidazol-4-ylethylimino)ethyl]pyridine}copper(I) cation, [Cu(I)(imidH)$_2$DAP]$^+$, has previously been reported to react reversibly with O$_2$ in a 2:1 stoichiometry under ambient conditions in solution, thus providing a copper(I) complex to model the active site function of hemocyanin [J. Chem. Soc. (Dalton), 1827 (1980)]. The reactivity of O$_2$ with other closely related derivatives of this complex has been previously studied, with those derivatives found to be either less reversible in their reactivity with O$_2$ or to be unreactive toward O$_2$. In the present work, a new, closely related series of copper(I) derivatives, [Cu(I)(imidH)$_2$PDA]$^+$, [Cu(I)(imidR)$_2$PDA]$^+$, and [Cu(I)(py)$_2$PDA]$^+$, have been synthesized, characterized, and their reaction with O$_2$ studied in order to better understand what determines the degree of reversible O$_2$ reactivity. These new complexes were found to be either unreactive with O$_2$ or their reactivity to be less reversible than that of the previously studied parent complexes. It was found possible to relate the O$_2$ reactivity and degree of reversibility to the E$_{1/2}$ of the
copper center for a series of closely related complexes. The zinc(II) and copper(II) complexes were also synthesized and characterized for comparison.

In a continuing study of $O_2$ reactivity with transition metal complexes, the ligand systems [(imidH)$_2$DAP] and [(py)$_2$DAP] were studied with iron(II) to investigate the possibility that these complexes might also serve as model compounds for the active site function of hemerythrin. Whereas [Fe(II)(py)$_2$DAP](BF$_4$)$_2$ was found to be unreactive with $O_2$, [Fe(II)(imidH)$_2$DAP](BF$_4$)$_2$ was found to react slowly and irreversibly under ambient conditions in a ratio of one $O_2$ molecule per iron center.

As there are now many known cobalt(II) $O_2$-carriers, these same ligands were also studied with cobalt as the metal center. The [Co(II)-(py)$_2$DAP](BF$_4$)$_2$ complex was found to be unreactive toward $O_2$, whereas both [Co(I)(py)$_2$DAP](BF$_4$) and [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$ reacted slowly and irreversibly with $O_2$ in a ratio of one $O_2$ molecule per cobalt center. In addition, [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$ yielded an isolatable and characterizable monomeric cobalt-$O_2$ complex.

In summary, a total of fifteen new complexes of zinc(II), copper(II), copper(I), iron(II), cobalt(II) and cobalt(I) were synthesized, characterized, and studied for reversible reactivity with $O_2$, with some insight gained into the mechanism responsible for irreversible oxidation of the $O_2$ reactive complexes.
DEDICATION

To James and Evelyn, my parents.
ACKNOWLEDGMENTS

I would like to thank Lon J. Wilson, my research director, for his guidance through this challenging work.

I am indebted to Robert J. Saxton for the Mössbauer spectra, and to Kevin Carter for the epr spectra.

Several of the organic precursors were synthesized by Timothy Doyle, to whom I owe a great debt of appreciation.

My heartfelt thanks go to Claire Lampard who worked so diligently and so closely with me to complete the typed manuscript.

I want to thank Johanna Tanner, a dear friend, who helped me to see the real world outside of academia and who supplied emotional support.

And finally, to K. S. C. and S. B. for just being there.
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INTRODUCTION

Transition metal complexes and their reactivity with O\textsubscript{2} play important roles in sustaining life, with one of the most important being the transport of O\textsubscript{2} from outside the organism to the locations within where it is utilized. This involves the necessity of being able to reversibly bind O\textsubscript{2}.\textsuperscript{1} At present iron and copper are the only two metals known to be involved in O\textsubscript{2}-transport proteins in living systems. The hemoglobins, where the active (or O\textsubscript{2}-binding) site consists of an iron atom in a porphyrin ligand system, are found in the higher forms of life and are the best characterized of the transition metal O\textsubscript{2}-transport proteins.\textsuperscript{2} In addition, erythrocyruorin and chloro-cruorin occur in some of the lower forms of life and are also based on an iron-heme system at the active site.\textsuperscript{3} Although their names would seem to indicate the presence of a heme group, both hemerythrin\textsuperscript{4} (based on iron) and hemocyanin\textsuperscript{5} (based on copper) are O\textsubscript{2}-transport proteins which do not contain a heme at the active site. They occur exclusively in lower forms of life such as mollusks and arthropods.

The hemocyanins have been investigated by many physical techniques, but the most conclusive piece of evidence for the elucidation of the active site structure, an x-ray crystal structure, is not available and is not likely to be forthcoming in the near future due to the large molecular weights (~ 10\textsuperscript{6}) of the hemocyanins. Some recent workers have begun crystallographic work, but as to date a structure has not been resolved in enough detail to shed much light on the active
site structure. The active site therefore has to be determined by
more indirect physical methods such as IR spectroscopy, EXAFS,
resonance Raman spectroscopy, epr spectroscopy, chemical analysis, and
chemical modification. By complementary use of these techniques, it
has been possible to infer much about the active site structure.

Hemocyanin (Hc) is known to reversibly bind one molecule of O₂ per
two copper centers. It is also known to bind NO and CO, among other
small molecules. The location of the binding site for O₂ has been
determined by the combination of several techniques. A study of the
effect of iodine on the fluorescence of hemocyanin indicates that the
binding site is by the solvent accessible tryptophans, near the ex-
terior of the protein. On the other hand, IR data on CO adducts
indicate that the binding site is in a hydrophobic pocket. This
arrangement, a solvent accessible site in a hydrophobic pocket, would
seem a very reasonable combination of requirements in that access of
solvent dissolved O₂ to the active site is allowed, but at the same
time the hydrophobic pocket helps to prevent the irreversible oxidation
of the copper centers.

Deoxyhemocyanin (deoxy-Hc) is colorless and diamagnetic, consist-
ent with the formulation that it contains copper(I). Oxyhemocyanin
(oxy-Hc) is blue and also diamagnetic. The reaction of O₂ with
deoxy-Hc is believed to involve formation of a µ-peroxo bridge with the
concurrent oxidation of the two copper(I) centers to copper(II). The
diamagnetism of oxy-Hc is consistent with strong antiferromagnetic
coupling through a µ-peroxo bridge resulting in a S=0 ground state.
Low temperature magnetic susceptibility work has shown this to be the case, with the lower limit of \(-J\) (the \textit{antiferromagnetic coupling constant}) to be \(\geq 625 \text{ cm}^{-1}\).\(^{14}\)

Furthermore, the use of resonance Raman spectroscopy has produced detailed information about the manner in which the \(O_2\) is bound at the active site. The resonance Raman peak of oxy-Hc occurring around \(745 \text{ cm}^{-1}\) (depending on the source of the Hc) is not characteristic of proteins, and is known to shift to around \(705 \text{ cm}^{-1}\) when \(^{18}O_2\) is used in place of unenriched \(O_2\). The \(745 \text{ cm}^{-1}\) resonance Raman peak is in resonance with the band around \(575 \text{ cm}^{-1}\) in the electronic spectrum of oxy-Hc. Based on model studies this resonance Raman absorption peak has been assigned to an \(O=O\) vibration and is very characteristic of the peroxide-ion in an anhydrous environment.\(^{15,16}\) Further work has also shown that both oxygen atoms in the bound peroxide are in essentially equivalent environments, unlike the peroxide linkage in hemerythrin.\(^{17}\)

The overall conclusion of the resonance Raman work supports the theory of oxidative addition of the \(O_2\) to form a \(\mu\)-peroxo bridge between the two copper centers which have been oxidized to copper(II). Other resonance Raman experiments using \(^{63}\text{Cu}^{65}\text{Cu}\) and \(D_2O/H_2O\) show the resonance Raman bands which are in resonance with the \(345 \text{ nm}\) absorption peak to be assignable to a copper-\(N(\text{imidazole})\) stretching frequency, with an asymmetrical arrangement of the imidazoles (from histidine) around the copper, supporting a square-pyramidal model with an apical imidazole.\(^{18}\)
The use of extended x-ray absorption fine structure (EXAFS) spectra near the Cu K edge has also shown that the copper is in the +2 oxidation state in oxy-Hc.\(^{19}\) Oxy-Hc and deoxy-Hc give spectra very similar to model compounds containing copper(II) imidazole and copper(I) imidazole, respectively. This again supports the proposal that the active site of Hc contains imidazoles (histidines) and that deoxy-Hc contains copper(I) and oxy-Hc contains copper(II). The copper center is found to have a higher coordination number in the oxy form than the deoxy form with a smaller copper to copper distance in deoxy-Hc than in oxy-Hc. Based on this EXAFS data, along with resonance Raman data, Spiro and workers have proposed a model for the copper site in hemocyanin (Figure 1A). They propose that in the deoxy form the copper(I) centers are each bound to three histidines with no bridging ligand between the copper centers. Upon oxygenation a bridging ligand is formed by the O\(_2\) (now peroxide-like) and an additional bridging ligand endogenous to the protein (perhaps tyrosine) comes into play.\(^{19}\) The \(\mu\)-peroxo bridge is believed to be non-planar.

Based on the spectroscopic work done on different derivatives of hemocyanin (met, apo, dimer, oxy, deoxy, etc.), Solomon and co-workers have arrived at a very similar but slightly different model for the active site. They propose essentially the same model as Spiro but with water replacing one of the histidine ligands on each copper (Figure 1B).\(^{20}\)

The study of model compounds is another method which is gaining importance as a means to elucidate the structure of protein active
Figure 1
Proposed Active Site Structures for Hemocyanin

deoxyhemocyanin

oxyhemocyanin
(A) Spiro Model
\[ X = \text{Tyrosine (phenol)} \]

(B) Solomon Model
\[ X = \text{Tyrosine (phenol)} \]
\[ N = \text{Histidine (imidazole)} \]
sites when no direct structural information is available. In this approach small complexes which can be well characterized are designed so as to possess many of the essential physical features and/or reactivities of the protein active sites. The analogy can sometimes then be made that these small complexes contain the essence of the active sites. A tribute to the success of this method of attack is seen in the "picket-fence porphyrin" model compounds which were designed by Collman and workers and model the active site structure and function of hemoglobin. By modifications of the ligand structure it has been possible to "fine-tune" the model to better mimic the native protein.

Recently several attempts have been made to model hemocyanin or to shed light upon the active site structure by the synthesis and study of copper(II) peroxide complexes or copper(I) complexes which mimic hemocyanin's reactivity with O₂ or other small molecules. Due to the difficulty of stabilizing copper(I) complexes, the study of copper(I) complexes with nitrogenous ligands such as found in deoxy-Hc is still in its infancy.

Among other workers, Brubaker et al. and Thompson et al. have studied copper(II)/copper(I) pairs to elucidate the change in structure in going from one oxidation state to the other. Brubaker et al. found by x-ray crystallography that in the (1,8-bis(2-pyridyl)3,6-dithiaoctane)copper(I) complex the geometry was tetrahedral, while in the copper(II) analog it was square pyramidal, supporting the contention that a copper system which is reversible between
copper(I) and copper(II) must be able to undergo geometrical change. Other authors have reported the isolation of copper peroxide dimers as an aid in understanding the μ-peroxo bridge in oxy-Hc.\textsuperscript{26,27}

Bosnich and workers\textsuperscript{28} have studied an extensive series of copper(II) complexes containing sulfur and nitrogen in the coordination sphere, and based upon their work they have postulated yet another model for oxy-hemocyanin that consists of a coordination sphere containing two imidazoles and a thioether at each copper center, bridged by a peroxide moiety and an oxygen atom from a phenolate moiety (Figure 2). Several more recent studies, however, have shown that sulfur is not likely to be present in the coordination sphere in either deoxy-Hc or oxy-Hc.\textsuperscript{29}

A copper(II) complex reported by McKee \textit{et al.}\textsuperscript{30} has many of the essential features proposed to exist in oxy-Hc. It is a copper(II) dinuclear complex with the coppers bridged by an alkoxide moiety and X (X = OAc\textsuperscript{-}, N\textsubscript{3}\textsuperscript{-}, pyrazolate, HCOO\textsuperscript{-}, or NO\textsubscript{2}\textsuperscript{-}) with each copper being coordinated, in addition to the bridges, to two imidazole nitrogens and a tertiary amine. When X = NO\textsubscript{2}\textsuperscript{-} or pyrazolate, there is a reduced magnetic moment, indicative of antiferromagnetic coupling, while the azide complex is diamagnetic at room temperature.

Arcus \textit{et al.}\textsuperscript{31} have reported that bis[[hydrotris(1-pyrazolyl)borato]copper(I)] reacts irreversibly with O\textsubscript{2} in a ratio of one O\textsubscript{2} per two copper centers. Cagné \textit{et al.}\textsuperscript{32} have reported the irreversible reaction of O\textsubscript{2} with (carbonyl)\textit{(1,3-bis[2-(4-methylpyridyl)imino]isoindoline)copper(I)}. Burnett \textit{et al.}\textsuperscript{33} have reported the irreversible re-
Figure 2

The Bosnich Model for the Active Site

Structure of Oxyhemocyanin
action of $O_2$ with a macrocycle complex containing two copper(I) atoms, and propose a mechanism for the ligand decomposition by means of oxidation of the N=C bonds to N=C.

Nishida et al.\textsuperscript{34} have reported that a copper(I) system containing benzoimidazole groups reacts somewhat reversibly with $O_2$ although the reaction is not well characterized. Bulkowski et al.\textsuperscript{23} have also reported the somewhat reversible behavior of a copper(I) macrocycle, although it was found to react only in the solid state.

There are several well established properties that an idealized copper(I) model system for hemocyanin might possess. First, a multi-dentate ligand system would favor the formation of isolatable compounds by helping to eliminate the possibility of ligand exchange and dimerization. Also the ligand system should have enough flexibility to allow any geometrical changes that occur during the formal copper(I) $\rightleftharpoons$ copper(II) cycling which accompanies reversible oxygenation. Furthermore, the ligand system must stabilize copper(I), but at the same time not to the exclusion of copper(II). Based on an electrochemical study of copper(II) complexes with and without imines in the ligand system, it has been found that imines tend to stabilize copper(I), probably due to $\pi$ backbonding decreasing the electron density on the copper center.\textsuperscript{35} To date only one model system has been reported which possesses all of these properties.

The synthesis of the first well characterized copper(I) compound, [Cu(I)(imidH)$_2$DAP](BF$_4$), to reversibly bind $O_2$ was achieved by Dr. Miriam G. Simmons, formerly of our research group (Figure 3A).\textsuperscript{36}
Figure 3

Copper(I) Model Compounds Studied by Simmons\textsuperscript{36} and Merrill\textsuperscript{37}

(A) The \{Bis-2,6-[1-(2-imidazol-4-ylethylimino)ethyl]pyridine\}-copper(I) Cation.

(B) The \{2-[1-(2-imidazol-4-ylethylimino)ethyl],6-[1-(2-pyridin-2-ylethylimino)ethyl]pyridine\}copper(I) Cation.

(C) The \{Bis-2,6-[1-(2-pyridin-2-ylethylimino)ethyl]pyridine\}-copper(I) Cation.

(D) The \{Bis-2,6-[1-(2-(N\textsubscript{1}-p-methylbenzyl)imidazol-4-ylethylimino)ethyl]pyridine\}copper(I) Cation.

(E) The \{2-[1-(2-(N\textsubscript{1}-p-methylbenzyl)imidazol-4-ylethylimino)ethyl],6-[1-(2-pyridin-2-ylethylimino)ethyl]pyridine\}copper(I) Cation.

(F) The \{2-[1-(2-(N\textsubscript{1}-p-methylbenzyl)imidazol-4-ylethylimino)ethyl],6-[1-(2-imidazol-4-ylethylimino)ethyl]pyridine\}copper(I) Cation.
A solution of the copper(I) deoxy form is red, but upon bubbling with
\( O_2 \) turns green within a few minutes, and can be deoxygenated by
application of vacuum or bubbling with \( N_2 \). The \( O_2 \) uptake stoichiometry
as characterized by Warburg manometry was found to be one molecule of
\( O_2 \) per two copper centers. The EPR (100 K) data for the copper(I)
red deoxy form and for the green oxygenated form show both forms to be
essentially diamagnetic. These EPR results, along with the manometry
measurements, are indicative of the formation of a \( \mu \)-peroxo bridge with
strong antiferromagnetic coupling between two copper(II) centers
similar to that observed in oxy-Hc. Dr. Connie L. Merrill,\(^{37}\) also
formerly of our research group, reported antiferromagnetic coupling
between the two Cu(II) centers in the oxy form and found the \(-J\) value
to be approximately 70 cm\(^{-1}\). In the original work done by Simmons,\(^{36}\)
the related derivative \([\text{Cu(I)}(\text{py})_2\text{DAP}](\text{BF}_4)\) (Figure 3C) was found to
irreversibly react with \( O_2 \) over a much longer period of time (hours).
This may be due to oxidation of the ligand or to irreversible oxidation
of the copper center. In order to better understand the reasons behind
the difference in the \( O_2 \) reactivity of \([\text{Cu(I)}(\text{imidH})_2\text{DAP}](\text{BF}_4)\) as
compared with that of \([\text{Cu(I)}(\text{py})_2\text{DAP}](\text{BF}_4)\), Dr. Merrill investigated
derivatives in which the \( N_1 \) imidazole proton was substituted by a
\( p \)-methylbenzyl group to study the effect of the imidazole proton on
the oxygenation process. Several mixed-ligand derivatives were also
prepared and studied, using all possible pairings of imidazole, sub-
stituted imidazole, and pyridine moieties (Figure 3B, D, E, F).

Table 1 summarizes some of the results of Simmons and Merrill concern-
## Table 1

**Summary of the Copper Work of Simmons** and Merrill

<table>
<thead>
<tr>
<th>Complex(^a)</th>
<th>Reacts with O(_2)</th>
<th>% Reversible</th>
<th>(E_{1/2}) (vs. S.C.E.)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Cu(I)(imidH)}_2\text{DAP}</a>)</td>
<td>yes</td>
<td>85</td>
<td>-0.35</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Cu(I)(imidH)(imidR)DAP}</a>)</td>
<td>yes</td>
<td>65</td>
<td>-0.33</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Cu(I)(imidR)}_2\text{DAP}</a>)</td>
<td>yes</td>
<td>very little</td>
<td>-0.32</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Cu(I)(imidH)(py)DAP}</a>)</td>
<td>yes</td>
<td>none</td>
<td>-0.27</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Cu(I)(imidR)(py)}</a>)</td>
<td>no</td>
<td></td>
<td>-0.25</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Cu(I)(py)}_2\text{DAP}</a>)</td>
<td>slow/irr.</td>
<td></td>
<td>-0.20</td>
</tr>
</tbody>
</table>

\(^a\) See Figure 3 for ligand abbreviations.

\(^b\) In CH\(_3\)CN at 10\(^{-3}\) M and 0.1 M in TBAP.
ing observed reactivity with $O_2$ as well as the $E_{1/2}'s$ of the Cu(II)/Cu(I) redox couples.

In a continuing study of what determines the reactivity of $O_2$ with these unique Cu(I) compounds, a series of related derivatives has been synthesized (Figure 4) to investigate the effect of ligand modification and the accompanying change of the redox potential of the Cu(II)/Cu(I) redox couple. Overall, the redox couples for these new compounds have been found to be $\sim 0.25 \text{ V}$ more positive than those of the analogous derivatives previously described. This shift in potential has served to lengthen the time for the oxygenation process and at the same time drastically reduce the reversibility of the systems. These copper(I) complexes and their zinc(II) and copper(II) analogs have also been studied by various methods (spectroscopy, manometry, electrochemistry, etc.) to better understand their $O_2$ reactivity or lack thereof.

Since the $[\text{Cu(I)}(\text{imidH})_2\text{DAP}]^+$ complex proved to be the first well characterized copper(I) system to reversibly bind $O_2$, this ligand set, along with other related derivatives, was investigated using iron(II) as the metal center as a possible model of hemerythrin, and with cobalt as the metal center for comparison with other well characterized cobalt $O_2$-carriers.

Hemerythrin (Hr) is an iron based $O_2$-transport protein which despite its name does not contain a heme group. Like hemocyanin, it also reacts reversibly with $O_2$ in the ratio of one $O_2$ per two iron centers. Based on resonance Raman studies using isotopically
Figure 4

Copper Model Compounds Studied in this Work

(A) The \{Bis-2,6-[(2-imidazol-4-ylethylimino)methyl]pyridine\}-copper(I) Cation.

(B) The \{Bis-2,6-[(2-pyrid-2-ylethylimino)methyl]pyridine\}-copper(I) Cation.

(C) The \{Bis-2,6-[(2-N\textsubscript{1}-p-methylbenzyl)imidazol-4-ylethylimino)-methyl]pyridine\}copper(I) Cation.

(D) The \{2-[(2-Imidazol-4-ylethylimino)methyl],6-[(2-pyrid-2-ylethylimino)methyl]pyridine\}copper(II) Cation.
labeled O₂ \((^{18}O_2, ^{16}_2^{18}_0, ^{16}_0^{18}_2)\) it was found that O₂ is bound in a peroxide-like manner to what is most probably two Fe(III) centers.\(^{39,40}\) Unlike oxy-Hc though, it has been found that the two ends of the bound O₂ molecule are not in equivalent environments.\(^{40}\) Based on Mössbauer studies the irons in deoxy-Hr are probably best described as Fe(II)'s in equivalent environments, but in oxy-Hr the irons are probably Fe(III)'s in nonequivalent environments.\(^{41}\) It therefore has been postulated that the ligands from the protein are essentially the same around both iron atoms in both the oxy and deoxy forms, but in oxy-Hr O₂ is bound to the two iron centers in an asymmetric manner, perhaps end-on to one of the iron centers in a Pauling manner.\(^{42}\) This end-on mode of binding for O₂ has been found to be the case in model compounds of hemoglobin.\(^{43}\)

Although much information has been gathered concerning the active site in hemerythrin, the most informative results have been based on x-ray crystallographic results. Since Hr has a smaller molecular weight (\(~10^5\)) than hemocyanin and also has a monomer form (similar to myoglobin vs. hemoglobin), it has been possible to obtain crystals for fairly well resolved crystal structures. Based on sequencing of the amino acids and chemical modification studies, x-ray structures have been solved for azidometmyohemerythrin from *Thermiste zostericola*\(^1\) (Figure 5A) and for metaquohemerythrin from *T. dyscritum*\(^44\) (Figure 5B). It can be seen that both structures are essentially the same and agree with each other as to the basic structure of the active site. The ligands from the protein are three histidines, one tyrosine, one
Figure 5

Models of the Active Site Structure of Hemerythrin Based on X-ray Diffraction Results

(A) From studies on azidometmyohemerythrin from Themiste zostericola.

(B) From studies on methemerythrin from T. dyscrita.
aspartate, and one glutamate. The main discrepancy arises as to whether or not the aspartate and glutamate are bridging ligands.

There has been much work done on the reactivity of O₂ with synthetic iron-porphyrin derivatives, but there has been very little success in developing a reversible O₂-transport system containing non-heme iron(II). For example, Baldwin et al.⁴⁵ reported a system containing 9,10-bridged-9,10-dihydroanthracene which is reversible only at -85°C and is irreversibly oxidized at -50°C. Herron et al.⁴⁶ have recently reported a system containing a persistent void which reversibly reacts with O₂ at -35°C in a ratio of one O₂ per one iron center, having characterized the reversibility by means of electronic spectra. This system is irreversibly oxidized at 20°C. Kimura et al. have recently reported characterizing a non-porphyrin iron-O₂ complex.⁴⁷

It was hoped that the ligand system incorporated in the work of Simmons (Figure 3A) when coordinated with iron(II) would perhaps serve as a functioning model for the reactivity of O₂ with hemerythrin. As mentioned above, this ligand system with copper(I) has already shown itself to be of some value as a model for the reaction of O₂ with copper in the hemocyanin proteins. The complex [Cu(I)(imidH)₂DAP](BF₄) reacts quickly and reversibly with O₂, whereas [Fe(II)(imidH)₂DAP]-(BF₄)₂ (Figure 6A) reacts slowly (hours) and apparently irreversibly. The [Fe(II)(py)₂DAP](BF₄)₂ derivative (Figure 6B) was also prepared and characterized for purposes of comparison. Both compounds have
Figure 6
Iron and Cobalt Model Systems

(A) The Bis-2,6-[1-(2-imidazol-4-ylethylamino)ethyl]pyridine Complex.

(B) The Bis-2,6-[1-(2-pyrid-4-ylethylamino)ethyl]pyridine Complex.
\[ [\text{M} \ (\text{py})_2 \ DAP]^n^+ \]  

(B)  

\[ [\text{M} \ (\text{imid H})_2 \ DAP]^n^+ \]  

(A)  

\( n = 1 \) or 2
been characterized by a variety of spectroscopic methods, magnetic susceptibility measurements, electrochemistry, and manometry.

Cobalt does not occur in nature as the basis of an \(O_2\)-transport protein, although it is the transition metal whose reactivity with \(O_2\) is probably best understood as synthetic Co(II) \(O_2\)-carrying compounds have been known and studied for over 100 years. While cobalt complexes and their reversible reactivity with \(O_2\) are not models of naturally occurring proteins, they still serve to elucidate the nature of \(O_2\) reactivity with the metal centers in these proteins. In addition to being studied as models for \(O_2\)-transport proteins, cobalt-\(O_2\) systems have also been investigated as a means to obtain pure \(O_2\) from the atmosphere and as a storage system for \(O_2\).\[21h\] Molecular oxygen was first observed to react with a cobalt complex in 1852 by Fremy.\[48\] This complex was isolated by Werner and Mylius in 1898\[49\] and identified as \([\text{H}_3\text{N}]_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5\]\[4^+\]. The first characterized reversible cobalt-\(O_2\) carrier was reported by Tsumki in 1938,\[50\] who showed that the color change of \(N,N'\)-bis(salicylidene)ethylenediamine cobalt(II) when exposed to \(O_2\) was due to reversible \(O_2\) binding by the complex. The observation of this color change had been first reported by Pfeiffer and co-workers\[51\] in 1933. This system was based on a Schiff base ligand (Figure 7C) as were almost all of the early cobalt-\(O_2\) systems. A Schiff base is made by condensing a ketone or aldehyde with an amine to form an imine and water.

Almost all of the early cobalt-\(O_2\) carriers could be divided into two groups (Figure 7A and B). Type A was characterized as being
Figure 7

Type A and Type B Cobalt O₂-Carriers

and the Schiff Base Condensation Reaction

(A) Type A cobalt O₂-carrier.
(B) Type B cobalt O₂-carrier.
(C) Formation of a Schiff base.
TYPE A

(A)

TYPE B

(B)

(C)

\[ R'\text{C}O + R''\text{NH}_2 \rightarrow R'\text{C}N + H_2O \]
tetradentate, square-planar, with paramagnetism equivalent to one unpaired electron. Upon oxygenation type A complexes react with the stoichiometry of one $O_2$ per two cobalt centers, to yield a diamagnetic substance (Figure 8A). Based upon kinetic studies Calvin and co-workers$^{52}$ found the oxygenation reaction to proceed through a two-step process. The first step involves formation of an activated monomeric

$$\text{A} + \text{O}_2 \rightarrow \text{A} \text{O}_2^* \quad (1)$$

$$\text{A} \text{O}_2^* + \text{A} \rightarrow \text{A} \text{O}_2 \text{A} \quad (2)$$

$O_2$ complex, with the second step involving dimerization. Which step was rate determining varied, depending upon the nature of A.

Type B complexes were characterized as being pentadentate, trigonal bipyramid, with paramagnetism equivalent to three unpaired electrons [high spin Co(II)]. Reaction with $O_2$ occurs with a stoichiometry of one $O_2$ per one cobalt center, forming a monomeric species whose paramagnetism is consistent with one unpaired electron (Figure 8C). These monomeric complexes are usually stable below 0°C, being irreversibly oxidized at higher temperatures.

Many studies have been done on type A complexes where the coordination sphere is made five coordinate by the addition of a base at an axial position, where the bases are imidazole, substituted imidazole, or pyridine, among others. It was found that the reactivity of these complexes and the degree of reversibility of the oxygenation process could be changed depending upon both the axial ligand and the solvent system. Axial bases, such as imidazole, which are good π
Figure 8
Modes of $O_2$ Bonding to Metal Centers

A

B

C

D
donors, were found to enhance the desired reactivity. A correlation was also found between the redox potential (E$_{1/2}$) of the cobalt(II)/cobalt(III) redox couple in neutral complexes and the reactivity with O$_2$. Vogt had postulated some time before that if the redox potential were too negative, irreversible oxidation would occur, but if the potential were too positive no reaction would occur. Thus it could be seen that by modifying the ligand system to change the redox potential of the cobalt center, the O$_2$ reactivity could be "fine-tuned."

The cobalt-O$_2$ dimers were postulated to go through a monomeric intermediate, but a question remained as to how to stop the reaction at the monomer stage and prevent the formation of the dimer. Several methods were reported to enhance monomer formation, with the first isolated monomer being reported by Floriani and Calderazzo, and Basolo and Crumbliss. Generally, the formation of monomers could be enhanced by the use of bulky ligands which would prevent dimer formation due to steric reasons, the use of low concentrations, low temperatures, and nonpolar solvents.

The isolation of monomeric cobalt-O$_2$ complexes generated great interest when first discovered because the method of binding O$_2$ in the monomer species was thought to be analogous to that in hemoglobin, which was still not clearly understood at that time. The existence of a monomer, rather than a dimer, was confirmed by IR, ESR, magnetic susceptibility, and above all x-ray crystal structures. Solid state measurements showed the two oxygen atoms to be in non-equivalent environments, which would be very consistent with a Pauling type of binding (Figure 8C). The oxidation state of the O$_2$ was pro-
posed to be superoxo \((O_2^-)\) which meant that the cobalt had been oxidized to cobalt(III), with the unpaired electron residing on the superoxide. Among the chemical tests used to determine the oxidation states of the \(O_2\) and cobalt, it was found that the addition of electrochemically generated superoxide \((O_2^-)\) to the cobalt(II) complex gave

\[
\text{Co(III)} + O_2^- \rightarrow \text{Co(III)}O_2^-
\]

(3)

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

(4)

the same result as addition of \(O_2\) to the cobalt(II) complex.\(^{58}\) It was also found that lithium superperoxide \((\text{LiO}_2)\) could be formed by the addition of a lithium salt to a solution of \(\text{Co(III)}O_2^-\).\(^{59}\)

In the dimer species, it was seen by EPR results that the oxygen atoms were in equivalent environments,\(^{60}\) and had O–O stretching frequencies in the IR very much like that of peroxide.\(^{61}\) X-ray crystal structures on \([\text{Co}_2(\text{NH}_3)_10(O_2)](\text{SO}_4)_2\cdot 4\text{H}_2\text{O}\) among many other cobalt–\(O_2\) dimers gave an O–O distance also in agreement with a peroxide formulation.\(^{62}\) The reactivity of \(O_2\) with cobalt complexes which form dimers is therefore taken to be an oxidative addition reaction with the formation of a non-planar \(\mu\)-peroxo bridge between the two cobalts which have been oxidized to cobalt(III). Those dimeric species which have a coordination site \textit{cis} to the \(\mu\)-peroxo bridge are known to form a hydroxo-bridge (Figure 8B) so that the two cobalts are doubly bridged. These doubly bridged complexes are known to be less reversible due to the stabilization provided by the additional bridge.\(^{21e}\)
Although much of the work on cobalt-O₂ carriers has involved Schiff base ligands which have a -2 charge so that a neutral complex results when used with cobalt(II), work has been reported using other types of ligands such as amino acids and polypeptides.⁶³ Martell⁶⁴ has reported a series of compounds which uses pentadentate ligands which are neutral, thus when complexed with cobalt(II) give salts.

Most of the work on cobalt-O₂ carriers involves cobalt(II) systems, but there have been a few reports of cobalt(I) complexes. The cobalt(I) complexes are generally reported to be green to yellow in color and are either diamagnetic or have magnetic moments of ~ 3.1 μ_B, depending on the type of ligand set used.⁶⁵ The reactivity of these cobalt(I) complexes with O₂ is thought to involve the formation of monomeric species with the O₂ bound side one (Figure 8D), with the cobalt oxidized to Co(III) and the O₂ reduced to O₂⁻.²¹f,⁶⁶

As stated earlier, very little work in this area has involved pentadentate ligands which are neutral. One of the advantages of using a pentadentate ligand is negating the possibility that the ligand used to fill the fifth coordination site is also binding to the sixth site, thus preventing O₂ access to the cobalt center. The use of a pentadentate ligand system will also prevent the formation of a μ-hydroxide bridge in addition to the μ-peroxo bridge, the presence of which has been shown to reduce the degree of reversibility due to the stabilizing influence of two bridges.

Based on the success of the use of the pentadentate ligand [(imidH)₂DAP] with copper(I) (Figure 3A) in mimicking the reversible
oxygenation reactivity of hemocyanin, the properties of this ligand system with cobalt(II) (Figure 6A) were investigated in this work. It was found that from a methanolic solution a rust brown solid could be obtained which characterized to be a monomeric O₂ adduct [Co(imidH)₂-DAP](BF₄)₂·O₂. This complex is stable for about one day in the solid state, with its physical characteristics being consistent with those reported previously for other monomeric cobalt-O₂ complexes. [Co(II)(py)₂DAP](BF₄)₂ (Figure 6B) was also prepared and found to be insensitive to O₂. The complex [Co(I)(py)₂DAP](BF₄) (Figure 6B) was prepared by controlled potential electrolysis from the analogous Co(II) complex and was found to react with O₂ in the ratio of one O₂ per one cobalt center, over several hours time. Some evidence has also been found for ligand oxidation in the presence of O₂ in the case of O₂ active species. These four cobalt complexes were characterized by spectroscopic methods, epr, magnetic susceptibility, manometry, conductivity, and electrochemistry.

In summary, fifteen new compounds of copper(I), copper(II), zinc(II), iron(II), cobalt(II), and cobalt(I) have been synthesized, isolated, characterized by physical techniques, and their reactivity with O₂ studied by various methods, with insight gained into the necessary components of a system which will reversibly react with O₂. Additionally, insight has also been gained into a possible mechanism for the irreversible oxidation of the ligand in the O₂ reactive species.
EXPERIMENTAL SECTION

Materials

All solvents used were reagent grade. Acetonitrile (CH$_3$CN) was distilled from KMnO$_4$ and Na$_2$CO$_3$, methanol (CH$_3$OH) from sodium metal, and methylene chloride (CH$_2$Cl$_2$) from P$_2$O$_5$. Dimethyl sulfoxide (DMSO) was stored over molecular sieves then distilled from BaO or NaOH. The CD$_3$DN used for pmr studies was obtained from Aldrich Chemicals. Boron trifluoride etherate, 2,6-diacetylpypyridine (DAP), 2-(2-aminoethyl)-pyridine, 2,6-pyridinedimethanol, α-chloro-para-xylene, and histamine hydrochloride were all obtained from Aldrich Chemicals. Histamine free base (grade B) was obtained from Calbiochem. AgBF$_4$, Cu$_2$O, Co(BF$_4$)$_2$·6H$_2$O, Zn(BF$_4$)$_2$·6H$_2$O, and NaBF$_4$ were obtained from Alpha Products. The NaBF$_4$ was recrystallized from water and dried with vacuum and heat over P$_2$O$_5$. Tetrabutylammonium perchlorate (TBAP) was obtained from G. Frederick Smith Chemical Company, Eastman Chemicals, or Alpha Products. Tetrabutylammonium fluoroborate (TBABF$_4$) was obtained from Fisher Scientific Company. FeCl$_2$·4H$_2$O was obtained from Mallinckrodt.

Argon, nitrogen, and oxygen gases were purchased from Big Three Industries. The argon and nitrogen were scrubbed through a train consisting of drierite, H$_2$SO$_4$, KOH, drierite, a heated copper catalyst, and P$_2$O$_5$ to insure dry, O$_2$ free gases. The oxygen gas was run through a train of H$_2$SO$_4$ and KOH to insure dryness.

Syntheses

All complexes which were O$_2$ sensitive or highly hygroscopic were prepared under argon using Schlenk line techniques or in a Vacuum/
Atmospheres dry box under N\textsubscript{2}. It was found that all ligands could be prepared on the open lab bench, with the ligand solutions deoxygenated before addition of the metal salts.

2,6-Pyridinedicarboxaldehyde. 2,6-Pyridinedicarboxaldehyde (PDA) was prepared by oxidizing 2,6-pyridinedimethanol with freshly prepared MnO\textsubscript{2} as described in the literature.\textsuperscript{67} Commercially available MnO\textsubscript{2} would not perform the desired oxidation. The MnO\textsubscript{2} used was prepared as reported in the literature\textsuperscript{68} by dissolving 80 g of MnSO\textsubscript{4} in 300 ml of hot water and 58 g of KMnO\textsubscript{4} in 400 ml of hot water. Both solutions were then heated to 90°C. The KMnO\textsubscript{4} solution was added slowly with stirring to the MnSO\textsubscript{4} solution, with the dark brown MnO\textsubscript{2} forming immediately. After completion of the addition, the solution was heated and stirred for an additional 15 min. The MnO\textsubscript{2} was collected by filtration on a Büchner funnel, washed with a solution of 8 g of KMnO\textsubscript{4} in 100 ml of hot water and washed again with hot water until the filtrate was colorless. The MnO\textsubscript{2} was dried in an oven at 100°C until constant weight was obtained. MnO\textsubscript{2} prepared in this manner retained its reactivity for several months when stored in a tightly sealed container.

The 2,6-pyridinedicarboxaldehyde (PDA) was prepared by refluxing a suspension of 80 g of MnO\textsubscript{2} with 7.6 g of 2,6-pyridinedimethanol in 600 ml of CHCl\textsubscript{3} for 5 h. Longer reflux times appeared to have no affect on the yield. After reflux, the solution was filtered hot using a Büchner funnel. The remaining solid was washed with five 100 ml portions of hot CHCl\textsubscript{3} and five 100 ml portions of hot ligroin
(bp 60-80°C). All filtrates were combined, filtered again, and taken to dryness under reduced pressure. The remaining solids were sublimed at 70°C and finally recrystallized from hot ligroin. The resulting product was a white crystalline solid with a melting point of 122-123°C (lit. 124°C),\textsuperscript{69} yield 32%. Upon standing for several weeks, the compound turned brown or blue, but could be repurified by sublimation. No color change was noted when the compound was protected from light.

\[ N_1-(p\text{-}methylbenzyl)\text{histamine, free base.} \] The compound was prepared by the modified method of Averill,\textsuperscript{70} which involves the substitution of the \(R = p\text{-}methylbenzyl\) group at the \(N_1\) position of histamine to give the \(N_1\text{-}R\) isomer. Approximately 750 ml of liquid ammonia were collected in a 1 liter three-neck round bottom flask containing several small pieces of sodium metal and equipped with a dry ice condenser. Sufficient sodium was used so that after all of the ammonia was collected it was a deep royal blue color. 300 ml of ammonia were then distilled over into a second round bottom flask equipped with a dry ice condenser and containing 10 g of histamine dihydrochloride. Small pieces of sodium metal were added until the blue color just remained. This blue solution was titrated with a solution of 1 ml of \(\alpha\text{-}chloro-para\text{-}xylene\) in 10 ml of anhydrous diethyl ether, until the blue color of the solution just disappeared. The resulting color varied from white to pink. Five ml of \(\alpha\text{-}chloro-para\text{-}xylene\) were then added slowly by syringe, and the solution allowed to stir overnight until all of the ammonia had evaporated.
After standing overnight, the resulting golden colored oil was dissolved in a minimum amount of 1 M HCl (about 200 ml). This solution was extracted with 60 ml portions of CH$_2$Cl$_2$ until the CH$_2$Cl$_2$ layer was colorless and clear (usually about three portions). NaOH pellets were then added to the aqueous layer until pH 10, at which point the crude free base substituted histamine could be seen forming as droplets of oil. This solution was stripped to dryness under vacuum and the resulting oily solids washed with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ filtrates were reduced to dryness to yield the crude free base substituted histamine as a golden brown oil. The oil was weighed, dissolved in a minimum amount of absolute ethanol (10 ml), and concentrated HCl added in a stoichiometric amount to form the hydrochloride salt. This salt precipitated upon stirring and cooling, leaving the undesired N$_3$-R isomer in solution. The precipitate was evaluated for purity based upon the presence of a doublet or a singlet peak at about 5.2 ppm relative to TMS in the pmr spectrum: the presence of a doublet was indicative of the presence of the undesired N$_3$-R isomer, which could be removed by recrystallization from absolute ethanol.

The pure substituted histamine hydrochloride salt was dissolved in a minimum amount of water (10 ml) and NaOH pellets added until pH 10. This aqueous solution was reduced to dryness and the remaining oily solids washed with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ filtrates were taken to dryness to yield the pure free base substituted histamine as a golden oil, which would occasionally solidify. Purity was verified by pmr spectroscopy.
Tetra(acetonitrile)copper(I) Tetrafluoroborate, [Cu(I)(CH₃CN)₄](BF₄).  

The compound was prepared using the methods of Hemmerich and Sugwart. All of the preparation and handling were done using inert atmosphere techniques. 1.43 g of Cu₂O were added to a solution of 10 ml of water, 25 ml CH₃CN, and 3 ml of boron trifluoride etherate, and refluxed gently for 1 h until the majority of the copper oxide had dissolved. The solution was cooled and the white precipitate collected and recrystallized from CH₃CN.

{Bis-2,6-[(2-pyrid-2-yethylamino)methyl]pyridine}zinc(II) Tetrafluoroborate, [Zn(II)(py)₂PDA](BF₄)₂. A ligand solution was prepared by dissolving 0.2702 g (2 mmol) of PDA in 50 ml of CH₃OH, adding 0.4887 g (4 mmol) of 2-(2-aminoethyl)pyridine, and allowing the solution to stir at room temperature for 2 h, by which time it had turned golden yellow. To this solution was added 0.6941 g (2 mmol) of solid Zn(II)(BF₄)₂·6H₂O. The solution was stirred an additional 15 min, and then reduced to dryness under vacuum. The compound was recrystallized by dissolving in a minimum amount of room temperature MeOH, then adding a small additional amount (1 ml) of MeOH with cooling and scratching, whereupon a white solid precipitated. Application of heat at any time caused decomposition of the product. Analysis calculated for ZnC₂₁N₂₁H₂₁B₂F₈: C, 43.31%; H, 3.63%; N, 12.02%; Zn, 11.22%. Found: C, 43.24%; H, 3.57%; N, 11.96%; Zn, 11.13%.

{Bis-2,6-[(2-pyrid-2-yethylamino)methyl]pyridine}copper(II) Tetrafluoroborate, [Cu(II)(py)₂PDA](BF₄)₂. The compound was prepared and
treated the same as the zinc derivative, using Cu(II)(BF₄)₂·6H₂O instead of the zinc salt. The application of heat at any time caused decomposition. The recrystallized, blue-green solid gave μₐ (solid), 298 K) = 1.94 μₜ. Analysis calculated for CuC₂₁N₂₇H₂₁B₂F₈: C, 43.44%; H, 3.65%; N, 12.06%; Cu, 10.94%. Found: C, 43.47%; H, 3.53%; N, 12.01%; Cu, 11.05%.

{Bis-2,6-[(2-pyrid-2-ylethylimino)methyl]pyridine}copper(I) Tetrafluoroborate·methanol, [Cu(I)(py)₂PDA](BF₄)·0.5CH₃OH. The ligand solution was prepared as described for the zinc derivative followed by deoxygenation on a Schlenk line using alternating applications of vacuum and argon. The [Cu(I)(CH₃CN)₄](BF₄) (0.6291 g, 2 mmol) was dissolved in a minimum amount (20 ml) of deoxygenated CH₃CN and added to the ligand solution via a U-tube connector, causing an immediate color change to dark red. Application of heat had to be avoided at all times to prevent decomposition. The solution was reduced to dryness under vacuum, but the resulting solid could not be recrystallized due to its O₂ sensitivity. However, the solid was reconstituted by dissolving it in a minimum amount of room temperature MeOH, filtering, and reducing the resulting solution to dryness to yield a dark red solid with μₐ (solid, 298 K) = 0.72 μₜ. Analysis calculated for CuC₂₁.₅N₂₅H₂₃BF₄O₅: C, 50.66%; H, 4.55%; N, 13.73%; Cu, 12.87%. Found: C, 50.66%; H, 4.40%; N, 13.63%; Cu, 12.50%.

{Bis-2,6-[(2-imidazol-4-ylethylimino)methyl]pyridine}zinc(II) Tetrafluoroborate, [Zn(II)(imidH)₂PDA](BF₄)₂. The ligand solution was pre-
pared by dissolving 0.2702 g (2 mmol) of PDA in 50 ml of MeOH, adding 0.4446 g (4 mmol) of histamine free base and stirring at room temperature for 2 h. To this golden yellow solution, 0.6941 g (2 mmol) of solid Zn(II)(BF$_4$)$_2$·6H$_2$O was added and the solution stirred an additional 15 min before being taken to dryness. The complex was recrystallized from a minimum amount of room temperature MeOH to yield a white crystalline product. The application of heat at any time caused decomposition. Analysis calculated for ZnC$_{17}$H$_{19}$B$_2$F$_8$: C, 36.44%; H, 3.42%; N, 17.50%; Zn, 11.67%. Found: C, 36.63%; H, 3.34%; N, 17.32%; Zn, 11.90%.

{Bis-2,6-[(2-imidazol-4-ylethylimino)methyl]pyridine}copper(II) Tetrafluoroborate, [Cu(II)(imidH)$_2$PDA](BF$_4$)$_2$. The compound was prepared the same as the zinc derivative, using Cu(II)(BF$_4$)$_2$·6H$_2$O instead of the zinc salt. Upon addition of the copper salt to the ligand solution, the initial color was emerald green which later turned to royal blue. While reducing the solution to dryness, a lime green solid precipitated. The compound was not recrystallized per se, but rather "digested" in a small amount of room temperature MeOH. The solution was filtered to give a lime green solid product, while the filtrate was royal blue.

The application of heat at any time caused decomposition of the product. The product gave $\mu_{\text{eff}}$ (solid, 298 K) = 2.20 $\mu_B$. Analysis calculated for CuC$_{17}$H$_{19}$B$_2$F$_8$: C, 36.56%; H, 3.43%; N, 17.55%; Cu, 11.38%. Found: C, 36.73%; H, 3.32%; N, 17.53%; Cu, 11.74%.
{Bis-2,6-[(2-imidazol-4-ylethylamino)methyl]pyridine}copper(I) tetrafluoroborate·methanol, \([\text{Cu(I)(imidR)}_2\text{PDA}]\text{(BF}_4\text{)}\cdot\text{CH}_3\text{OH}\). The ligand solution was prepared as for the zinc derivative and then deoxygenated on the Schlenk line. The \([\text{Cu(I)(CH}_3\text{CN)}_4\text{]}\text{(BF}_4\text{)}\) (0.6921 g, 2 mmol) was dissolved in a minimum amount of deoxygenated CH\(_3\)CN (20 ml) and added to the ligand solution via a U-tube, causing an immediate color change to dark red. The solution was taken to dryness, but the resulting red solid was not recrystallized due to its extreme O\(_2\) sensitivity. The application of heat at any time caused decomposition. The dark red solid gave \(\mu_{\text{eff}}\) (solid, 298 K) = 0.71 \(\mu\)\(_B\). Analysis calculated for \(\text{Cu}_1\text{8N}_7\text{H}_{23}\text{BF}_4\text{O}\): C, 42.92%; H, 4.60%; N, 19.46%; Cu, 12.63%. Found: C, 42.65%; H, 4.24%; N, 19.59%; Cu, 13.21%.

{Bis-2,6-[(2-(\(N\)\(_1\)-p-methylbenzyl)imidazol-4-ylethylamino)methyl]pyridine}zinc(II) tetrafluoroborate·monohydrate, \([\text{Zn(II)(imidR)}_2\text{PDA}]\text{(BF}_4\text{)}_2\cdot\text{H}_2\text{O}\). The ligand solution was prepared by dissolving 0.2702 g (2 mmol) of PDA in 50 ml of MeOH, adding 0.8611 g (4 mmol) of [\(N\)\(_1\)-(p-methylbenzyl)]histamine free base, and stirring the solution at room temperature for 2 h. To this golden yellow solution 0.6941 g (2 mmol) of Zn(II)(BF\(_4\))\(_2\)·6H\(_2\)O, was added and the solution stirred for an additional 15 min, before being reduced to dryness. The resulting light tan solid was recrystallized from a minimum amount of MeOH at room temperature. Application of heat at any time caused decomposition. Analysis calculated for \(\text{ZnC}_{33}\text{N}_7\text{H}_{37}\text{B}_2\text{F}_8\text{O}\): C, 50.39%; H, 4.74%; N, 12.49%; Zn, 8.31%. Found: C, 50.20%; H, 4.58%; N, 12.17%; Zn, 7.76%.
(Bis-2,6-\{(1-(2-(N\textsubscript{1}-p-methylbenzyl)imidazol-4-ythlylimino)methyl\}pyridine)copper(II) Tetrafluoroborate\textsuperscript{1.5} hydrate, [Cu(II)(imidR\textsubscript{2})\textsubscript{PDA}](BF\textsubscript{4})\textsubscript{2} \cdot 1.5H\textsubscript{2}O. The compound was prepared the same as the zinc derivative, using Cu(II)(BF\textsubscript{4})\textsubscript{2} \cdot 6H\textsubscript{2}O in place of the zinc salt to yield a green solution. Reduction of this solution to dryness produced a green solid. This product, although not very soluble in MeOH, was dissolved in MeOH and the solution filtered and cooled in ice. The blue mother liquor was decanted from the green oil that resulted. This green oil was then dissolved in a MeOH:CH\textsubscript{3}CN (50:50) mixture, and the solution filtered and reduced to dryness to yield the desired compound as a green solid with \(\mu_{\text{eff}}\) (solid, 298 K) = 2.15 \(\mu_B\). Application of heat at any time caused decomposition. Analysis calculated for CuC\textsubscript{33}N\textsubscript{7}H\textsubscript{38}B\textsubscript{2}F\textsubscript{8}O\textsubscript{1.5}: C, 49.94%; H, 4.82%; N, 12.35%; Cu, 8.00%. Found: C, 49.88%; H, 4.52%; N, 12.15%; Cu, 8.24%.

(Bis-2,6-\{(2-(N\textsubscript{1}-p-methylbenzyl)imidazol-4-ythlyliminomethyl\}pyridine)copper(I) Tetrafluoroborate\textsuperscript{0.5} methanol, [Cu(I)(imidR\textsubscript{2})\textsubscript{PDA}](BF\textsubscript{4})\textsubscript{0.5}CH\textsubscript{3}OH. The ligand solution was prepared as for the zinc derivative and was deoxygenated on the Schlenk line. The [Cu(I)(CH\textsubscript{3}CN)\textsubscript{4}](BF\textsubscript{4}) (0.6921 g, 2 mmol) was dissolved in a minimum amount of deoxygenated CH\textsubscript{3}CN (20 ml) and added to the ligand solution via a U-tube, producing an immediate color change to dark red. The solution was reduced to dryness, but the solid was not recrystallized due to its extreme \(O_2\) sensitivity. Application of heat at any time caused decomposition. The resulting dark red solid gave \(\mu_{\text{eff}}\) (solid, 298 K) = 0.55 \(\mu_B\).
Analysis calculated for CuC\(_{33.5}\)N\(_7\)H\(_{39}\)BF\(_4\)O\(_{0.5}\): C, 57.81%; H, 5.36%; N, 14.09%; Cu, 9.13%. Found: C, 57.76%, H, 5.60%; N, 13.88%; Cu, 9.40%.

\[\text{[2-[(2-imidazol-4-ylethylamino)methyl],6-[(2-pyrid-2-ylethylamino)-methyl]pyridine)copper(II) Tetrafluoroborate}(\text{methanol/monohydrate}), \text{[Cu(II)(imidH)(py)PDA}(\text{BF}_4)_2\cdot(\text{CH}_3\text{OH/H}_2\text{O})]\]. The compound was prepared by dissolving 0.2702 g (2 mmol) of PDA in 50 ml of MeOH and adding drop-wise to this solution a solution of 0.2442 g (2 mmol) of 2-(2-aminoethyl)pyridine and 0.2222 g (2 mmol) of histamine free base in 50 ml of MeOH. The addition took about 1 h, followed by 1 h of additional stirring, all at room temperature. To this golden yellow solution, 0.6905 g (2 mmol) of solid Cu(BF\(_4\))\(_2\cdot6\text{H}_2\text{O}\) was added to give a blue solution which was stirred an additional 15 min before being reduced to dryness at room temperature. The compound was recrystallized by dissolving it in a minimum amount of room temperature MeOH, followed by cooling and scratching of the flask to yield the blue-green product. Application of heat at any time caused decomposition. The \(\mu_{\text{eff}}\) (solid, 298 K) = 2.11 \(\mu_\text{B}\). Analysis calculated for CuC\(_{20}\)N\(_{6}\)H\(_{26}\)B\(_2\)F\(_8\)O\(_2\): C, 38.77%; H, 4.22%; N, 13.56%; Cu, 10.25%. Found: C, 38.95%; H, 3.82%; N, 13.61%; Cu, 10.37%.

\[\text{[Bis-2,6-[1-(2-pyrid-2-ylethylamino)ethyl]pyridine)iron(II) Tetrafluoroborate}0.5\text{hydrate}, [Fe(II)(py)\(_2\)DAP}(\text{BF}_4)_2\cdot0.5\text{H}_2\text{O}\]. A ligand solution was prepared by dissolving 0.6527 g (4 mmol) of 2,6-diacetylpyridine (DAP) in 75 ml of MeOH, adding 0.9774 g (8 mmol) of 2-(2-aminoethyl)-pyridine and refluxing gently for 1 h to give a golden yellow solution.
Fe(II)(BF₄) was not commercially available and had to be freshly prepared in situ for each synthesis, with all manipulations of the re-agents being executed under inert atmospheric conditions. 0.795 g of Fe(II)Cl₂·4H₂O (4 mmol) was dissolved in 100 ml of MeOH and added to 1.7132 (8 mol) of solid AgBF₄, with the immediate precipitation of AgCl. The solution was reduced in volume to about 75 ml, cooled, and the filtrate [containing Fe(II)(BF₄)₂] added directly into the deoxygenated ligand solution. The intensely purple solution that resulted was reduced to dryness, and the resulting purple solid recrystallized from hot MeOH. The μ eff (solid, 298 K) = 5.28 μ B. Analysis calculated for FeC₂₅J₃₅H₂₅.5B₂F₁₇₂₂O₂₂.5; C, 45.29%; H, 4.30%; N, 11.48%; Fe, 9.17%. Found: C, 45.31%; H, 4.23%; N, 11.14%; Fe, 10.00%.

{Bis-2,6-[1-(2-imidazol-4-yylethylimino)ethyl]pyridine}iron(II) Tetra-fluoroborate·methanol, [Fe(II)(imidH)₂DAP](BF₄)₂·CH₃OH. A ligand solution was prepared by dissolving 0.6527 g (4 mmol) of DAP in 75 ml of MeOH, adding 0.8892 g (8 mmol) of histamine free base, and refluxing gently for 1 h to give a golden yellow solution. The Fe(BF₄)₂ solution was prepared as above for [Fe(II)(py)₂DAP](BF₄)₂. The addition of the iron salt to the ligand solution gave a dark purple solution which was reduced to dryness. The resulting purple solid was dissolved in a minimum amount of hot MeOH, the solution filtered hot, cooled, and the volume reduced until a small amount of oil formed. The mother liquor was decanted from the oil and reduced to dryness under vacuum to yield the desired purple solid. The μ eff (solid, 298 K) = 4.59 μ B. Analysis
calculated for FeC$_{20}$N$_7$H$_{27}$B$_2$F$_8$: C, 39.32%; H, 4.45%; N, 16.05%; Fe, 9.15%. Found: C, 39.36%; H, 4.26%; N, 16.02%; Fe, 9.67%.

{Bis-2,6-[l-(2-pyrid-2-ylethylimino)ethyl]pyridine)cobalt(II) Tetrafluoroborate, [Co(II)(py)$_2$DAP](BF$_4$)$_2$.} A ligand solution was prepared by dissolving 0.6527 g (4 mmol) of 2,6-diacetylpyridine (DAF) in 75 ml of MeOH, adding 0.9774 g (8 mmol) of 2-(2-aminoethyl)pyridine and refluxing gently for 1 h to give a golden yellow solution. The Co(II)(BF$_4$)$_2$·6H$_2$O (1.3625 g, 4 mmol) was placed under vacuum during this time. After refluxing, the ligand solution was cooled and deoxygenated by alternating applications of vacuum and argon. All further manipulations were made under inert atmosphere conditions. The solid cobalt salt was added to the ligand solution via a U-tube, immediately giving a ruby red solution which was stirred an additional 15 min before being reduced to dryness under vacuum. The compound recrystallized easily from hot MeOH to give a dark purple solid. The $\mu_{\text{eff}}$ (solid, 298 K = 2.22 $\mu_B$). Analysis calculated for CoC$_{23}$N$_5$H$_{25}$B$_2$F$_8$: C, 45.74%; H, 4.17%; N, 11.59%; Co, 9.76%. Found: C, 45.45%; H, 3.96%; N, 11.41%; Co, 9.77%.

{Bis-2,6-[1-(2-imidazol-4-ylethylimino)ethyl]pyridine)cobalt(II) Tetrafluoroborate, [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$.} A ligand solution was prepared by dissolving 0.6527 g (4 mmol) of DAP in 75 ml of MeOH, adding 0.8892 g (8 mmol) of histamine free base, and refluxing gently for 1 h to give a golden yellow solution. The Co(II)(BF$_4$)$_2$·6H$_2$O was placed under vacuum during this time. After refluxing, the ligand solution
was cooled and deoxygenated and added to the solid cobalt salt via a U-tube to immediately produce a ruby red solution (note: if the solution was contaminated by O₂ at this state, a rust colored precipitate began to form immediately). The clear, ruby red solution was reduced to dryness and the resulting solid recrystallized from hot MeOH to give a dark purple solid. The μₐeff (solid, 298 K = 3.50 μₐ).

Analysis calculated for CoC₁⁹N₁⁻H₂₃B₂F₈: C, 39.21%; H, 3.98%; N, 16.85%; Co, 10.13%. Found: C, 39.37%; H, 3.83%; N, 16.73%; Co, 9.30%.

{Bis-2,6-[1-(2-pyrid-2-ylethylimino)ethyl]pyridine)cobalt(I) Tetrafluoroborate|methylene chloride, [Co(I)(py)₂DAP](BF₄)·CH₂Cl₂.} The compound was prepared by controlled potential electrolysis of the cobalt(II) analog. A saturated solution of NaBF₄ in CH₃CN served as the supporting electrolyte solution. In order to first electrolyze any contaminates in the solution, the supporting electrolyte solution was purged with N₂ for 1/2 h, then electrolyzed at -0.55 V (vs. S.C.E.) until a constant amperage was achieved. To this solution was added 0.1 g of [Co(II)(py)₂DAP](BF₄)₂ and the solution purged with N₂ for another 1/2 h. This solution was then electrolyzed at -0.55 V (vs. S.C.E.) until constant amperage was obtained, during which time the solution changed from a ruby red to a burnt orange color. The solution was transferred to a Schlenk flask under an argon/N₂ atmosphere, reduced to dryness, and placed under vacuum overnight. The resulting solid, containing both NaBF₄ and the cobalt(I) compound, was placed on a Schlenk filter and washed with one 5 ml portion of CH₂Cl₂, with the CH₂Cl₂ filtrates containing the burnt orange colored Co(I)
compound. The CH₂Cl₂ filtrates were taken to dryness to yield the dark brown solid. The \( \mu_{\text{eff}} \) (solid, 298 K) = 3.46. Analysis calculated for CoC₄₂H₂₇N₅BF₄Cl₄: C, 47.87%; H, 4.52%; N, 11.63%; F, 12.62%; Co, 9.79%. Found: C, 47.58%; H, 4.30%; N, 11.95%; F, 13.75%; Co, 8.67%.

{Bis-2,6-[1-(2-imidazol-4-yethylamino)ethyl]pyridine)cobalt Tetrafluoroborate·O₂, [Co(imidH)₂DAP](BF₄)₂·O₂. This compound was prepared exactly as the deoxygenated cobalt(II) compound, except that all of the synthesis was executed on the open lab bench. Upon addition of the cobalt salt to the ligand solution, the solution was momentarily ruby red, then a rust colored precipitate began to form. The solution was then bubbled with O₂ for 15 min to produce additional precipitate. This solid was collected by filtration and washed with several portions of MeOH and then absolute ether. The \( \mu_{\text{eff}} \) (solid, 298 K) = 2.16 \( \mu_B \). Analysis calculated for CoC₁₉N₂H₂₃B₂F₈O₂: C, 37.17%; H, 3.78%; N, 15.97%; Co, 9.61%. Found: C, 37.03%; H, 3.99%; N, 16.08%; Co, 8.97%.

Physical and Spectroscopic Measurements

Solid state infrared spectra were obtained as Nujol mulls on NaCl plates on a Beckman IR-4230 spectrophotometer. Solution spectra were obtained with solution IR cells with NaCl plates and CH₃CN as the solvent. All mulls other than those of zinc(II) and copper(II) complexes were prepared and maintained under N₂. UV-VIS spectra were obtained on a Cary 17 Recording Spectrophotometer using matched quartz cells of 1 cm or 2 cm path length. DMSO or CH₃CN were the solvents used. All solutions for electronic absorption spectroscopy
other than those of the copper(II) complexes were prepared in the dry box or on the Schlenk line. For recycling of the oxygenated solutions, the solutions were placed under vacuum with vigorous stirring for 30 min at room temperature.

Solution state conductivity measurements were obtained using a Model 31 YSI conductivity bridge using CH\textsubscript{3}CN solutions \(\sim 10^{-2}\) M in complex. All solutions were prepared on the Schlenk line and added to the argon flushed cell by way of septum caps and canula.

\textit{Pmr} spectra of the zinc(II) and copper(I) complexes were obtained in CD\textsubscript{3}CN at room temperature at 90 MHz using a Varian EM-390 spectrometer. The spectra of the hydrochloride salt and the free base \(N\textsubscript{1}-(p\text{-methylbenzyl})\)histamine were run using D\textsubscript{2}O or CDC\textsubscript{3} as the solvent. \textit{Pmr} spectra of the paramagnetic cobalt(II), cobalt(I), and iron(II) complexes were run in CD\textsubscript{3}CN at 90 MHz on a Joel FX90Q spectrometer using CDC\textsubscript{3} as the reference. \textit{Pmr} spectra used in the Evans' method\textsuperscript{72} determination of the solution magnetic susceptibility for the cobalt and iron complexes were obtained at 90 MHz on a Varian EM-390 instrument with CH\textsubscript{3}CN as the solvent and CHCl\textsubscript{3} as the reference solvent. All samples other than those of the zinc(II) complexes and the organic precursors were prepared either in the dry box or on the Schlenk line.

Chemical analyses for nonmetal elements were performed either by Schwarzkopf Microanalytical Laboratory or on a Perkin-Elmer 240C elemental analyzer. Metal analyses were obtained by atomic absorption spectrometry on an Instrumentation Laboratory model IL253 instrument.
The Warburg manometers used for measuring $O_2$ uptake were purchased from Precision Scientific (Model #66662). The flasks were paired with a manometer and the flask constant determined using triply distilled Hg. The manometer fluid consisted of a solution of distilled water containing a few drops of bromothymol blue and a few grams of Alconox as a surfactant. DMSO was the solvent used for all $O_2$ uptake experiments.

The complex was weighed (4-10 mg) into the side arm of the flask, the flask attached to the manometer, and flushed with $N_2$ for 3 min. Then 3 ml of deoxygenated DMSO were syringed into the main compartment and the flask lowered into the constant temperature bath (23°C) and flushed with $N_2$ for an additional min. The flask was then flushed with $O_2$ for 1 min, quickly stoppered, and the stopcock closed. After 1 min both the manometer and thermobarometer were adjusted to atmospheric pressure and sealed. The manometer was then shaken and tilted for 30 sec to mix the DMSO thoroughly with the complex in the side arm. The solution was stirred with a small magnetic stirrer until $O_2$ uptake had ceased or until such time (about 2 h) that blanks had shown the manometer to be unreliable. The $O_2$ uptake ceased after 15 min to 2 h, depending on the compound. A blank was treated in exactly the same manner and its $O_2$ uptake, along with the uptake by the thermobarometer on each run, was subtracted from the $O_2$ uptake of the complex.

For recycling runs 4-10 mg of complex was dissolved in 3 ml of DMSO and the solution oxygenated, then placed under vacuum with vigorous stirring for 30 min. The solution was then syringed into the
manometer flask which had been flushed with N₂ and the procedure followed as before, except that the O₂ flush lasted only 30 sec. A blank was treated in the same manner.

X-band EPR spectra were recorded at 12 K on a Varian E-line spectrometer. The samples were prepared in the dry box by dissolving the complex in DMSO to yield an \( \sim 10^{-4} \) M solution. The oxygenated samples were bubbled with O₂ for about 10 min, and the redeoxygenated samples placed under vacuum with vigorous stirring for 30 min.

Magnetic susceptibility in the solid state was measured using the Faraday method on a Cahn model 6600-1 Research Magnetic Susceptibility System, using Hg[Co(NCS)₄] as the calibrant. Measurements were made under 1 atm of helium using a cryogenic system consisting of an Air Products Interface model DMS-19 vacuum shroud, an LT-3-110 B Heli-tran system, and an APD-TL digital temperature readout monitoring an iron-doped gold vs. chromel thermocouple. The molar susceptibilities of the corresponding zinc(II) complexes were used to correct for ligand and anion diamagnetism in the copper, cobalt, and iron complexes:

\[
\begin{align*}
[Zn(\text{imidH})_2\text{PDA}](BF_4)_2: \\
[Zn(py)\text{PDA}](BF_4)_2: \\
[Zn(\text{imidR})_2\text{PDA}](BF_4)_2: \\
[Zn(\text{imidH})(py)\text{PDA}](BF_4)_2: \\
[Zn(\text{imidH})_2\text{DAP}](BF_4)_2: \\
[Zn(py)_2\text{DAP}](BF_4)_2: \\
\end{align*}
\]

\[
\begin{align*}
X_M &= -2.830 \times 10^{-4} \text{ cgsu mol}^{-1} \\
X_M &= -2.338 \times 10^{-4} \text{ cgsu mol}^{-1} \\
X_M &= -4.224 \times 10^{-4} \text{ cgsu mol}^{-1} \\
X_M &= -2.584 \times 10^{-4} \text{ cgsu mol}^{-1} \\
X_M &= -3.378 \times 10^{-4} \text{ cgsu mol}^{-1} \\
X_M &= -2.386 \times 10^{-4} \text{ cgsu mol}^{-1} \\
\end{align*}
\]
Electrochemical studies were conducted at room temperature in CH₃CN or MeOH using NaBF₄, tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium tetrafluoroborate (TBABF₄) as the supporting electrolyte. Solutions used for cyclic voltammetry or differential pulse polarography were 10⁻³ M in compound and ~ 0.025 M in supporting electrolyte. Solutions were purged with N₂ or O₂ and kept under a blanket of the appropriate gas depending upon the desired conditions. Cyclic voltammograms and differential pulse polarograms were obtained using a PAR model 174A Polarographic Analyzer with the current voltage curves recorded on a Houston Instruments Omnicraphic 2000 X-Y recorder. The electrolysis cell was a PAR polarographic model K60, using a three electrode arrangement. The counter and working electrodes were platinum button electrodes, interfaced through mercury to copper wires. The reference electrode was a Fischer Scientific model 13-639-56 Saturated Calomel Electrode (S.C.E.) and was separated from the bulk solution by a fritted glass bridge containing supporting electrolyte solution.

Controlled potential electrolysis (C.P.E.) was used for synthetic purposes to prepare [Co(I)(py)₂DAP](BF₄) from the corresponding cobalt(II) derivative. The potential was set using a PAR model 173 Potentiostat/Galvanostat and the integration of the current, with respect to time to yield coulombs, was performed by a PAR model 179 Coulometer. The value (coulombs) displayed by the coulometer was corrected to account for background by subtracting the value represented by the residual current (in amps) times the length of the electrol-
ysis (in seconds). A Labchron digital timer was used for all time measurements. The synthesis cell consisted of a main compartment into which the solution to be electrolyzed was placed, a fritted glass bridge for the counter electrode, and a series of two fritted glass bridges for the S.C.E. reference electrode, with the entire system constructed to allow for interface to a Schlenk line. The counter electrode consisted of a coil of platinum wire interfaced to copper wire. The working electrode was a cylinder of platinum gauze attached to a platinum wire. For synthetic purposes, CH$_3$CN solutions saturated with NaBF$_4$ served as the supporting electrolyte solution with about 0.1 g of compound used per 150 ml of solution. N$_2$ saturated with CH$_3$CN was bubbled through the solution to be electrolyzed, and the solution stirred by a magnetic stir bar. The supporting electrolyte solution was electrolyzed at the selected voltage previous to compound addition in order to electrolyze any impurities and to determine the background amperage. The complex was added and the electrolysis continued until a constant amperage was obtained. The voltage to be used was selected so as to fall on the plateau occurring after the cathodic peak on the cyclic voltammogram of the complex to be electrolyzed, usually about 0.25 V negative of the E$_{1/2}$. All redox potentials are reported vs. S.C.E. and are uncorrected for junction potentials.

Mössbauer spectra were obtained using a previously described spectrometer$^{76}$ and computer analyzed by the program of Chrisman and Tumolillo.$^{77}$ Temperatures were measured by a copper vs. constantan thermocouple imbedded into the sample. Sodium nitroprusside (SNP) was used
as a reference standard for the isomer shift parameters. Computer-generated plots of the Mössbauer spectra were obtained using a Calcomp plotting program.
RESULTS AND DISCUSSION

The Copper Chemistry

Synthesis and Characterization of the Complexes

The copper derivatives were prepared as outlined in Figure 9. The organic precursors, 2,6-pyridinedicarboxaldehyde (PDA) and free base \([N_1-(p\text{-methylbenzyl})]\text{histamine were prepared in advance of the Schiff base condensations which formed the pentadentate ligands. The 2,6-pyridinedicarboxaldehyde (PDA) was prepared by the oxidation of 2,6-pyridinedimethanol with freshly prepared MnO}_2\). It was found that PDA is light sensitive, decomposing upon exposure to light for long periods of time, as evidenced by a color change from white to light blue. The free base \([N_1-(p\text{-methylbenzyl})]\text{histamine was prepared by the addition of } \alpha\text{-chloro}\_p\text{-xylene to a solution of histamine hydrochloride in liquid ammonia in which sodium metal had been dissolved. This yielded the hydrochloride salt of the } N_1\text{-substituted histamine (substituted in the } N_1\text{ position with a } p\text{-methylbenzyl group) along with a side product in which the } N_3\text{ position was substituted. The reaction mixture was worked up to remove the undesired isomer by means of fractional recrystallization, and to convert the hydrochloride salt to the free base. Both organic precursors were characterized by pmr with their spectra given in Figures 10 and 11 and the spectral assignments in Table 2.}

The Schiff base condensation to form the ligands (Figure 4A, B, C) involved the condensation of one part of PDA with two parts of the appropriate amine [either free base histamine, free base substituted
Figure 9

Synthesis Scheme for [Cu(I)(imidH)₂PDA](BF₄)

PDA

\[
\text{H}_2\text{N} - \text{CH} - \text{CN} \quad \text{histamine}
\]

\[
\begin{array}{c}
\text{CH}_3\text{OH} \\
\end{array}
\]

\[
[\text{imidH}_2\text{PDA}]
\]

\[
\begin{array}{c}
\text{CH}_3\text{OH/} \\
\end{array}
\]

\[
[\text{Cu(I)(CH}_3\text{CN})_4](\text{BF}_4)
\]

\[
[\text{Cu(I)(imidH)₂PDA}(\text{BF}_4)]
\]
Figure 10

PMR Spectrum of 2,6-Pyridinedicarboxaldehyde in CDCl₃ Relative to TMS at Room Temperature
Figure 11

PMR Spectrum of $[N_1-(p$-methylbenzyl)]histamine

in CDCl$_3$ Relative to TMS at Room Temperature
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift, p.p.m.*</th>
<th>Spectral Assignment**</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-Pyridinedicarboxaldehyde</td>
<td>8.05 (m)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>10.10 (s)</td>
<td>b</td>
</tr>
<tr>
<td>([N_1-(p\text{-methylbenzyl})\text{histamine}])</td>
<td>2.30 (s)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>2.69 (t)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2.93 (t)</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>3.33 (s)</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>4.87 (s)</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>6.60 (s)</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>7.00 (m)</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>7.33 (s)</td>
<td>h</td>
</tr>
</tbody>
</table>

*p.p.m. given relative to TMS at zero, s = single, t = triplet, m = multiplet.

**Assignments shown in Figures 10 and 11.
histamine, or 2-(2-aminoethyl)pyridine] in room temperature MeOH for
two hours. The mixed derivative (Figure 4D) was prepared from one
part of PDA, one part of free base histamine and one part of
2-(2-aminoethyl)pyridine. The order of addition of the amines made no
difference in the final product. In the case of the $[\text{Cu(I)}(\text{py})_2\text{PDA}]$
($\text{BF}_4$), $[\text{Cu(I)}(\text{imidH})_2\text{PDA}]($BF$_4$), and the $[\text{Cu(I)}(\text{imidR})_2\text{PDA}]($BF$_4$) deriva-
tives, the ligand solution was deoxygenated, the $[\text{Cu(I)}($CH$_3$CN)$_4]$($\text{BF}_4$)
added dissolved in CH$_3$CN, and the solution reduced to dryness at room
temperature under vacuum. All of the copper(II) and zinc(II) deriva-
tives were prepared in the same manner, although no precautions against
O$_2$ exposure were taken, and the metal salts, Cu($\text{BF}_4$)$_2$·6H$_2$O or
Zn($\text{BF}_4$)$_2$·6H$_2$O, were added as solids. The copper(I) derivatives could
not be recrystallized without some decomposition due to their O$_2$ sensi-
tivity. The copper(II) and zinc(II) derivatives were either recrystall-
lized from room temperature MeOH or were purified by dissolving in a
minimum amount of room temperature MeOH, oiling out a small quantity
of the compound with ether, then decanting off the mother liquor and
reducing it to dryness to obtain the desired compound. After purifica-
tion, all of the complexes exhibited markedly different solubilities
from the analogs reported by Merrill$^{37}$ and Simmons,$^{36}$ in that they were
very much less soluble in MeOH but with similar solubility in CH$_3$CN.
Attempts were made to synthesize the copper(I) mixed-ligand derivative
by controlled potential electrolysis of the copper(II) analog, but this
yielded products which when isolated corresponded to the $[\text{Cu(I)}(\text{py})_2$
PDA]($\text{BF}_4$) and the $[\text{Cu(I)}(\text{imidH})_2\text{PDA}]($BF$_4$) derivatives.
It was found important to keep the complexes made with PDA at room temperature or below at all times; at higher temperatures decomposition occurred, with the zinc(II) complexes turning green and the copper(II) complexes turning brown. No attempt was made to determine the products of the decomposition, since elemental analyses (C, H, N, metal) on these materials varied from batch to batch and were inconsistent with reasonable possibilities. The fact that aldehydes undergo Schiff base condensation more readily than ketones explains why the PDA derivatives can be prepared without heat, whereas gentle reflux is usually needed in the case of the ketones to bring about complete condensation.\textsuperscript{78} It is also known that imine bonds are sensitive to hydrolysis and attack by alcohols.\textsuperscript{79} In the presence of heat, these two properties of Schiff bases may explain the observed "decomposition," either through polymerization because of the greater reactivity of aldehydes, or to hydrolysis or methanolysis of the imine bond.

The infrared data for the copper(II), copper(I), and zinc(II) complexes is given in Table 3. The infrared spectra show that the Schiff base condensation occurred by the presence of a C=N stretch and the absence of a C=O stretch. Also in the case of the [(imidR)\textsubscript{2}PDA] derivatives and the [(py)\textsubscript{2}PDA] derivatives, the N–H stretch disappears. The O=N stretching frequency occurs between 1580 cm\textsuperscript{-1} and 1615 cm\textsuperscript{-1} in all cases.\textsuperscript{80} For those cases where analyses showed the presence of water or MeOH, a peak around 3500 cm\textsuperscript{-1} to 3600 cm\textsuperscript{-1} due to an O–H stretching frequency was also observed.\textsuperscript{80} All of the derivatives are hygroscopic, as a peak in the O–H stretching frequency region was
<table>
<thead>
<tr>
<th>Complex</th>
<th>O-H(st)(^c)</th>
<th>N-H(st)</th>
<th>C=N(st)</th>
<th>anion(^d) BF(_4)(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF(_4)">Zn(II)(py)(_2)PDA</a>(_2)</td>
<td></td>
<td></td>
<td></td>
<td>1615(s) 1050(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(II)(py)(_2)PDA</a>(_2)</td>
<td></td>
<td></td>
<td></td>
<td>1605(s) 1055(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(I)(py)(_2)PDA</a></td>
<td>3600(w)</td>
<td></td>
<td>1600(s)</td>
<td>1050(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Zn(II)(imidH)(_2)PDA</a>(_2)</td>
<td></td>
<td>3345(s)</td>
<td>1595(s)</td>
<td>1050(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(II)(imidH)(_2)PDA</a>(_2)</td>
<td></td>
<td>3330(s)</td>
<td>1585(s)</td>
<td>1050(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(I)(imidH)(_2)PDA</a></td>
<td>3600(w)</td>
<td>3340(s)</td>
<td>1590(s)</td>
<td>1050(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Zn(II)(imidR)(_2)PDA</a>(_2)</td>
<td>3500(s)</td>
<td></td>
<td>1600(s)</td>
<td>1050(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(II)(imidR)(_2)PDA</a>(_2)</td>
<td>3610(m)</td>
<td></td>
<td>1580(s)</td>
<td>1050(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3350(m)</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(I)(imidR)(_2)PDA</a></td>
<td>3600(w)</td>
<td></td>
<td>1585(s)</td>
<td>1050(s)</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(II)(imidH)(py)PDA</a>(_2)(^e)</td>
<td>3600(w)</td>
<td>3320(s)</td>
<td>1595(s)</td>
<td>1055(s) (3285(s))</td>
</tr>
<tr>
<td><a href="BF(_4)">Cu(II)(imidH)(py)PDA</a>(_2)(^f)</td>
<td>3600(w)</td>
<td>3310(s)</td>
<td>1600(s)</td>
<td>1040(s) (1585(s))</td>
</tr>
</tbody>
</table>

a) s = strong, m = medium, w = weak
b) all values are given in cm\(^{-1}\)
c) from lattice MeOH or H\(_2\)O
d) center of a broad envelope
e) compound obtained from a MeOH solution
f) compound obtained from a CH\(_3\)CN solution, also a C=N(st) at 2240 cm\(^{-1}\)
observed when the Nujol mulls were prepared on the open bench on a humid day. In the [(imidH)₂PDA] complexes, an N-H stretching frequency was observed between 3315 cm⁻¹ and 3360 cm⁻¹, and in all cases a broad (~ 200 cm⁻¹) band was observed between 1000 cm⁻¹ and 1100 cm⁻¹, corresponding to a B-F stretching frequency.⁸⁰

The infrared data was also used to investigate the [Cu(II)(imidH)-(py)PDA](BF₄)₂ derivative, which appeared to be unstable, unlike [Cu(II)(imidH)(py)DAP](BF₄)₂ discussed by Merrill.⁷⁷ In the case of [Zn(II)(imidH)(py)PDA](BF₄)₂, the IR spectrum obtained for what was believed to be the pure mixed ligand derivative corresponded exactly to the IR spectrum obtained for pure [Zn(II)(imidH)₂PDA](BF₄)₂. This assignment is also supported by NMR and elemental analysis (vide infra).

In the case of [Cu(II)(imidH)(py)PDA](BF₄)₂ recrystallized from MeOH, the IR spectrum shows a sharp doublet at 3320 cm⁻¹ and 3285 cm⁻¹, with a sharp singlet at 1595 cm⁻¹, whereas the analogous derivative, [Cu(II)(imidH)(py)DAP](BF₄)₂, prepared by Merrill⁷⁷ shows only a single peak at 3320 cm⁻¹ and a doublet at 1610 cm⁻¹ and 1590 cm⁻¹. A 1:1 mixture of the [Cu(II)(imidH)₂PDA](BF₄)₂ and [Cu(II)(py)₂PDA](BF₄)₂ derivatives shows the same spectral features obtained by Merrill,⁷⁷ as would be expected, but not as obtained for the mixed ligand derivative described here. After dissolving the supposed [Cu(II)(imidH)(py)PDA]-(BF₄)₂ derivative in CH₃CN and reducing the solution to dryness, the infrared spectrum changes to give a singlet around 3300 cm⁻¹ and a doublet at 1600 cm⁻¹ and 1585 cm⁻¹, with an additional peak due to the C≡N stretching frequency of CH₃CN at 2240 cm⁻¹ (Figure 12). Elemental
Figure 12

Infrared Spectra of [Cu(II)(imidH)(py)PDA](BF₄)₂ as Nujol Mulls

(A) Compound recovered from MeOH.
(B) Compound recovered from CH₃CN.
analyses support the fact that the complex is affected by the solvents in which it is dissolved. After being in MeOH, one MeOH and one H$_2$O are indicated as being in the formula of the complex, whereas after being dissolved in CH$_3$CN, approximately one CH$_3$CN and one H$_2$O are indicated as being present. These changes were also investigated electrochemically and are described later.

The pmr spectra for all of the zinc(II) and copper(I) complexes were obtained and are shown in Figures 13-18, with the spectral assignments given in Tables 4 and 5. The copper(I) spectra are generally of poor quality due to contamination of the copper(I) species by O$_2$, producing some oxygen adduct or other copper(II) compounds, thus broadening the lines in the spectra. This broadening of the spectra of copper(I) species due to the presence of minute quantities of copper(II) has been observed before. $^{81}$ Proof that the Schiff base condensation has occurred is the lack of the pmr peak corresponding to the aldehydic proton present in unreacted PDA. The pmr's of the complexes, due to their cleanliness and sharpness, attest to the fact that the metal centers are fully five coordinated (at least) with both arms of the ligand attached, otherwise a greater number of peaks would be expected to appear due to the inequivalency of the two arms unless a five coordinate ⇨ four coordinate equilibrium is faster than the pmr time scale. The [Cu(II)(imidH)$_2$DAP](BF$_4$)$_2$ and [Zn(II)(imidH)$_2$DAP]·(BF$_4$)$_2$ complexes are five coordinate in the solid state as shown by x-ray crystallography. $^{82}$ When the spectra of the [(imidH)$_2$PDA] complexes are obtained under very dry conditions, the imidazole proton
Figure 13

PMR Spectrum of $\text{[Zn(II)(imidH)$_2$PDA](BF}_4)_2$

in CD$_3$CN Relative to TMS at Room Temperature
Figure 14

PMR Spectrum of $[\text{Zn(II)}(\text{py})_2\text{PDA})(\text{BF}_4)_2$

in $\text{CD}_3\text{CN}$ Relative to TMS at Room Temperature
Figure 15

PMR Spectrum of \([\text{Zn(II)}(\text{imidR})_2\text{PDA}]\text{(BF}_4\text{)}_2\)
in CD$_3$CN Relative to TMS at Room Temperature
Figure 16

PMR Spectrum of [Cu(I)(imidH)₆FDA](BF₄)
in CD₃CN Relative to TMS at Room Temperature
Figure 17

PMR Spectrum of \([\text{Cu(I)}(\text{py})_2\text{PDA}]\text{(BF}_4\text{)}\)

in CD$_3$CN Relative to TMS at Room Temperature
Figure 18

PMR Spectrum of \[\text{Cu(I)(imidR)_2PDA}(BF_4)\]
in CD_3CN Relative to TMS at Room Temperature
Table 4

PMR Spectral Data for the Zinc(II) Complexes

in CD$_3$CN at Room Temperature

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Chemical Shift, p.p.m.*</th>
<th>Spectral Assignment**</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF$_4$">Zn(II)(py)$_2$PDA</a>$_2$</td>
<td>3.45 (t)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>4.41 (t)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>7.40–8.20 (m)</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>8.20–8.55 (m)</td>
<td>d</td>
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<tr>
<td></td>
<td>8.75 (m)</td>
<td>e</td>
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<tr>
<td><a href="BF$_4$">Zn(II)(imidH)$_2$PDA</a>$_2$</td>
<td>3.15 (t)</td>
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<td>4.25 (t)</td>
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<td>7.10 (s)</td>
<td>c</td>
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<tr>
<td></td>
<td>7.95 (s)</td>
<td>d</td>
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<td></td>
<td>8.05–8.50 (m)</td>
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<td></td>
<td>8.70 (m)</td>
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<tr>
<td></td>
<td>10.85 (broad)</td>
<td>g</td>
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<td>7.95 (s)</td>
<td>g</td>
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<tr>
<td></td>
<td>7.95–8.35 (m)</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>8.60 (s)</td>
<td>i</td>
</tr>
</tbody>
</table>

* p.p.m. given relative to TMS, s = singlet, t = triplet, m = multiplet
** assignments relate to Figures 13–15.
Table 5
PMR Spectral Data for the Copper(I) Complexes
in CD$_3$CN at Room Temperature

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Chemical Shift, p.p.m.*</th>
<th>Spectral Assignment**</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF$_4$">Cu(I)(py)$_2$PDA</a></td>
<td>3.00 (t)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>4.00 (t)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>7.05-7.75 (m)</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>7.75-8.10 (m)</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>8.45 (s)</td>
<td>e</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(imidH)$_2$PDA</a></td>
<td>2.80 (t)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>3.70 (t)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>6.55 (s)</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>7.20-7.80 (m)</td>
<td>d,e</td>
</tr>
<tr>
<td></td>
<td>8.10 (s)</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>9.69 (broad)</td>
<td>g</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(imidR)$_2$PDA</a></td>
<td>2.35 (s)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>2.83 (m)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>3.33 (s)</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>3.80 (m)</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>4.95 (s)</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>6.10 (s)</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>6.95 (s)</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>7.35 (s)</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>7.35-7.85 (m)</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>8.20 (s)</td>
<td>j</td>
</tr>
</tbody>
</table>

* p.p.m. given relative to TMS, s = singlet, t = triplet, m = multiplet. ** assignments shown in Figures 16-18.
signal was evident around 10 ppm. The pmr spectra also support the conclusion that MeOH is occluded in some of the complexes by the appearance of a peak assignable to MeOH.

The difficulty of obtaining the pure [Cu(I)(imidH)(py)PDA](BF₄)₂ derivative is shown by the pmr spectrum. After electrolysis of the supposed [Cu(II)(imidH)(py)PDA](BF₄)₂ derivative, the products isolated can be assigned to be the [Cu(I)(imidH)₂PDA](BF₄) complex and the [Cu(I)(py)₂PDA](BF₄) complex, with the separation of these two being accomplished due to differing solubilities in CH₃CN. Little, if any, of the [Cu(I)(imidH)(py)PDA](BF₄) derivative was recovered. The pmr spectra of what should be the [Zn(II)(imidH)(py)PDA](BF₄)₂ complex is essentially that of the [Zn(II)(imidH)₂PDA](BF₄)₂ complex. These results, along with the infrared spectral data, leave some doubt as to the true nature of the [Cu(II)(imidH)(py)PDA](BF₄)₂ derivative.

**Electrochemical Studies**

Since the reactivity of O₂ with the copper(I) complexes possibly proceeds by way of the oxidative addition mechanism shown in Figure 19, the complexes were studied by electrochemistry, not only to observe the reaction of O₂ with the complexes, but also to investigate the possibility that the reactivity with O₂ is related to the E₁/₂ of the metal center, as found previously for a series of cobalt(II) derivatives.⁵³

The zinc(II) complexes were studied by cyclic voltammetry (Figure 20) to insure that any of the redox couples observed in the region of interest (+1.0 V to −0.6 V vs. S.C.E.) were not due to ligand redox reactions. The only redox couples seen for the zinc(II) com-
Figure 19

Proposed Reaction Mechanism of $\text{O}_2$ with $\text{Cu(I)L}$

to Form a $\mu$-Peroxo Bridge

$$2 \text{Cu(I)L} + \text{O}_2 \rightarrow \text{Cu(II)L} - \text{Cu(II)L}$$
Figure 20

Cyclic Voltamograms of the Zinc(II) Complexes

in CH\textsubscript{3}CN at 10\textsuperscript{-3} M and 0.025 M TBABF\textsubscript{4} at Room Temperature

(A) [Zn(II)(imidH)\textsubscript{2}PDA](BF\textsubscript{4})\textsubscript{2}

(B) [Zn(II)(py)\textsubscript{2}PDA](BF\textsubscript{4})\textsubscript{2}

(C) [Zn(II)(imidR)\textsubscript{2}PDA](BF\textsubscript{4})\textsubscript{2}

Scan Rate = 200 mV/sec
plexes are negative of this region of interest, and are assigned to ligand centered reductions rather than to reduction of the zinc(II) center. Therefore, any redox couples observed in the region of interest can confidently be assigned to the Cu(II) ⇌ Cu(I) redox process.

One of the primary reasons for investigating this particular set of ligands was to determine the effect of a change in the $E_{1/2}$ of the metal center on the oxygenation process, while leaving the major portion of the ligand intact, in particular the imidazole protons. As would be expected, replacement of the methyl groups attached to the imine carbons by hydrogens shifts the $E_{1/2}$ of the metal center to more positive values. This is due to a proton being more electron withdrawing than a methyl group, thus increasing delocalization of the electron density of the electron rich copper(I) center and stabilizing the copper(I) state. Comparing the $E_{1/2}$ values for the systems described here (Table 6) and those systems described by Merrill and Simmons (Table 1), it can be seen that all of the complexes described here have $E_{1/2}$'s ca. 0.25 V positive of those analogs described by Merrill and Simmons. If indeed there is a correlation between $E_{1/2}$'s and the reactivity with $O_2$, the complexes described here should all be less reactive with $O_2$ than the previously described analogs, and, indeed, this is the case, as discussed below.

Cyclic voltammograms of the copper(II) complexes were employed to investigate the $O_2$ reactivity of the copper(I) species without having to actually synthesize the copper(I) species. The copper(II) species were studied under $N_2$ and $O_2$ to investigate the effect of exposure to
Table 6
Cyclic Voltammetry Data for the Copper Complexes

in CH$_3$CN at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

<table>
<thead>
<tr>
<th>Complex</th>
<th>Volts (vs. S.C.E.)</th>
<th>Cu(II) $\leftrightarrow$ Cu(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF$_4$">Cu(II)(py)$_2$PDA</a>$_2$</td>
<td>+0.04</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(py)$_2$PDA</a></td>
<td>+0.04</td>
<td></td>
</tr>
<tr>
<td>oxygenated</td>
<td>$-\ldots$</td>
<td>$\ldots^a$</td>
</tr>
<tr>
<td>deoxygenated</td>
<td></td>
<td>+0.04</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(II)(imidR)$_2$PDA</a>$_2$</td>
<td>-0.09</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(imidR)$_2$PDA</a></td>
<td>-0.09</td>
<td></td>
</tr>
<tr>
<td>oxygenated</td>
<td>$-\ldots$</td>
<td>$\ldots^a$</td>
</tr>
<tr>
<td>deoxygenated</td>
<td></td>
<td>-0.09</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(II)(imidH)$_2$PDA</a>$_2$</td>
<td>-0.11</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(imidH)$_2$PDA</a></td>
<td>-0.11</td>
<td></td>
</tr>
<tr>
<td>oxygenated</td>
<td>$-\ldots$</td>
<td>$\ldots^a$</td>
</tr>
<tr>
<td>deoxygenated</td>
<td>$-\ldots$</td>
<td>$\ldots^a$</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(II)(imidH)(py)PDA</a>$_2$</td>
<td>$b$</td>
<td></td>
</tr>
<tr>
<td>initially</td>
<td></td>
<td>-0.11</td>
</tr>
<tr>
<td>after 10 minutes</td>
<td></td>
<td>-0.11 and -0.04</td>
</tr>
<tr>
<td>after 30 minutes</td>
<td></td>
<td>-0.04</td>
</tr>
</tbody>
</table>

Scan rate = 200 mV/s

a) No wave seen.

b) The voltammogram obtained is determined by the length of time in solution.
O₂ upon the redox couple. All of the Cu(II) ⇌ Cu(I) redox couples under N₂ were found to be nearly reversible one electron processes, as verified by controlled potential electrolysis. The peak to peak separation was found to be slightly larger than 0.59 mV as in an idealized reversible reaction, but less than 100 mV. Under O₂, the cyclic voltammogram of the [Cu(II)(py)₂PDA](BF₄)₂ complex does not change appreciably from that obtained under N₂ (Figure 21). However, if the potential is held at -0.6 V (vs. S.C.E.) for 10 seconds during the forward part of the scan, the anodic wave in the return oxidation scan is greatly reduced in amplitude and shifted to more positive values. At a hold of 20 seconds at -0.6 V (vs. S.C.E.) the anodic wave is almost lost completely. This observation can be rationalized if the copper(I) formed at the electrode surface reacts with the O₂ in solution to form copper(II), so that there is no copper(I) available to produce an oxidation wave. It should also be noted that this [Cu(II)(py)₂PDA](BF₄)₂ derivative seems to undergo a much faster reaction with O₂ than the [Cu(II)(py)DAP](BF₄)₂ derivative reported by Simmons, as that derivative does not lose its anodic wave under similar conditions. It has been confirmed by manometric studies (vide infra) that this [Cu(I)(py)₂PDA](BF₄) derivative does indeed react faster with O₂ than the [Cu(I)(py)DAP](BF₄) analog described by Simmons, although it takes on the order of 60 minutes to come to equilibrium. The cyclic voltammogram of the isolated copper(I) species is also available (Figure 22) and is the same as that obtained from the copper(II) complex. As would be expected there is loss of the anodic
Figure 21

Cyclic Voltammograms of [Cu(II)(py)$_2$PDA](BF$_4$)$_2$

in CH$_3$CN at 10$^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.
(B) Under O$_2$.
(C) Under O$_2$, with a 10 second hold at -0.6 V.
(D) Under O$_2$, with a 20 second hold at -0.6 V.

Scan Rate = 200 mV/sec
**Figure 22**

Cyclic Voltammograms of $[\text{Cu(I)(py)}_2\text{PDA}](\text{BF}_4)$

in CH$_3$CN at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.

(B) Under O$_2$.

(C) Solution (B) deoxygenated by bubbling with N$_2$.

Scan Rate = 200 mV/sec
wave when a solution of the copper(I) complex is bubbled with O₂, although the cathodic wave is still visible but reduced in amplitude. However, there is no color change when this copper(I) solution is exposed to O₂. After long periods of purging with N₂ the original cyclic voltammogram is recovered. This recovery may not necessarily be related to the reversible oxygenation of the copper(I) complex in solution, but rather to the long length of time necessary for complete oxygenation of a sample. After purging with N₂, the apparent recovery of the cyclic voltammogram is probably due to copper(I) which was never oxygenated in the first place, not an oxygenated species which has undergone reversible oxygenation.

As would be expected, based upon the results of Merrill and Simmons, the [Cu(I)(imidH)₂PDA](BF₄) complex is shown to be much more reactive than the [Cu(I)(py)₂PDA](BF₄) complex. After saturation of the solution with O₂, scanning the cyclic voltammogram without a hold (Figure 23) shows the anodic wave to be diminished and shifted positively by about 0.70 mV. In a scan which is held at -0.6 V for 10 seconds in the presence of O₂, the anodic wave is completely lost, indicating rapid reactivity of the copper(I) formed at the electrodes with the O₂ in solution, forming copper(II) and thus no anodic (oxidation) wave is observed. A cyclic voltammogram for the isolated copper(I) complex is available (Figure 24) and under N₂ it is the same as that obtained for the copper(II) complex. Upon saturation of the solution with O₂, the solution turns from red to green, and a cyclic voltammogram scan shows complete loss of both the anodic and cathodic
Figure 23

Cyclic Voltammograms of [Cu(II)(imidH)$_2$PDA](BF$_4$)$_2$

in CH$_3$CN at 10$^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.

(B) Under O$_2$.

(C) Under O$_2$, with a 10 second hold at -0.6 V.

Scan Rate = 200 mV/sec
Figure 24

Cyclic Voltammograms of $[\text{Cu(I)(imidH)}_2\text{PDA}]^+\text{BF}_4^-$
in CH$_3$CN at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.
(B) Under O$_2$.
(C) Solution (B) deoxygenated by bubbling with N$_2$.

Scan Rate = 200 mV/sec
waves. Upon prolonged purging with \( \text{N}_2 \) there is no color change and the cyclic voltammogram is not recoverable, thus indicative of an irreversible oxygenation reaction under these conditions.

The \([\text{Cu(II)}(\text{imidR})_2\text{PDA}]\text{(BF}_4\text{)}_2\) derivative shows a cyclic voltammogram very much like that of the \([\text{Cu(II)}(\text{py})_2\text{PDA}]\text{(BF}_4\text{)}_2\) derivative under \( \text{O}_2 \) (Figure 25). There is little change in the cyclic when scanned under \( \text{O}_2 \) with no hold, but complete loss of the anodic wave when the scan is held at \(-0.6 \text{ V}\) for 10 seconds. A cyclic voltammogram is available for the isolated \([\text{Cu(I)}(\text{imidR})_2\text{PDA}]\text{(BF}_4\text{)}\) species (Figure 26), and is identical to that for the \([\text{Cu(II)}(\text{imidR})_2\text{PDA}]\text{(BF}_4\text{)}_2\) species under \( \text{N}_2 \). After exposure to \( \text{O}_2 \), there is some loss of the anodic wave, but not as much as would be expected based on how quickly the anodic wave is lost under \( \text{O}_2 \) with the copper(II) species. After purging the solution with \( \text{N}_2 \), the original voltammogram is again obtained. Again, recovery of the voltammogram is believed not to be due so much to reversible oxygenation, but rather the presence in solution of copper(I) which was never oxygenated due to the slow rate of reaction with \( \text{O}_2 \).

Based on the time involved in the disappearance of the anodic wave under \( \text{O}_2 \), the compounds may be ordered in terms of their relative rates of reactivity with \( \text{O}_2 \). Thus it can be said that the \([\text{Cu(I)}(\text{imidH})_2\text{PDA}]\text{(BF}_4\text{)}\) complex reacts fastest, followed by the \([\text{Cu(I)}(\text{imidR})_2\text{PDA}]\text{(BF}_4\text{)}\) derivative, and finally the \([\text{Cu(I)}(\text{py})_2\text{PDA}]\text{(BF}_4\text{)}\) derivative, which is the same ordering as the \( E_{1/2} \)'s.

Electrochemistry also serves as a tool to investigate the lack of stability of the \([\text{Cu(II)}(\text{imidH})(\text{py})\text{PDA}]\text{(BF}_4\text{)}_2\) derivative (Figures 27 and
Figure 25

Cyclic Voltammograms of \([\text{Cu(II)(imidR)}_2PDA](\text{BF}_4)_2\)

in CH$_3$CN at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.
(B) Under O$_2$.
(C) Under O$_2$, with a 10 second hold at -0.6 V.
(D) Under O$_2$, with a 10 second hold at -0.6 V.

Scan Rate = 200 mV/sec
Figure 26

Cyclic Voltammograms of $[Cu(I)(imidR)_{2}PDA](BF_4)$
in CH$_3$CN at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$
(B) Under O$_2$
(C) Solution (B) deoxygenated by bubbling with N$_2$

Scan Rate = 200 mV/sec
Figure 27

Cyclic Voltammograms of [Cu(II)(imidH)(py)PDA](BF₄)₂
in CH₃CN at 10⁻³ M and 0.025 M TBABF₄ at Room Temperature

(A) Cyclic voltammogram obtained initially.
(B) Cyclic voltammogram obtained after 10 minutes in solution.
(C) Cyclic voltammogram obtained after 15 minutes in solution.
(D) Cyclic voltammogram obtained after 30 minutes in solution.

Scan Rate = 200 mV/sec
28). When the [Cu(II)(imidH)(py)PDA](BF₄)₂ derivative recrystallized from MeOH is first placed in the supporting electrolyte solution (Figure 27A), an E₁/₂ of -0.1 V (vs. S.C.E.) is obtained, the same value as obtained for the [Cu(II)(imidH)₂PDA](BF₄)₂ derivative. After standing for several minutes a cyclic voltammogram may be obtained which shows peaks corresponding to E₁/₂'s of -0.04 V (vs. S.C.E.) and -0.1 V (Figure 27B). After an additional period of time, only a single peak at -0.04 V is seen (Figure 27D). Based upon the relationships shown between the PDA derivatives investigated here, and the DAP complexes investigated by Simmons 36 and Merrill, 37 the [Cu(II)(imidH)(py)-PDA](BF₄)₂ derivative in this case would be expected to have an E₁/₂ of -0.04 V. If the blue [Cu(II)(imidH)(py)PDA](BF₄)₂ derivative recrystallized from MeOH is dissolved in CH₃CN and allowed to stand for an hour before being recovered from solution, the resulting green solid when first placed in the supporting electrolyte solution shows only one peak at -0.04 V. This difference in behavior depending upon the solvent history is also evidenced by changes in the IR spectrum (Figure 12) and the elemental analysis as discussed above. The first explanation that was proposed for this phenomenon was that when recrystallized from MeOH a MeOH molecule became coordinated to the copper (as evidenced by the elemental analysis). Upon exposure to CH₃CN this MeOH was replaced by CH₃CN, accounting for the change in E₁/₂'s. If this were so, controlled potential electrolysis of the mixed derivative, whether with MeOH or CH₃CN, should yield the [Cu(I)(imidH)(py)PDA](BF₄) derivative, which could be verified by its pmr spectra. This was not found to be
Figure 28

Differential Pulse Polarograms of $[\text{Cu(II)}(\text{imidH})(\text{py})\text{PDA}](\text{BF}_4)_2$

in CH$_3$CN at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Differential pulse polarogram obtained initially.

(B) Differential pulse polarogram obtained after 10 minutes in solution.

(C) Differential pulse polarogram obtained after 15 minutes in solution.

(D) Differential pulse polarogram obtained after 30 minutes in solution.

Scan Rate = 2 mV/sec
the case. Isolation of the products from controlled potential electrolysis and separation by means of solubility differences yielded only the 
[Cu(I)(imidH)_2PDA](BF_4) complex and the [Cu(I)(py)_2PDA](BF_4)_2 complex, with little if any of the [Cu(I)(imidH)(py)PDA](BF_4) derivative present. The only possible explanation that can be proposed at this time would involve hydrolysis of the imine bond in the mixed ligand derivative, with some driving force favoring the formation of the [Cu(I)(imidH)_2PDA](BF_4) and [Cu(I)(py)_2PDA](BF_4) derivatives as opposed to reforming the mixed ligand derivative. To better understand what could be occurring, a solution of one part [Cu(II)(imidH)_2PDA](BF_4)_2 complex and one part [Cu(II)(py)_2PDA](BF_4)_2 was prepared, and monitored electrochemically for a period of over 24 hours. There was no change in the cyclic scans; in other words, the [Cu(II)(imidH)(py)PDA](BF_4)_2 derivative would not form from a mixture of [Cu(II)(py)_2PDA](BF_4)_2 and [Cu(II)-(imidH)_2PDA](BF_4)_2 derivatives. It is of interest to note that if an aliquot of the reaction mixture is taken before being reduced to dryness and recrystallized the main peak seen is that corresponding to [Cu(II)-(py)(imidH)PDA](BF_4)_2 with smaller peaks corresponding to [Cu(II)-(imidH)_2PDA](BF_4)_2 and [Cu(II)(py)_2PDA](BF_4)_2, as would be expected from a statistical mixture. None of these difficulties were seen in the mixed ligand DAP derivative analogs prepared by Merrill, with the only difference being the presence of a methyl group on the imine carbon as opposed to a proton in the present PDA case.

From the comparison of the E_{1/2}'s of the complexes studied here (Table 6) with those studied by Merrill and Simmons (Table 1), a
correlation can be made between the $E_{1/2}$'s of metal centers having like types of ligands and the reactivity of the metal center with $O_2$. It is not valid to compare the $E_{1/2}$ of the $[\text{Cu}(I)(\text{imidH})_2\text{PDA}](\text{BF}_4)$ complex described here with the $E_{1/2}$ of the $[\text{Cu}(I)(\text{py})_2\text{DAP}](\text{BF}_4)$ complex described by Simmons,\textsuperscript{36} as that would lead one to incorrectly believe that the $[\text{Cu}(I)(\text{imidH})_2\text{PDA}](\text{BF}_4)$ complex would be $O_2$ inactive. However, it is valid to compare the $E_{1/2}$ of the $[\text{Cu}(I)(\text{imidH})_2\text{PDA}](\text{BF}_4)$ complex with the $E_{1/2}$ of the $[\text{Cu}(I)(\text{imidH})\text{DAP}](\text{BF}_4)$ complex, and the correct assumption, borne out by manometry, is that the $[\text{Cu}(I)(\text{imidH})_2\text{PDA}](\text{BF}_4)$ complex described here would be the less reactive of the two. Thus a correlation can be made for a series of complexes with like ligands: those with the more positive $E_{1/2}$'s will react slower and with a smaller degree of reversibility than those with more negative $E_{1/2}$'s.

**Warburg Manometry Results**

The stoichiometry of $O_2$ uptake was determined by Warburg manometry. $[\text{Cu}(I)(\text{py})_2\text{PDA}](\text{BF}_4)$ reacts over a period of about 1 hour (Figure 29) to give a final reaction stoichiometry of one $O_2$ per two copper centers, although there is no color change associated with this $O_2$ uptake as with the other $O_2$ reactive species. The $[\text{Cu}(I)(\text{imidH})_2\text{PDA}](\text{BF}_4)$ complex and the $[\text{Cu}(I)(\text{imidR})_2\text{PDA}](\text{BF}_4)$ complex both react with a stoichiometry of one $O_2$ per two copper centers, with a concurrent change in color from red to green. The $[\text{Cu}(I)(\text{imidH})_2\text{PDA}](\text{BF}_4)$ complex completes its reaction within about 5 minutes, while the $[\text{Cu}(I)(\text{imidR})_2\text{PDA}](\text{BF}_4)$ derivative takes on the order of 15 minutes for complete reaction. In general, these relative rates of reaction are consistent
Figure 29

$O_2$ Uptake of $[Cu(I)(py)_2PDA](BF_4)$ in DMSO

versus Time at Room Temperature
with the conclusions drawn from the electrochemical studies. The 
[Cu(I)(imidH)$_2$PDA](BF$_4$) derivative was found to be approximately 20% 
reversible, consistent with the electronic spectral data, based upon the 
O$_2$ uptake of a sample which had been oxygenated then placed under 
vacuum with vigorous stirring for 1 hour. The [Cu(I)(imidR)$_2$PDA](BF$_4$) 
complex was found to be irreversible under the same conditions, again 
consistent with electronic spectral data. The stoichiometries for the 
reaction of O$_2$ with the copper(I) centers is consistent with the 
mechanism proposed by Simmons$^{36}$ and Merrill,$^{37}$ which involves the oxida-
tion of two copper(I) centers to copper(II), concurrent with the 
reduction of the O$_2$ molecule to a peroxide group bridging the two 
copper(II) centers (Figure 19). The irreversibility is thought to be 
due to either irreversible oxidation of the copper centers, or to 
oxidation of the ligand system.

Burnett et al.$^{33}$ have reported the investigation of a copper(I) 
system which contains a ligand which has some of the essential features 
of the ligand systems involved here. A proposed mechanism for the 
irreversible oxidation of the ligand, due to oxidation of a CH$_2$–CH$_2$ 
linkage to CH–CH (Figure 30) was put forth. This assignment of the 
oxidation process was based upon the observation of a new IR peak 
corresponding to O=C which is not present in the deoxygenated species.

In order to test the applicability of this mechanism to the 
copper(I) chemistry under investigation here, a solution IR spectrum 
was taken of undeoxygenated [Cu(I)(imidH)$_2$DAP](BF$_4$) and of the oxy-
genated form. There does appear to be a change in the IR spectrum in
Figure 30

Proposed Mechanism for the Irreversible Oxidation of the Ligand in the Copper(I) Complexes
the region of interest (1550 cm\(^{-1}\) to 1650 cm\(^{-1}\)), with a doublet appearing in the spectrum of the oxygenated complex where only a singlet was present before (Figure 31). This mechanism is consistent with an initial uptake of one O\(_2\) per two copper centers as observed for the complexes investigated here.

**Electronic Spectral Studies**

Since the most obvious change upon oxygenation of the \([\text{Cu(I)-(imidH)}_2\text{PDA}]\text{(BF}_4\text{)}\) and \([\text{Cu(I)(imidR)}_2\text{PDA}]\text{(BF}_4\text{)}\) derivatives is the color change from red to green, the study of the electronic spectra should provide information about the completeness of the oxygenation and the degree of reversibility of the system when deoxygenation is attempted. This can by done by monitoring the intense peak (\(\varepsilon \approx 2000\)) that occurs at \(~500\) nm in all of the copper(I) species (Figures 32, 33, and 34). The copper(II) species (Figures 35, 36, and 37) do not exhibit a 500 nm feature. Upon oxygenation of the \([\text{Cu(I)(imidH)}_2\text{PDA}]\text{(BF}_4\text{)}\) and \([\text{Cu(I)(imidR)}_2\text{PDA}]\text{(BF}_4\text{)}\) derivatives, the absorption peak at \(~500\) nm disappears completely, explaining the change in color from red to green upon oxygenation. The spectra of a sample of the oxygenated \([\text{Cu(I)-(imidH)}_2\text{PDA}]\text{(BF}_4\text{)}\) derivative which had been placed under vacuum with vigorous stirring for an hour in an attempt to deoxygenate it shows a recovery in intensity of about 25% of the \(~500\) nm peak, consistent with the \(~25\%\) reversibility factor observed manometrically. The spectra of the \([\text{Cu(I)(imidR)}_2\text{PDA}]\text{(BF}_4\text{)}\) complex which had been oxygenated, followed by attempts to deoxygenate it, showed little, if any,
Figure 31

Solution State Infrared Spectra Supporting the Proposed Mechanism for the Irreversible Oxidation of the Ligand of $[\text{Cu}(I)(\text{imidH})_2\text{DAP}](\text{BF}_4)$

(A) Spectrum obtained in deoxygenated $\text{CH}_3\text{CN}$.

(B) Solution (A) bubbled with $\text{O}_2$ for 15 minutes.
Figure 32

Electronic Absorption Spectra of [Cu(I)(py)$_2$PDA](BF$_4$)
in DMSO at 10$^{-4}$ M at Room Temperature

(A) In deoxygenated DMSO.

(B) Solution (B) bubbled with O$_2$ for 15 minutes.
Figure 33

Electronic Absorption Spectra of \([\text{Cu(I)}(\text{imidH})_2\text{PDA}]\text{BF}_4\) in DMSO at \(10^{-4}\) M at Room Temperature

(A) In deoxygenated DMSO.

(B) Solution (A) bubbled with \(O_2\) for 15 minutes.

(C) Solution (B) placed under vacuum for 30 minutes in an attempt to deoxygenate the complex.
Figure 34

Electronic Absorption Spectra of [Cu(I)(imidR)₂PDA](BF₄) in DMSO at 10⁻⁴ M at Room Temperature

(A) In deoxygenated DMSO.

(B) Solution (A) bubbled with O₂ for 15 minutes.

(C) Solution (B) placed under vacuum for 30 minutes in an attempt to deoxygenate the complex.
Figure 35

Electronic Absorption Spectra of $[\text{Cu(II)}(\text{py})_{2}\text{PDA}]\text{BF}_4_2$

in DMSO at $10^{-4}$ M at Room Temperature
Figure 36

Electronic Absorption Spectra of [Cu(II)(imidH)₂PDA](BF₄)₂

in DMSO at 10⁻⁴ M at Room Temperature
Figure 37

Electronic Absorption Spectra of [Cu(II)(imidR)$_2$PDA](BF$_4$)$_2$

in DMSO at 10$^{-4}$ M at Room Temperature
recovery of the ~500 nm peak, consistent with the irreversible nature of the oxygenation, as shown by manometric studies.

The slow reactivity of [Cu(I)(py)$_2$PDA](BF$_4$) is shown by monitoring its spectra with time after exposure to O$_2$ (Figure 38). Even after 80 minutes, the ~500 peak is still evident (~50% of original). This explains why the complex retains its color after exposure to O$_2$ for moderate lengths of time, even though uptake of O$_2$ is occurring. Along with some loss of the ~500 nm peak, there is also the appearance of another peak at ~400 nm, which is not observed in the spectra of the other oxygenated derivatives. This is suggestive that the oxygenation of [Cu(I)(py)$_2$PDA](BF$_4$) is occurring by a different mechanism than the other derivatives.

The electronic spectra for all of the complexes are tabulated in Table 7.

Conclusions for the Copper Chemistry

A systematic study has been made of a series of three copper(I) complexes and four copper(II) complexes having closely related pentadentate ligands in order to better understand the effect that small changes in the ligand structure has upon the reversibility of the oxygenation reaction. Based upon the derivatives studied here, in conjunction with those described by Merrill$^{37}$ and Simmons,$^{36}$ it can be seen that there exists a correlation between the E$_{1/2}$'s of the copper(I) complexes with like ligands and their reactivity with O$_2$. Also within a series of ligands in which one change has been made (i.e., methyl group vs. proton on the imine carbon) the reactivity of the copper(I)
Figure 38

Electronic Absorption Spectra of $[\text{Cu(I)}(\text{py})_2\text{PDA}](\text{BF}_4)$

in MeOH at $10^{-4}$ M at Room Temperature

(A) In deoxygenated MeOH.

(B) Solution (A) in the presence of $O_2$ for 10 minutes.

(C) Solution (A) in the presence of $O_2$ for 30 minutes.

(D) Solution (A) in the presence of $O_2$ for 80 minutes.
Table 7

Electronic Spectral Data for the Copper Complexes

at Room Temperature in DMSO

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$, nm</th>
<th>$\varepsilon$, M$^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF$_4$">Cu(II)(py)$_2$PDA</a>$_2$</td>
<td>675</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>490</td>
<td>63</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(II)(imidR)$_2$PDA</a>$_2$</td>
<td>665</td>
<td>152</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(II)(imidH)$_2$PDA</a>$_2$</td>
<td>610</td>
<td>108</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(py)$_2$PDA</a></td>
<td>470</td>
<td>2650</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(imidR)$_2$PDA</a></td>
<td>470</td>
<td>1895</td>
</tr>
<tr>
<td><a href="BF$_4$">Cu(I)(imidH)$_2$PDA</a></td>
<td>500</td>
<td>1920</td>
</tr>
</tbody>
</table>
complex with O\textsubscript{2} can be correlated to the $E_{1/2}$ of the metal center, although there may be other factors involved such as the presence or absence of an imidazole proton. It has become evident based on the work described here and the work of Merrill\textsuperscript{35} that, although the imidazole proton is not essential for some degree of reversible behavior of the oxygenation process, its presence seems to greatly enhance the reversibility to a degree that is not likely to be due only to the effect it has upon the $E_{1/2}$ of the metal center.

Some insight has also been gained into the manner in which ligand oxidation may occur to give irreversible oxygenation of the copper(I) complexes. Based upon IR spectral results it appears there may be formation of a C=C bond, which could occur by oxidation of the CH\textsubscript{2}CH\textsubscript{2} bonds on the ligand arms during the oxygenation process.
The Iron(II) Chemistry

Synthesis and Characterization of the Complexes

The ligand synthesis for [Fe(II)(imidH)₂DAP](BF₄)₂ and [Fe(II)-(py)₂DAP](BF₄)₂ was carried out as described for the copper derivatives, using DAP in place of PDA. The Fe(BF₄)₂ was prepared in situ immediately prior to use by dissolving FeCl₂·4H₂O in a minimum amount of MeOH and adding this solution to a stoichiometric amount of AgBF₄ to yield a methanolic solution of Fe(BF₄)₂ with AgCl as a precipitate. All of this was done under argon. The solution was filtered to remove AgCl and the filtrate added directly to the appropriate deoxygenated ligand solution, whereupon the solution immediately became intensely purple in color. The solution was reduced to dryness, the resulting solid dried overnight under vacuum, and, in the case of [Fe(II)(py)₂DAP](BF₄)₂, recrystallized from MeOH. The [Fe(II)(imidH)₂DAP](BF₄)₂ was purified by dissolving it in a minimum amount of MeOH, reducing the volume while cooling until a small amount of material oiled out of solution, decanting off the mother liquor, and taking the mother liquor to dryness to yield the desired crystalline product.

The infrared spectral data for the iron(II) complexes is given in Table 8. As in the case of the other metal derivatives with the same ligands, the infrared spectra give evidence, by way of a new C=N stretching frequency and the absence of the C=O stretching frequency, that the Schiff base condensation has been completed. For the iron derivatives, the C=N stretching frequency is found at 1605 cm⁻¹ for [Fe(II)(py)₂DAP](BF₄)₂ and 1590 cm⁻¹ for [Fe(imidH)₂DAP](BF₄)₂, with
### Table 8

Infrared Spectral Data for the Iron(II) Complexes as Solid State Nujol Mulls\(^{a,b}\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>O-H (st)</th>
<th>N-H (st)</th>
<th>C=N (st)</th>
<th>anion (\text{BF}_4^-)</th>
<th>(\text{BF}_4^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Fe(II)(py)}_2\text{DAP}</a>_2)</td>
<td>3425 (s)(^c)</td>
<td>1695 (s)</td>
<td>1060 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Fe(II)(imidH)}_2\text{DAP}</a>_2)</td>
<td>3600 (w)(^d)</td>
<td>3340 (w)</td>
<td>1590 (s)</td>
<td>1060 (s)</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{a}\)  s = strong, \(m = \) medium, \(w = \) weak

\(\text{b}\) All values in \(\text{cm}^{-1}\).

\(\text{c}\) From \(\text{H}_2\text{O}\).

\(\text{d}\) From MeOH.

\(\text{e}\) Center of a broad envelope.
the relative placement of these peaks being the same as in the copper
derivatives. In addition, \([\text{Fe(II)}(\text{imidH})_2\text{DAP}] (\text{BF}_4)_2\) displays a sharp
peak at 3340 cm\(^{-1}\) as expected for the N-H stretching of the imidazole
proton. Again this observation is consistent with that of other metal
derivatives of the \(((\text{imidH})_2\text{DAP})\) ligand system. The iron(II) complexes
have elemental analyses which indicate the presence of water in the case
of \([\text{Fe(II)}(\text{py})_2\text{DAP}] (\text{BF}_4)_2\) and MeOH in the case of \([\text{Fe(II)}(\text{imidH})_2\text{DAP}] (\text{BF}_4)_2\) (see Experimental Section). The presence of water in the
\([\text{Fe(II)}(\text{py})_2\text{DAP}] (\text{BF}_4)_2\) derivative is substantiated by the presence of
an O-H stretching frequency at 3425 cm\(^{-1}\), although there is no analogous
peak in the spectra of the imidazole derivative, unless it is obscured
by the N-H stretching frequency of the imidazole moiety. Lastly, the
region around 1060 cm\(^{-1}\) shows a very broad (~ 200 cm\(^{-1}\)) band typical of
the B-F stretching frequencies for the BF\(_4^-\) anion.\(^{80}\)

The pmr spectra of the analogous Zn(II) complexes have been pre-
viously reported by Simmons.\(^{36}\) The pmr spectra of \([\text{Fe(II)}(\text{py})_2\text{DAP}] (\text{BF}_4)_2\) is shown in Figure 39 and tabulated in Table 9. \([\text{Fe(imidH)}_2\text{DAP}] (\text{BF}_4)_2\) did not give a pmr spectrum under similar conditions, although
it is unclear as to why no spectrum could be obtained. It is known,
however, that when the electron spin relaxation time is slow, the re-
sulting pmr is often very broad, sometimes to the extent of being un-
detectable.\(^{86}\) This can occur with d\(^6\) systems [such as Fe(II)] which
are distorted from octahedral symmetry. It should also be noted that
the \([\text{Fe(II)}(\text{py})_2\text{DAP}] (\text{BF}_4)_2\) and \([\text{Fe(II)}(\text{imidH})_2\text{DAP}] (\text{BF}_4)_2\) complexes have
solution state \(\mu_{\text{eff}}\)'s that are significantly different.
Figure 39

PMR Spectrum of [Fe(II)(py)$_2$DAP](BF$_4$)$_2$ in CD$_3$CN/CDCl$_3$

Relative to TMS at Room Temperature
<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical Shift, p.p.m. a</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(II)(py)$_2$DAP]$_2$(BF$_4$)$_2$·H$_2$O</td>
<td>17.32</td>
</tr>
<tr>
<td></td>
<td>14.37</td>
</tr>
<tr>
<td></td>
<td>11.56</td>
</tr>
<tr>
<td></td>
<td>10.16</td>
</tr>
<tr>
<td></td>
<td>3.31</td>
</tr>
<tr>
<td><a href="BF$_4$">Fe(II)(imidH)$_2$DAP</a>$_2$·MeOH</td>
<td>spectra not obtainable</td>
</tr>
</tbody>
</table>

a  

p.p.m. relative to TMS at zero.
Magnetic Susceptibility Studies

The solid state magnetic susceptibility of the iron(II) derivatives was studied from room temperature down to liquid N\textsubscript{2} temperatures (~ 80 K) (Figure 40). Appendix A gives this data. [Fe(II)(py)\textsubscript{2}DAP]- (BF\textsubscript{4})\textsubscript{2} has a $\mu_{\text{eff}} = 5.34$ B at room temperature, decreasing according to the Curie-Weiss law to 5.18 B at 8.6 K with a Weiss constant $\theta = -4.10$ K. [Fe(II)(imidH)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} has a $\mu_{\text{eff}}$ of 4.69 B at room temperature, decreasing to 4.42 B at 81.6 K, with a slight curve in the plot of temperature vs. $\mu_{\text{eff}}$ indicating non-Curie-Weiss law behavior. While [Fe(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} appears to remain high-spin (S=2) throughout the temperature range studied, [Fe(II)(imidH)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} has a $\mu_{\text{eff}}$ between the spin only values for an S=2 system and S=1 system. This indicates that the [Fe(II)(imidH)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} system may be a spin-equilibrium system, intermediate between the high-spin state and low-spin state at the temperatures studied here. It can be seen that as the temperature approaches ~ 80 K, there is a noticeable curve in the plot of $\mu_{\text{eff}}$ vs. temperature. Earlier magnetic susceptibility work down to 15 K on the dihydrate of this complex showed the curve to continue downward giving a $\mu_{\text{eff}} = 2.8$ B at 15 K,\textsuperscript{87} thus it may be possible that the complex is a spin-equilibrium system between S=2 and S=1, as reported for some other five coordinate systems.\textsuperscript{88} The reported five coordinate spin-equilibrium systems include complexes of the ligand system 2,6-bis-(2-diphenylphosphinoethyl)pyridine (pnp) to give [Fe(pnp)I\textsubscript{2}] and [Fe(pnp)I(NCS)]. These complexes show equilibrium between S=2 $\neq$ S=1,
Figure 40

Solid State Magnetic Susceptibility of the Iron Complexes versus Temperature

(A) \([\text{Fe(II)(py)}_2\text{DAP}](\text{BF}_4)_2\)

(B) \([\text{Fe(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2\)
unlike what is usually found for hexacoordinate Fe(II) systems, where the spin-equilibrium is between $S=2 \neq S=0$.\textsuperscript{89}

The solution magnetic susceptibility ($\text{CH}_3\text{CN/CHCl}_3$) for the iron derivatives differs from the values obtained for the solid state (Table 10). It has previously been shown by Wilson et al.\textsuperscript{90} that for Fe(II), Fe(III), and Co(II) spin-equilibrium systems the $\mu_{\text{eff}}$ (solid state) is often different from the $\mu_{\text{eff}}$ (solution state), with the $\mu_{\text{eff}}$ (solution state) being independent of anion effects, although solvent dependency of the $\mu_{\text{eff}}$ was also often found. The room temperature solution $\mu_{\text{eff}}$ for [Fe(II)(py)$_2$DAP](BF$_4$)$_2$ is 1.87 $\mu_B$, and although this value is indicative of one unpaired electron, it is believed that this is more probably indicative of a spin-equilibrium situation, with the $\mu_{\text{eff}}$ at this particular temperature indicative of a mole fraction weighted average between the $S=0$ and $S=2$ states. Assuming $\mu_{\text{eff}} = 0.5$ for the $S=0$ state and $\mu_{\text{eff}} = 5.2 \mu_B$ for the $S=2$ spin state, populations of $\sim 71\%$ $S=0$ and $\sim 29\%$ $S=2$ would adequately explain the data. The $\mu_{\text{eff}}$ (solution, room temperature) of [Fe(II)(imidH)$_2$DAP](BF$_4$)$_2$ is 2.89 $\mu_B$, again intermediate between $S=0$ and $S=2$, but corresponding closely to $S=1$, although the intermediate spin state is not known to exist in very many cases. Some solid state five coordinate species do have $S=1$, as discussed earlier. However, it is believed that the RT $\mu_{\text{eff}}$ obtained for [Fe(imidH)$_2$DAP](BF$_4$)$_2$ is probably indicative of a spin-equilibrium system, where the $\mu_{\text{eff}}$ at this one particular temperature is intermediate between $S=2$ and $S=0$, but possibly $S=1$. 
### Table 10

Magnetic Susceptibility Data for

\([\text{Fe}(\text{py})_2\text{DAP}]\,(\text{BF}_4)_2\) and \([\text{Fe}(\text{imidH})_2\text{DAP}]\,(\text{BF}_4)_2\)^a

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solid (RT, (\mu_B))(^b, c)</th>
<th>Solid (81.6 K, (\mu_B))</th>
<th>Solution (RT, (\mu_B))(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}(\text{II})(\text{py})_2\text{DAP}],(\text{BF}_4)_2)</td>
<td>5.34</td>
<td>5.18</td>
<td>1.87</td>
</tr>
<tr>
<td>([\text{Fe}(\text{II})(\text{imidH})_2\text{DAP}],(\text{BF}_4)_2)</td>
<td>4.68</td>
<td>4.42</td>
<td>2.89</td>
</tr>
</tbody>
</table>

\(^a\) A complete listing of a \(\chi_g\), \(\chi_M\), \(\chi_M'\), and \(\mu_{\text{eff}}\) at temperatures between RT and 81.6 K is given in Appendix A.

\(^b\) RT refers to room temperature.

\(^c\) Determined by the Faraday method.

\(^d\) Determined by the Evan's method,\(^73\) with solvent system \(\text{CH}_3\text{CN/CH}_3\text{Cl}\).
Mössbauer Spectral Studies

To further investigate the magnetic properties of the iron complexes, they were studied by Mössbauer spectroscopy, the data of which is tabulated in Table 11 and the low temperature spectra are shown in Figures 41 and 42. The chemical shift ($\delta$) vs. SNP for [Fe(II)(py)$_2$DAP]-($\text{BF}_4$)$_2$ was found to be 1.28 mm/sec and the quadrupole splitting ($\Delta E_q$) to be 1.32 mm/sec, consistent with a high-spin iron(II) complex, and also consistent with the solid state magnetic susceptibility work. The chemical shift ($\delta$) for [Fe(imidH)$_2$DAP]($\text{BF}_4$)$_2$ at room temperature is 0.81 mm/sec vs. SNP with a quadrupole splitting ($\Delta E_q$) of 0.55 mm/sec. At 100 K the parameters are $\delta$ 0.78 mm/sec and $\Delta E_q$ = 0.51 mm/sec. From the spectra obtained here it is difficult to determine if a spin-equilibrium system is present as suggested by magnetic susceptibility work. In an Fe(II) S=2 $\leftrightarrow$ S=1 spin equilibrium system it would be expected that a widely spaced doublet for the S=2 component would be present along with a sharp singlet for the S=0 component. When the temperature is lowered sufficiently the doublet should become less intense, with the sharp singlet becoming the main feature. By looking at the plot of $\mu_{\text{eff}}$ vs. temperature for [Fe(imidH)$_2$DAP]($\text{BF}_4$)$_2$ (Figure 40), it can be seen that there is very little change in the $\mu_{\text{eff}}$ of the complex from RT to 100 K, thus a large change in the Mössbauer spectrum is not expected between RT and 100 K. It appears that the Mössbauer spectra of the [Fe(II)(imidH)$_2$DAP]($\text{BF}_4$)$_2$ system is supporting evidence for the assignment of S=1 rather than a mixture of S=0 and S=2.
**Table 11**

Mössbauer Parameters for the Iron(II) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp. (^a)</th>
<th>(\delta) (mm/s) vs. SNP</th>
<th>(\Delta E_q) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe(II)(py)\textsubscript{2}DAP]}(\text{BF}_4\textsubscript{2})]</td>
<td>RT</td>
<td>2.28</td>
<td>1.32</td>
</tr>
<tr>
<td>([\text{Fe(II)(imidH)}\textsubscript{2}DAP]}(\text{BF}_4\textsubscript{2})]</td>
<td>RT</td>
<td>0.81</td>
<td>0.55</td>
</tr>
<tr>
<td>([\text{Fe(II)(imidH)}\textsubscript{2}DAP]}(\text{BF}_4\textsubscript{2})]</td>
<td>100 K</td>
<td>0.78</td>
<td>0.51</td>
</tr>
</tbody>
</table>

\(^a\) RT refers to room temperature.
Mössbauer Spectrum of [Fe(II)(py)$_2$DAP](BF$_4$)$_2$ at 100 K
Mössbauer Spectra of \([\text{Fe(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2\) at 100 K
[Fe(imidH)₂DAP](BF₄)₂ 100 K
Electrochemical Studies

Since the reactivity of O₂ with the metal center in metal complexes has been related to the electron density on the metal center, and the \( E_{1/2} \) of the metal complex is correlated to the electron density on the metal center, the iron complexes, as in the case of the copper derivatives, were investigated by electrochemical techniques (Figures 43 and 44 and Table 12). It is possible to observe both the Fe(II)/Fe(I) redox couple and the Fe(II)/Fe(III) redox couple, and it is known that each of the peaks so assigned are not due to ligand redox reactions based upon electrochemical studies of the analogous zinc complexes, which showed that the ligand redox reactions occur at potentials cathodic (negative) of those observed here. The assignment of the Fe(II)/Fe(III) wave is supported by \( E_{1/2} \) values obtained for other Fe(II) complexes, which show the Fe(II)/Fe(III) oxidation to occur around 0.9 V \( \text{vs. S.C.E.} \), close to the values obtained for the complexes studied here (see Table 12). The \( E_{1/2} \) of the \([\text{Fe(II)(py)}_2\text{DAP}](\text{BF}_4)_2\) Fe(II)/Fe(I) redox couple is -0.66 V \( \text{vs. S.C.E.} \), and the Fe(II)/Fe(III) couple is +1.05 \( \text{vs. S.C.E.} \). In the case of the imidazole derivative, the value of the Fe(II)/Fe(I) redox couple is -0.78 V \( \text{vs. S.C.E.} \) and for the Fe(II)/Fe(III) redox couple +0.86 V \( \text{vs. S.C.E.} \). The redox couples for \([\text{Fe(imidH)}_2\text{DAP}](\text{BF}_4)_2\) are cathodic of those for \([\text{Fe(py)}_2\text{DAP}](\text{BF}_4)_2\), as is the case in the copper derivative. The Fe(II)/Fe(III) redox couple is not as resolved as the Fe(II)/Fe(I) redox couple, with the Fe(II)/Fe(III) redox couple displaying little cathodic wave (reduction), perhaps indicative of an irreversible oxida-
Figure 43

Cyclic Voltammograms of [Fe(II)(py)$_2$DAP](BF$_4$)$_2$

in CH$_3$CN at 10$^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.

(B) Under O$_2$.

(C) Solution (B) deoxygenated by bubbling with N$_2$.

Scan Rate = 200 mV/sec
Figure 44

Cyclic Voltammograms of \([Fe(II)(imidH)_2DAP](BF_4)_2\) in CH$_3$CN

at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.

(B) Under O$_2$.

(C) Solution (B) deoxygenated by bubbling with N$_2$.

Scan Rate $= 200$ mV/sec
<table>
<thead>
<tr>
<th>Complex</th>
<th>Volts (vs. S.C.E.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Fe(II) ↔ Fe(I))</td>
</tr>
<tr>
<td><a href="BF%E2%82%84">Fe(II)(py)₂DAP</a>₂</td>
<td>-0.73</td>
</tr>
<tr>
<td>oxygenated</td>
<td>----- a</td>
</tr>
<tr>
<td>deoxygenated</td>
<td>-0.73</td>
</tr>
<tr>
<td><a href="BF%E2%82%84">Fe(II)(imidH)₂DAP</a>₂</td>
<td>-0.78</td>
</tr>
<tr>
<td>oxygenated</td>
<td>----- a</td>
</tr>
<tr>
<td>deoxygenated</td>
<td>----- b</td>
</tr>
</tbody>
</table>

Scan rate = 200 mV/s

a  Cyclic voltammogram obscured by the $O_2 + e^- + O_2^-$ reaction.
b  No cyclic voltammogram observed.
tion in going from Fe(II) to Fe(III). In the presence of $O_2$, $[\text{Fe(II)-(py)}_2\text{DAP}](\text{BF}_4)_2$ shows little or no change in the Fe(II)/Fe(III) redox couple, while the Fe(II)/Fe(I) redox couple is obscured by the reduction of $O_2$ ($O_2 + e^- \rightarrow O_2^-$) in solution. After purging the solution of $O_2$, the Fe(II)/Fe(I) wave is essentially recovered, unchanged from the original cyclic voltammogram, indicative of no irreversible reaction between the Fe(II) center and $O_2$.

When a solution of $[\text{Fe(imidH)}_2\text{DAP}](\text{BF}_4)_2$ is bubbled with $O_2$, the Fe(II)/Fe(I) couple is obscured by the reduction of $O_2$ in the solution ($O_2 + e^- \rightarrow O_2^-$ at $-0.6$ V) and the Fe(II)/Fe(III) couple appears ill defined. Upon purging the solution of $O_2$, some of the cyclic voltammogram is recovered, but it is not as resolved as that originally obtained, being very broadened and with the peak heights diminished. This change in the cyclic voltammogram can best be explained by reaction of $[\text{Fe(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2$ with $O_2$, especially since there is a color change of the solution upon bubbling with $O_2$ from purple to brown/purple. This color change is observed only in the presence of supporting electrolyte, not being observed during manometry measurements on the pure compound. This increased $O_2$ reactivity in the presence of supporting electrolyte has been noticed before in the copper analogs. 92

These results bear out the qualitative relationship between $O_2$ reactivity and the $E_{1/2}$ of the metal center, although the difference in reactivity could also be explained by involvement of the imidazole protons in the imidazole derivative. It has already been shown in the
case of the copper derivative that the imidazole proton is not necessary for reaction with $O_2$.\textsuperscript{37}

**Manometric Studies**

The stoichiometry of the oxygenation of $[\text{Fe(imidH)}_2\text{DAP}](\text{BF}_4)_2$ was determined by Warburg manometry, while the nonreactivity of $[\text{Fe(II)(py)}_2\text{DAP}](\text{BF}_4)_2$ was confirmed. The stoichiometry was found to be one $O_2$ per one iron center after almost 1 hour, the same stoichiometry as obtained by Herron et al.\textsuperscript{46} for their reversible iron(II) non-porphyrin $O_2$ system. There was an initial rapid uptake of $O_2$, followed by a continuously slower rate of uptake. The plot of $O_2$ per cobalt center vs. time is shown in Figure 45. Attempts at recycling the iron complex showed essentially no uptake of $O_2$ by a sample which had been oxygenated and then placed under vacuum with rapid stirring for 1 hour. No color change was seen at any point during the manometry experiments, unlike the color change recorded in the presence of supporting electrolyte.

The electronic spectra of the iron complexes were studied to observe the effect of exposure to $O_2$ on the complexes. Table 13 gives the data in tabular form, while Figures 46 and 47 show the actual spectra. Both complexes exhibit strong peaks at 500 nm ($\varepsilon = 7000$-$8000$), at ~ 600 nm-620 nm ($\varepsilon = 3000$-$3600$), and at ~ 290 nm-300 nm ($\varepsilon = 14,000$-$23,000$), with many small less resolvable shoulder peaks. Based upon the large intensity of these peaks, they are assigned to be metal to ligand charge transfer bands obscuring any d-d bands. Upon oxygenation the peaks at ~ 500 nm and ~ 600 nm lose intensity, but are still clearly resolvable.
Figure 45

$O_2$ Uptake of $[\text{Fe(II)(py)$_2$DAP}](\text{BF}_4)_2$ in DMSO

versus Time at Room Temperature
Table 13
Electronic Spectral Data for the Iron Complexes at Room Temperature in CH₃CN

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$, nm</th>
<th>$\varepsilon$, M⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(II)(py)$_2$DAP]BF$_4$)₂</td>
<td>600</td>
<td>3636</td>
</tr>
<tr>
<td></td>
<td>545</td>
<td>4150 (sh)$^a$</td>
</tr>
<tr>
<td></td>
<td>490</td>
<td>7800</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>8582</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>23400</td>
</tr>
<tr>
<td>[Fe(II)(imidH)$_2$DAP]BF$_4$)₂</td>
<td>620</td>
<td>3004</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>3461 (sh)</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>6862</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>2318 (sh)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>14471</td>
</tr>
</tbody>
</table>

$^a$ sh = shoulder
Figure 46

Electronic Absorption Spectra of $[\text{Fe(II)(py)}_2\text{DAP}]\text{(BF}_4\text{)}_2$

in DMSO at $10^{-4}$ M at Room Temperature

(A) In deoxygenated DMSO.

(B) Solution (A) bubbled with $O_2$ for 15 minutes.
Figure 47

Electronic Absorption Spectra of \([\text{Fe(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2\)

in DMSO at \(10^{-4}\) M at Room Temperature

(A) In deoxygenated DMSO.

(B) Solution (A) bubbled with \(O_2\) for 15 minutes.
It would be of interest to be able to definitely assign the complexes here to being either five or six coordinate, since Fe(II) usually exists in a six coordinate manner. With the data obtained here, it would be very difficult, if not impossible, to make a positive assignment. The elemental analysis for the \([\text{Fe(py)}_2\text{DAP}](\text{BF}_4)_2\) complex indicates one-half \(\text{H}_2\text{O}\) per iron center, whereas the analysis for \([\text{Fe(imidH)}_2\text{DAP}](\text{BF}_4)_2\) indicates one MeOH per iron center. It may be possible for both complexes to be six coordinate, one with the sixth ligand being \(\text{H}_2\text{O}\), the other MeOH. Usually five coordinate iron(II) complexes occur only when the ligands are sufficiently bulky to sterically prevent coordination of a sixth ligand.

It might be possible to determine the coordination number based on electronic absorption spectra, but as discussed before the large charge transfer bands obscure any d-d bands which could be used for this determination.

If indeed the spin-equilibrium is \(S=2 \Leftrightarrow S=1\), as opposed to \(S=2 \Leftrightarrow S=0\), this would be supporting evidence for a five coordinate species, as six coordinate iron(II) species are usually spin-equilibrium \(S=2 \Leftrightarrow S=0\).\(^88\)

Conclusions

To date only two non-porphyrin iron(II) complexes have been found which react reversibly with \(O_2\),\(^{45,46}\) neither under ambient conditions, thus leaving the active site of hemerythrin, as to date, without a successful model. The iron complexes \([\text{Fe(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2\) and
[Fe(II)(py)$_2$DAP](BF$_4$)$_2$ have been investigated for their O$_2$ carrying properties, since the analogous copper(I) complex has been found to react reversibly with O$_2$ through several cycles, thus being a fairly good model for hemocyanin. [Fe(py)$_2$DAP](BF$_4$)$_2$ did not react with O$_2$, as was expected based upon the work with the analogous copper(I) complex. [Fe(II)(imidH)$_2$DAP](BF$_4$)$_2$ did react with O$_2$ at room temperature, although very slowly and in an irreversible manner, with a stoichiometry of one O$_2$ per one iron center. As in the case of the other metal derivatives with the [(imidH)$_2$DAP] ligand, the reason for the reactivity of [Fe(II)(imidH)$_2$DAP](BF$_4$)$_2$ and not [Fe(II)(py)$_2$DAP](BF$_4$)$_2$ can be attributed to either the $E_{1/2}$ of the metal center involved, or the presence of the imidazole moiety, or some combination of both. It has been shown previously in the case of the copper analogs that the presence of the imidazole proton is not necessary for O$_2$ reactivity, although reversibility is greatly reduced in its absence.

From the data gathered for these iron complexes, it can be seen that the reactivity of [Fe(II)(imidH)$_2$DAP](BF$_4$)$_2$ with O$_2$ does not provide a good model for the active site of hemerythrin, but it does give some insight into the path to follow to develop a more reversible system. Looking at the copper analogs, [Cu(I)(imidH)$_2$PDA](BF$_4$) reacts slower and less reversibly with O$_2$ than [Cu(I)(imidH)$_2$DAP](BF$_4$) which has a more negative $E_{1/2}$. It would be logical to conclude that in the case of the iron derivatives a system which possessed the imidazole moieties, and at the same time an $E_{1/2}$ negative of the current derivative, would be a more reversible system.
The Cobalt Chemistry

Synthesis and Characterization of the Complexes

The cobalt(II) derivatives were prepared as shown in Figure 48. The ligand was prepared by means of a Schiff base condensation reaction of one equivalent of 2,6-diacetylpyridine (DAP) with two equivalents of either free base histamine or 2-(2-aminoethyl)pyridine in refluxing MeOH. No attempt was made to exclude O₂ during the ligand preparation. The ligand solution was then cooled to room temperature, deoxygenated on a Schlenk line, and the solution added to solid Co(II)(BF₄)₂·6H₂O which had been placed under vacuum during the ligand preparation, giving a clear ruby red solution. This solution was reduced to dryness and the resulting red/purple solid recrystallized from hot MeOH to give the analytically pure compound.

Contamination of [Co(II)(imidH)₂DAP](BF₄)₂ by O₂ was evidenced by the formation of a rust colored precipitate. The pure, oxygenated form, [Co(imidH)₂DAP](BF₄)₂·O₂, was prepared and isolated in the same manner as the unoxygenated derivative, but with no attempt being made to exclude O₂. A solution of [Co(II)(imidH)₂DAP](BF₄)₂ was stirred in the open air for one-half hour, and the rust colored precipitate collected by filtration, washed with diethyl ether, and air dried on a filter frit equipped with a drying tower containing drierite. The initial formation of the rust colored precipitate was very rapid, but completion of the precipitation was very slow. The elemental analysis of the freshly prepared oxygenated compound was consistent with its formulation as [Co(imidH)₂DAP](BF₄)₂·O₂, but upon standing as a solid the compound
Figure 48

Synthesis Scheme for \([\text{Co(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2\)
\[
\text{DAP} + (2)\text{H}_2\text{N} - \text{N} \rightarrow \text{CH}_3\text{OH}
\]
\[
[(\text{imidH})_2\text{DAP}]
\]
\[
\text{CH}_3\text{OH} / \text{Co(BF}_4)_2
\]
\[
[\text{Co(II)(imidH)}_2\text{DAP}(\text{BF}_4)_2]
\]
decomposed to a material which consistently gave the same elemental analysis from batch to batch but was not interpretable.

The [Co(I)(py)₂DAP](BF₄) complex was prepared by controlled potential electrolysis of the parent cobalt(II) complex. An CH₃CN solution saturated with NaBF₄ and containing 0.1 g of [Co(II)(py)₂DAP]BF₄ was electrolyzed at a potential −0.25 V negative of the E₁/₂ of the Co(II)/Co(I) redox couple (i.e., at −0.55 V vs. S.C.E.) until the current reading was essentially the same as that obtained for a blank solution. The burnt orange colored solution was transferred to a Schlenk line, reduced to dryness, dried under vacuum overnight, and the resulting solids washed with a small amount of CH₂Cl₂. The analytically pure [Co(I)(py)₂DAP](BF₄)·CH₂Cl₂ was obtained by reducing the CH₂H₂ filtrate to dryness. A brown solution during the synthesis was indicative of O₂ contamination.

The infrared spectral data for the cobalt compounds is given in Table 14. The infrared spectra of the cobalt complexes give evidence, by the presence of the C= N stretching frequency and the absence of the C=O stretching frequency, that the Schiff base condensation has occurred. The C=N stretching frequency is found between 1580 cm⁻¹ and 1605 cm⁻¹ in all cases.¹⁰ This region also served as a means of identifying the desired complexes from O₂ contaminated forms. In the case of [Co(II)(imidH)₂DAP](BF₄)₂ and [Co(I)(py)₂DAP](BF₄) (Figure 49), a doublet appears in this region when the compounds have been exposed to air, whereas the pure, deoxy compounds display only a sharp singlet.
Table 14
Infrared Spectral Data for the Cobalt Complexes
as Solid State Nujol Mulls\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Complex</th>
<th>N=H (st)</th>
<th>O=N (st)</th>
<th>anion\textsuperscript{c} BF\textsubscript{4}⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF%5Ctextsubscript%7B4%7D">Co(II)(py)\textsubscript{2}DAP</a>\textsubscript{2}</td>
<td>1605 (s)</td>
<td>1040 (s)</td>
<td></td>
</tr>
<tr>
<td><a href="BF%5Ctextsubscript%7B4%7D">Co(I)(py)\textsubscript{2}DAP</a></td>
<td>1595 (s)</td>
<td>1050 (s)</td>
<td></td>
</tr>
<tr>
<td><a href="BF%5Ctextsubscript%7B4%7D">Co(I)(py)\textsubscript{2}DAP</a> + O\textsubscript{2}\textsuperscript{d}</td>
<td>1595 (s)</td>
<td>1050 (s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1580 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="BF%5Ctextsubscript%7B4%7D">Co(II)(imidH)\textsubscript{2}DAP</a>\textsubscript{2}</td>
<td>3300 (s)</td>
<td>1580 (s)</td>
<td>1050 (s)</td>
</tr>
<tr>
<td><a href="BF%5Ctextsubscript%7B4%7D">Co(II)(imidH)\textsubscript{2}DAP</a>\textsubscript{2} + O\textsubscript{2}\textsuperscript{e}</td>
<td>3300 (m)</td>
<td>1580 (s)</td>
<td>1060 (s)</td>
</tr>
<tr>
<td></td>
<td>3260 (m)</td>
<td>1590 (s)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} s = strong, m = medium, w = weak.
\textsuperscript{b} All values in cm\textsuperscript{-1}.
\textsuperscript{c} Center of a broad envelope.
\textsuperscript{d} Exposed to O\textsubscript{2} as a solid.
\textsuperscript{e} The isolated solid oxygenated cobalt complex, [Co(imidH)\textsubscript{2}DAP]-(BF\textsubscript{4})\textsubscript{2}·O\textsubscript{2}.  

Figure 49

Nujol Mull Infrared Spectra Supporting the Possibility of

Irreversible Oxidation of the Ligand

in [Co(I)(py)₂DAP](BF₄) upon Exposure to O₂

(A) Unoxygenated sample.

(B) Sample (A) exposed to O₂ as a solid.
[Co(II)(py)$_2$DAP](BF$_4$)$_2$ which does not react with O$_2$ does not show any change in the IR spectrum in this region when exposed to O$_2$.

[Co(II)(imidH)$_2$DAP](BF$_4$)$_2$ also displays a single absorption peak at 3300 cm$^{-1}$, whereas [Co(imidH)$_2$DAP](BF$_4$)$_2$.O$_2$ displays a doublet with peaks at 3300 cm$^{-1}$ and 3260 cm$^{-1}$, these peaks being in the region of the N–H stretching frequency.\textsuperscript{80} [Co(II)(py)$_2$DAP](BF$_4$)$_2$ and [Co(I)(py)$_2$DAP](BF$_4$)$_2$ show no peaks in this region due to the absence of imidazole protons. All of the compounds are hygroscopic, and if the Nujol mulls are prepared in the open air the spectra will possess an additional broad band around 3600 cm$^{-1}$, which can be assigned to the O–H stretching frequency of water.\textsuperscript{80} This region is devoid of signals when the mulls are prepared in the dry box. The last region of special interest in the IR spectra is the region around 1050 cm$^{-1}$ which shows a very broad (∼ 200 cm$^{-1}$) band, typical of B–F stretching frequencies.\textsuperscript{80}

The presence of the two peaks in the region of 1580 cm$^{-1}$ to 1605 cm$^{-1}$ in the oxygenated products may be indicative of the type of products formed when the O$_2$-reactive complexes are exposed to O$_2$. For example, Burnett et al.\textsuperscript{33} have reported that O$_2$ reacts with a similar ligand system containing copper(I) to yield a dehydrogenated ligand containing O=C, which has a stretching frequency very near that of O=N, thus giving rise to a new IR peak which does not appear in the deoxygenated form. This same sort of dehydrogenation mechanism might explain the additional peak seen in these compounds upon oxygenation, along with the slow, irreversible uptake of O$_2$ (vide infra).
The pmr spectra of the analogous Zn(II) complexes have been reported previously by Simmons.\textsuperscript{36} Since all of the cobalt complexes studied here are highly paramagnetic, the pmr spectra are very broad, covering a range of 110 ppm. The pmr spectra of the isolatable oxygenation product, [Co(imidH)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} - O\textsubscript{2}, could not be obtained due to the extremely low solubility of the compound. The peak positions for all of the other cobalt derivatives are given in Table 15, with the spectra given in Figures 50, 51, and 52. Both [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} and [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) have similar pmr spectra. The presence of occluded CH\textsubscript{2}Cl\textsubscript{2} in [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) is substantiated by the presence of a peak corresponding to CH\textsubscript{2}Cl\textsubscript{2} at 5.3 ppm,\textsuperscript{80} which does not occur in the spectra of [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2}.

To further substantiate the existence of the [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) derivative being unique from the [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} derivative, solution conductivity measurements were performed on the two complexes using 10\textsuperscript{-3} M solutions in CH\textsubscript{3}CN at 25°C. The [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} derivative has a \( \Lambda \) of 314 cm\textsuperscript{-1} ohm\textsuperscript{-1} M\textsuperscript{-1}, whereas [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) has a \( \Lambda \) of 193 cm\textsuperscript{-1} ohm\textsuperscript{-1} M\textsuperscript{-1}. These values are on the order of magnitude of \( \Lambda \) for the 2:1 and 1:1 electrolytes, respectively, of the analogous copper complexes.\textsuperscript{36} The value for the cobalt(II) derivative also compares favorably with values of other 2:1 electrolytes,\textsuperscript{93} while the value for the cobalt(I) derivative differs substantially from the value for a 2:1 electrolyte.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical Shift, p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF$_4$">Co(II)(py)$_2$DAP</a>$_2$</td>
<td>71.5</td>
</tr>
<tr>
<td></td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>13.1</td>
</tr>
<tr>
<td><a href="BF$_4$">Co(I)(py)$_2$DAP</a></td>
<td>70.6</td>
</tr>
<tr>
<td></td>
<td>42.1</td>
</tr>
<tr>
<td></td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
</tr>
<tr>
<td><a href="BF$_4$">Co(II)(imidH)$_2$DAP</a>$_2$</td>
<td>106.2</td>
</tr>
<tr>
<td></td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>55.8</td>
</tr>
<tr>
<td></td>
<td>34.0</td>
</tr>
<tr>
<td></td>
<td>21.4</td>
</tr>
</tbody>
</table>

a p.p.m. relative to TMS at zero.
Figure 50

PMR Spectrum of [Co(II)(py)_2DAP](BF_4)_2 in CD_3CN/CDCl_3

Relative to TMS at Room Temperature
Figure 51

PMR Spectrum of \([\text{Co(I)(py)}_2\text{DAP}](\text{BF}_4)_2\) in CD$_3$CN/CDC$_1$$_3$

Relative to TMS at Room Temperature
Figure 52

PMR Spectrum of [Co(II)(imidH)₂DAP](BF₄)₂ in CD₃CN/CDCl₃

Relative to TMS at Room Temperature
Magnetochemical and Electron Paramagnetic Resonance Spectroscopy Studies

The solid state magnetic susceptibility of the cobalt compounds was studied from liquid $N_2$ temperatures (~80 K) up to room temperature (Figures 53 and 54). [Co(II)(py)$_2$DAP](BF$_4$)$_2$ is unremarkable in that it is a low spin (S=1/2) system which nearly obeys the Curie-Weiss law with $\mu_{\text{eff}} = 2.22 \ \mu_B$ at 295 K, $\mu_{\text{eff}} = 2.02 \ \mu_B$ at 86 K, and a Weiss constant $\theta = -36$ K. However, the solution state magnetic moment at room temperature ($\mu_{\text{eff}} = 4.06 \ \mu_B$) shows that a spin state change occurs in going from solid to solution with the solution state value consistent with a fully high-spin S=3/2 state.

[Co(I)(py)$_2$DAP](BF$_4$) displays a different solid state magnetic susceptibility than [Co(II)(py)$_2$DAP](BF$_4$)$_2$ which is yet another piece of evidence that the cobalt(II) and cobalt(I) derivatives are different species. At 295 K in the solid state $\mu_{\text{eff}} = 3.50 \ \mu_B$ and at 81.5 K, $\mu_{\text{eff}} = 2.98 \ \mu_B$, showing a behavior which nearly obeys the Curie-Weiss law for a S=1 spin state where the Weiss constant is $\theta = -43.56$ K. These values are very typical of other S=1 cobalt(I) complexes reported in the literature which have $\mu_{\text{eff}}$'s around 3.3 $\mu_B$. At room temperature in the solution state $\mu_{\text{eff}} = 3.60 \ \mu_B$.

In the solid state at room temperature $\mu_{\text{eff}}$ for [Co(II)(imidH)$_2$-DAP](BF$_4$)$_2$ is 3.50 $\mu_B$, a value which is intermediate between an S=1/2 and an S=3/2 spin state, or, in other words, it is possibly a spin-equilibrium system. There are quite a few Co(II) spin-equilibrium systems known, although most are six coordinate. Among some of the five coordinate species known to exhibit the spin-equilibrium property
Figure 53

Solid State Magnetic Susceptibility of
\[ \text{[Co(II)(py)\textsubscript{2}DAP(BF\textsubscript{4})\textsubscript{2} and [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4})} \]

versus Temperature

(A) \[ \text{[Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4})}. \]

(B) \[ \text{[Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2}}. \]
Figure 54

Solid State Magnetic Susceptibility of $[\text{Co(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2$

and Its Isolated Oxygenation Product versus Temperature

(A) $[\text{Co(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2$

(B) $[\text{Co}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2\cdot\text{O}_2$
are \([\text{Co(pnp)Br}_2]\) and \([\text{Co(pnp)I}_2]\) where pnp is 2,6-bis-(2-diphenylphosphinoethyl)pyridine.\(^89\) At lower temperatures (80 K), \(\mu_{\text{eff}}\) decreases to 2.16 \(\mu_B\), or to a value typical of an \(S=1/2\) system. The plot of temperature vs. \(\mu_{\text{eff}}\) is non Curie-Weiss in nature and is reminiscent of other cobalt(II) systems which are spin-equilibrium in nature. The solution state magnetic susceptibility is 3.21 \(\mu_B\), again intermediate between \(S=1/2\) and \(S=3/2\), but no variable temperature studies were performed for the solution state.

In the solid state at room temperature, \(\mu_{\text{eff}}\) for \([\text{Co(imidH)}_2\text{DAP}](\text{BF}_4)_2\cdot\text{O}_2\) is 2.10 \(\mu_B\), and at 81.1 K, \(\mu_{\text{eff}} = 1.73 \mu_B\), with the magnetic susceptibility over these temperatures nearly following the Curie-Weiss law where the Weiss constant \(\Theta = -40.95\) K. These values for \(\mu_{\text{eff}}\) are indicative of a single unpaired electron and are consistent with the values obtained by other authors\(^{55,56}\) for the degree of paramagnetism present in monomeric cobalt-\(\text{O}_2\) complexes, where the unpaired electron has been assigned as principally residing on the \(\text{O}_2\) ligand \(\text{[i.e., formally an \(\text{O}_2^-\) species with the cobalt center Co(III)]}\). It should be noted that unlike the changing elemental analysis for the \([\text{Co(imidH)}_2\text{DAP}](\text{BF}_4)_2\cdot\text{O}_2\) derivative, which indicates decomposition of the complex one day after isolation, the magnetic susceptibility does not show any change. Table 16 gives the magnetic susceptibility data.

To further understand the properties of the cobalt complexes and their reactivity with \(\text{O}_2\), they were studied by epr spectroscopy at 11.7 K in frozen DMSO solutions. It is characteristic of complexes of \(S=1\) that they do not give strong epr spectra,\(^94\) and of course diamag-
Table 16
Magnetic Susceptibility Data for the Cobalt Complexes\textsuperscript{a}

<table>
<thead>
<tr>
<th>Complex</th>
<th>solid ((RT, \mu_B)^{a, b})</th>
<th>solid ((80 K, \mu_B)^{b})</th>
<th>solution ((RT, \mu_B)^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(II)(py)}_2\text{DAP}]\text{(BF}_4\text{)}_2)</td>
<td>2.22</td>
<td>2.02</td>
<td>4.06</td>
</tr>
<tr>
<td>([\text{Co(I)py)}_2\text{DAP}]\text{(BF}_4\text{)}\cdot\text{CH}_2\text{Cl}_2)</td>
<td>3.50</td>
<td>2.98</td>
<td>3.60</td>
</tr>
<tr>
<td>([\text{Co(II)(imidH)}_2\text{DAP}]\text{(BF}_4\text{)}_2)</td>
<td>3.50</td>
<td>2.16</td>
<td>3.21</td>
</tr>
<tr>
<td>([\text{Co(II)(imidH)}_2\text{DAP}]\text{(BF}_4\text{)}_2 + \text{O}_2)</td>
<td>2.10</td>
<td>1.73</td>
<td>1.96</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Please see Appendix A for complete listing of \(\chi_g\), \(\chi_M\), \(\chi_M'\), and \(\mu_{\text{eff}}\) for intermediate temperatures.

\textsuperscript{b} Refers to room temperature.

\textsuperscript{c} Determined by Faraday method.

\textsuperscript{d} Determined by Evan's method\textsuperscript{73} with solvent system \(\text{CH}_3\text{CN}/\text{CH}_3\text{Cl}\).
netic species are totally epr silent. S=1 systems often do not give epr spectra as the ground state is nondegenerate and the energy for the transition which gives rise to the epr spectrum is often outside of the microwave region. There is also the possibility for magnetic coupling between the electrons. The [Co(I)(py)$_2$DAP](BF$_4$) derivative is known to be an S=1 system based on variable temperature magnetic susceptibility measurements, at least down to liquid N$_2$ temperatures; therefore, it is not expected to give a strong epr spectrum (assuming that it does not become diamagnetic at liquid helium temperatures). Although the [Co(I)(py)$_2$DAP](BF$_4$) derivative described here does give an epr spectra (Figure 55), it is of very low intensity and poorly resolved, with noise obscuring much of the detail. It is possible that the small signal recorded may very well be due to contamination of the sample by oxidation products of the [Co(I)(py)$_2$DAP](BF$_4$) derivative, or small residual amounts of the parent [Co(II)(py)$_2$DAP](BF$_4$)$_2$ complex, rather than the [Co(I)(py)$_2$DAP](BF$_4$) complex itself. It is important to note, though, that the spectra of the [Co(I)(py)$_2$DAP](BF$_4$) and [Co(II)(py)$_2$DAP](BF$_4$)$_2$ derivatives (Figures 55 and 56) (at the same concentration) differ significantly enough to substantiate the claim that the [Co(I)(py)$_2$DAP](BF$_4$) derivative is indeed a unique species, different from the [Co(II)(py)$_2$DAP](BF$_4$)$_2$ parent complex. Upon oxygenation of the [Co(I)(py)$_2$DAP](BF$_4$) species, the very broad signal centered at g = 2.317 is lost, while the signal around g = 2 remains essentially unchanged.
Figure 55

EPR Spectra of $[\text{Co(I)(py)$_2$DAP}](\text{BF}_4)$

at 12 K as a DMSO Glass

(A) Unoxgenated.

(B) Solution (A) bubbled with $O_2$ prior to freezing.

(C) Solution (B) placed under vacuum for 30 minutes prior to freezing in an attempt to deoxygenate the complex.
Figure 56

EPR Spectrum of \([\text{Co(II)(py)}_2\text{DAP}](\text{BF}_4)_2\)

at 12 K as a DMSO Glass
Examination of the spectra (Figure 57) of the unoxgenated $[\text{Co(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2$ derivative shows a spectra of rhombic distortion. Oxygenation of $[\text{Co(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2$ derivative causes the loss of the $g = 2.3049$ signal, with the rest of the spectra having axial distortion. The loss of the $g \approx 2.3$ signal is seen in other cobalt(II) systems which have been exposed to $O_2$. The shape of the spectra for both of the oxygenated $[\text{Co(imidH)}_2\text{DAP}](\text{BF}_4)_2$ derivatives is very indicative of a monomeric cobalt oxygen species when compared with the spectra of such complexes reported in the literature. Among the many examples of cobalt(II) complexes which form 1:1 cobalt $O_2$ complexes, some examples include Co(II)salen, Co(II)(acacen) and modifications of these ligands, where a base, such as pyridine, constitutes the fifth ligand. Epr studies of these complexes and their oxygenation products, have assigned the oxygenation process to be an oxidation addition process whereby

$$\text{Co(II)L} + O_2 \rightarrow \text{Co(III)O}_2^{-}$$

Magnetic susceptibility measurements show that one unpaired electron is present in the oxygenated species. Based on epr data the unpaired electron is assigned to reside mainly on the $O_2^-$ moiety, due to the presence of an octet hyperfine around $g \approx 2$, which is due to the unpaired electron on the $O_2^-$ moiety interacting with the $^{59}\text{Co}$ nucleus. The existence of monomeric cobalt-$O_2$ species has been proved by x-ray crystal structures, which also show the O-O distance (~ 1.26 Å) to be consistent with the superoxide formalism. Although most monomeric cobalt-$O_2$ derivatives show a well defined octet as discussed above,
Figure 57

EPR Spectra of [Co(II)(imidH)$_2$DAP]$_2$(BF$_4$)$_2$ and Its Isolated Oxygenation Product at 12 K as a DMSO Glass

(A) [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$, unoxygenated.

(B) Solution (A) bubbled with O$_2$ prior to freezing.

(C) [Co(imidH)$_2$DAP](BF$_4$)$_2$.O$_2$. 
the spectra obtained here are not resolved in enough detail to detect this. The spectra obtained here, though, are conclusive evidence that the oxygenation of the \([\text{Co(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2\) complex does not result in a μ-peroxo dimer, as this would be assumed to be diamagnetic like the analogous copper derivatives and other cobalt systems, and thus epr silent. Thus the monomeric \((\text{Co(III)}-\text{O}_2^-)\) formalism as suggested by the manometric measurements is also supported by the epr spectra. Epr data is given in Table 17.

The stoichiometry of the \(\text{O}_2\) uptake of the complexes was determined by Warburg manometry. The plots of \(\text{O}_2\) uptake vs. time are shown in Figures 58 and 59. \([\text{Co(II)(py)}_2\text{DAP}](\text{BF}_4)_2\) was found to be insensitive to \(\text{O}_2\). Both \([\text{Co(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2\) and \([\text{Co(I)(py)}_2\text{DAP}](\text{BF}_4)_2\) reacted with \(\text{O}_2\) in a stoichiometry approaching one \(\text{O}_2\) per cobalt center. Based on data obtained for the isolated oxygenated cobalt(II) imidazole derivative, \([\text{Co(imidH)}_2\text{DAP}](\text{BF}_4)_2\cdot\text{O}_2\), this stoichiometry is supporting evidence for the formation of a monomeric cobalt-\(\text{O}_2\) adduct, \((\text{Co(III)}-\text{O}_2^-)\). Although the \([\text{Co(I)(py)}_2\text{DAP}](\text{BF}_4)_2\) derivative has essentially the same \(\text{O}_2\cdot\text{Co}\) stoichiometry as \([\text{Co(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2\) complex, it is not as easily explained. It has been postulated that a \(d^8\) system should react with \(\text{O}_2\) to go to a \(d^6\) system with a side bound peroxide. But based on the electrochemical evidence for the \([\text{Co(I)(py)}_2\text{DAP}](\text{BF}_4)_2\) derivative under \(\text{O}_2\), the oxidative addition does not seem to proceed all the way to a Co(III) species. It is also possible that the major reaction occurring here is oxidation of ligand, perhaps enhanced by the cobalt(I) center, since in the solid state reaction with \(\text{O}_2\) gives an additional
Table 17

EPR Parameters for the Cobalt Complexes\textsuperscript{a} at 12 K

<table>
<thead>
<tr>
<th>Complex</th>
<th>( g ) Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Co(II)}(\text{py})_2\text{DAP}</a>_2)</td>
<td>( g_x = 2.2929 )</td>
</tr>
<tr>
<td></td>
<td>( g_y = 2.013 )</td>
</tr>
<tr>
<td></td>
<td>( b_z = 1.922 )</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Co(II)}(\text{imidH})_2\text{DAP}</a>_2)</td>
<td>( g_x = 2.3049 )</td>
</tr>
<tr>
<td></td>
<td>( g_y = 2.0225 )</td>
</tr>
<tr>
<td></td>
<td>( g_z = 1.986 )</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Co(I)}(\text{py})_2\text{DAP}</a>_2)</td>
<td>( g_1 = 2.317 )</td>
</tr>
<tr>
<td></td>
<td>( g_2 = 2.0011 )</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BBF%7D_4">\text{Co(II)}(\text{imidH})_2\text{DAP}</a>_{2.0}^b)</td>
<td>( g_1 = 2.06 )</td>
</tr>
<tr>
<td></td>
<td>( g_2 = 2.0133 )</td>
</tr>
</tbody>
</table>

\textsuperscript{a} At 11.7 K in frozen DMSO solutions, 10\textsuperscript{-4} M.

\textsuperscript{b} For the isolated oxygenated cobalt complex.
Figure 58

$O_2$ Uptake of $[\text{Co(I)(py)$_2$DAP}](\text{BF}_4)$ in DMSO

\textit{versus Time at Room Temperature}
Figure 59

$O_2$ Uptake of $[\text{Co(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2$ in DMSO

versus Time at Room Temperature
peak in the IR spectrum, indicative of oxidation of the ligand at the methylene carbons to form a O=C moiety. In the unoxygenated form there is only one peak at 1595 cm\(^{-1}\), but in the oxygenated species there are two peaks, one at 1595 cm\(^{-1}\) and the other at 1580 cm\(^{-1}\) in the infrared spectrum (Figure 49).

**Electrochemical Studies**

As discussed above, electrochemical techniques can provide valuable information about transition metal complexes and their reactivity toward \(O_2\). For example, a compound can first be analyzed by means of controlled potential electrolysis to determine the purity of the complex based on metal content. This same technique on a larger scale can also be used as a means of synthesis of complexes not available by other means, with definitive assignment of redox couples established by isolation and characterization of the reduced species. Cyclic voltammetry in conjunction with differential pulse polarography can be used to determine the redox potential \((E_{1/2})\) of a system. Finally, the shape of the cyclic voltammogram can give information about the reactivity of a species or its reduced version with a potential ligand.

Since the cobalt complexes' reactivity with \(O_2\) is thought to involve an oxidative addition, they were investigated using electrochemical techniques in order to determine what correlations might be drawn between the redox potentials of the metal centers and their reactivity toward \(O_2\). Table 18 shows the redox potentials obtained in CH\(_3\)CN at room temperature with the cyclic voltammograms shown in Figures 60, 61, and 62. As would be expected based from the analogous
### Table 18
Cyclic Voltammetry Data for the Cobalt Complexes
in CH$_3$CN at 10^{-3} M and 0.025 M TBABF$_4$ at Room Temperature

<table>
<thead>
<tr>
<th>Complex</th>
<th>Volts (vs. S.C.E.)</th>
<th>Co(I) $\leftarrow$ Co(II)</th>
<th>Co(II) $\leftrightarrow$ Co(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="BF$_4$">Co(II)(py)$_2$DAP</a>$_2$</td>
<td>-0.32</td>
<td>+0.53</td>
<td></td>
</tr>
<tr>
<td>oxygenated</td>
<td>-0.18</td>
<td>+0.53</td>
<td></td>
</tr>
<tr>
<td>deoxygenated</td>
<td>-0.32</td>
<td>+0.53</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Co(I)(py)$_2$DAP</a></td>
<td>-0.31</td>
<td>+0.60</td>
<td></td>
</tr>
<tr>
<td>oxygenated</td>
<td>-0.18</td>
<td>+0.60</td>
<td></td>
</tr>
<tr>
<td>deoxygenated</td>
<td>-0.31</td>
<td>+0.60</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Co(II)(imidH)$_2$DAP</a>$_2$</td>
<td>-0.53</td>
<td>+0.35</td>
<td></td>
</tr>
<tr>
<td>oxygenated</td>
<td>-----$^a$</td>
<td>-----$^a$</td>
<td></td>
</tr>
<tr>
<td>deoxygenated</td>
<td>-0.18, -0.53</td>
<td>-----$^a$</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Co(imidH)$_2$DAP</a>$_2$.$O_2$$^b$</td>
<td>-0.18, -0.49</td>
<td>-----$^a$</td>
<td></td>
</tr>
</tbody>
</table>

Scan rate = 200 mV/s

$^a$ There is no redox couple observed.

$^b$ This refers to the isolated oxygenated cobalt complex.
Figure 60

Cyclic Voltammograms of $[\text{Co(II)(py)$_2$DAP]}\text{(BF}_4\text{)}_2$

in CH$_3$CN at $10^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.
(B) Under O$_2$.
(C) Solution (B) after bubbling with N$_2$ for 5 minutes.
(D) Solution (B) after bubbling with N$_2$ for 30 minutes.

Scan Rate = 200 mV/sec
The image displays a set of four electrochemical cyclic voltammograms labeled as a), b), c), and d). Each graph shows the current (mA) plotted against the potential (V vs SCE) with marked sweep directions. The voltage range spans from +1.2 V to -1.0 V. The labels and specific details of the voltammograms are not explicitly described in the image provided.
Figure 61

Cyclic Voltammograms of [Co(I)(py)$_2$DAP](BF$_4$)
in CH$_3$CN at 10$^{-3}$ M and 0.025 M TBABF$_4$ at Room Temperature

(A) Under N$_2$.
(B) Under O$_2$.
(C) Solution (B) deoxygenated by bubbling with N$_2$.

Scan Rate = 200 mV/sec
Figure 62

Cyclic Voltammograms of [Co(II)(imidH)_2DAP](BF_4)_2 and Its Isolated Oxygenation Product in CH_3CN at 10^{-3} M and 0.025 M TBABF_4 at Room Temperature

(A) [Co(II)(imidH)_2DAP](BF_4)_2 under N_2.
(B) Solution (A) under O_2.
(C) Solution (B) deoxygenated by bubbling with N_2.
(D) [Co(imidH)_2DAP](BF_4)_2·O_2 under N_2.

Scan Rate = 200 mV/sec
copper(I) species, discussed above, the redox potential for [Co(II)-(imidH)₂DAP](BF₄)₂ are more negative than those of [Co(II)(py)₂DAP]-
(BF₄)₂. Many other cobalt(II) complexes which have been studied
 electrochemically have the cobalt(II)/cobalt(III) redox couple situated
in the region where the cobalt(II)/cobalt(I) couple is found in these
complexes.⁵³ The E₁/₂ values found here do correspond to those found
by Simmons for the Co(II)/Co(I) couple in a series of similar cobalt
Schiff base complexes.³⁶b One of the major concerns of this work was
to verify that the E₁/₂'s assigned to cobalt(II)/cobalt(I) redox couple
were correctly assigned. This assignment was verified by controlled
potential electrolysis of [Co(II)(py)₂DAP](BF₄)₂ at a voltage 0.25 V
cathodic (negative) of the E₁/₂ proposed to correspond to the cobalt(II)/
cobalt(I) couple, and the isolation of pure [Co(I)(py)₂DAP](BF₄) from
the reaction mixture. The reduction process was shown to be a one
electron reduction process, although the cathodic to anodic peak to peak
separation (~1.0 V) was larger than theory (0.59 V). The cyclic
voltammograms of the analogous zinc(II) compounds have been previously
reported by Simmons,³⁶ with the ligand centered reductions seen to occur
in a region negative of the one of interest here (negative of ~1.0 V vs.
S.C.E.). Thus it seems safe to assume that the cobalt reductions re-
ported here are not simply the result of ligand reduction processes,
but rather are metal centered reductions.

It has been postulated that there would be an optimum redox
potential for a metal complex to react reversibly with O₂.⁵⁴ If the
redox potential is too negative, the metal center would be irreversibly
oxidized. If the redox potential is too positive, the metal center
would be too stable toward oxidation and therefore would not react with 
$O_2$. Basolo has shown, using a series of neutral cobalt(II) chelates, 
that there is indeed a linear correlation between the redox potential 
($E_{1/2}$) of the cobalt(II)/cobalt(III) couple of a series of similar 
complexes and their reactivity with $O_2$.\textsuperscript{53} He also demonstrated that a 
charged complex with the same $E_{1/2}$ as a neutral complex would be less 
reactive with $O_2$ than the neutral complex. In looking at his data, the 
$E_{1/2}$ values of the cobalt(II)/cobalt(III) couple range from around 
-0.3 V to about -0.7 V, while the $E_{1/2}$ values of the cobalt complexes 
described here are +0.35 V and +0.53 V. It would seem, based on 
Basolo's data, that both of the Co(II) complexes investigated here 
should be $O_2$ insensitive, which is the case with [Co(II)(py)$_2$DAP](BF$_4$)$_2$, 
but not [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$ which is $O_2$ reactive, although very 
slowly. However, it must be kept in mind that Basolo's data was for a 
series of type A compounds (Figure 7) with a fifth axial ligand which 
were neutral complexes, whereas the complexes described here have penta-
dentate ligands and are cationic. An interesting point though is that 
the $E_{1/2}$ for the cobalt(II)/cobalt(I) redox couple for [Co(I)(py)$_2$DAP]- 
(BF$_4$) is almost the same as that found for the reversible [Cu(I)(imidH)$_2$-
DAP](BF$_4$) system, and also falls in the middle of the range of co-
balt(II)/cobalt(III) couples of cobalt(II) complexes found by Basolo to 
be good $O_2$ carriers.\textsuperscript{36,54} On this basis [Co(I)(py)$_2$DAP](BF$_4$) was in-
vestigated to see if the $E_{1/2}$ of -0.3 V (vs. S.C.E.) might indeed be 
indictive of a reversible $O_2$ system.
The reactivity of a complex with $O_2$ or another ligand in solution can be studied using electrochemistry. Gagné has reported on the reactivity of some copper complexes with CO and has determined the binding constant for the reaction in this manner.\textsuperscript{85} A complex in solution with no other potential ligands will have a redox potential of $E_{1/2}$, but when an additional ligand which will coordinate to the metal center is added to the solution the new complex formed will have a different redox potential, $E_{1/2}'$, than the parent complex. Whether the addition of this ligand stabilizes the oxidized form or the reduced form of the metal complex will determine whether the redox potential shifts positive or negative. If the reduced form is stabilized, the shift of the redox potential will be to a more positive value, whereas if the oxidized form is stabilized, the shift will be to a more negative value. Nicholson and Shain\textsuperscript{96} have also written a comprehensive paper concerning the effects of chemical reactions on cyclic voltammograms and have shown that for a system which involves charge transfer followed by an irreversible chemical reaction (eq. 1)

$$0 + ne \rightarrow R$$

$$R \xrightleftharpoons[k_e^-]{\xi^+} Z$$

\hspace{1cm} (1)

that as $k_e$ increases (at constant scan rates) the cathodic (reduction) peak will shift to a more positive (anodic) value with concurrent loss of the anodic (oxidation) peak.

The cyclic voltammograms of $[\text{Co(II)(py)}_2\text{DAP}][\text{BF}_4]_2$ (Figure 60) under $N_2$ show both cathodic and anodic waves for both redox couples
with $E_{1/2}$'s of -0.32 V and +0.53 V for the assigned cobalt(II)/cobalt(I) and cobalt(II)/cobalt(III) couples, respectively. Saturation of the solution with $O_2$ produces a dramatic change in the cyclic voltammogram. The cobalt(II)/cobalt(III) redox couple is essentially unchanged, although somewhat less sharp, but the cobalt(II)/cobalt(I) redox couple is shifted in the positive direction by 0.14 V to -0.18 V (S.C.E.). Analysis of this data based on the discussion of Gagne$^{85}$ and Nicholson and Shain$^{98}$ would indicate that the observed effect might be caused by $O_2$ coordinat-ing with the cobalt(I) center formed at the electrode surface, and that the complex then undergoes an irreversible chemical reaction. It is known from manometry studies (vide infra) that the cobalt(II) derivative does not react with $O_2$. The absence of the anodic wave of the co-
balt(I)/cobalt(II) redox couple could be explained by the oxidation by
$O_2$ of the cobalt(I) formed at the electrode to cobalt(II), but since the
cobalt(II)/cobalt(III) couple is still present, the oxidation apparently
does not proceed all the way to cobalt(III), as has been previously
proposed for a $d^8$ system.$^{66}$ This same sort of argument has been used
to explain the loss of the anodic wave when a solution of $[Cu(II)\cdot$
$(imidH)_2DAP](BF_4)_2$ is saturated with $O_2$. $^{36}$ For the copper system,
however, there is no change in the position of the cathodic wave, indica-
tive of a very different kinetic rate, or perhaps even a different
reaction mechanism.

The original cyclic voltammogram may be recovered by bubbling the
solution with $N_2$. If a scan is taken when the deoxygenation of the
solution is incomplete, there are two cathodic peaks, which may be re-
solved by differential pulse polarography to correspond to the $E_{1/2}$'s of the oxygenated and deoxygenated forms.

The same cyclic voltammogram can be obtained from the isolated cobalt(I) pyridine (Figure 61) derivative as from the parent cobalt(II) complex, under both $N_2$ and $O_2$. Upon deoxygenation of the solution, essentially the same voltammogram is obtained as before oxygenation, but with great broadening of the waves, indicative perhaps of some irreversible process which occurred upon exposure to $O_2$. Since the cyclic voltammogram is recovered upon deoxygenation, the oxygenation process must have been fairly slow, thus oxidizing only a small portion of the available Co(I). This is supported by the slow reaction rate observed manometrically.

The redox couples of the [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$ derivative (Figure 62) are more cathodic than those of [Co(II)(py)$_2$DAP](BF$_4$)$_2$ and as would be expected, based on the argument of $E_{1/2}$'s, [Co(II)(imidH)$_2$-DAP](BF$_4$)$_2$ is indeed much more reactive with $O_2$ than the [Co(II)(py)$_2$-DAP](BF$_4$)$_2$ derivative. While the cobalt(II)/cobalt(I) redox wave is sharp; the cobalt(II)/cobalt(III) couple is always ill defined. This would perhaps be indicative that the cobalt(II)/cobalt(III) couple is irreversible. Upon saturation of the solution with $O_2$, the entire cyclic voltammogram disappears, but the electrochemical data collection is complicated by the fact that addition of $O_2$ to the solution produces a precipitation reaction. The cyclic voltammogram that remains (of very small amplitude) may be explained by an irreversible chemical reaction preceding the charge transfer, as described by Nicholson and Shain. $^{96}$ [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$ is known to react with $O_2$ based on
manometry studies. Upon deoxygenation of the solution by bubbling with \( N_2 \), some of the cobalt(II)/cobalt(I) redox wave is recovered, but at the same time another cathodic wave (very broad and ill defined) also appears at -0.18 V. This new wave may be characteristic of the newly formed irreversibly oxidized species. The cobalt(II)/cobalt(III) wave is not recovered upon deoxygenation of the solution.

The isolatable oxygen adduct of the cobalt(II) imidazole complex, \([\text{Co(imidH)}_2\text{DAP}](\text{BF}_4)_2 \cdot \text{O}_2\), was studied by cyclic voltammetry (Figure 62), but the data is not well resolved due to the extremely low solubility of the complex. It shows a cyclic voltammogram very much like that of \([\text{Co(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2\) oxygenated in situ, with \( E_{1/2} \)'s at -0.18 V and -0.49 V (vs. S.C.E.).

Using the method of Gagne\textsuperscript{85} to measure the equilibrium binding constant for CO to some copper(I) complexes, an equilibrium binding constant, \( K \), for the \([\text{Co(I)}(\text{py})_2\text{DAP}](\text{BF}_4)\) complex with \( \text{O}_2 \) may be derived. The assumption has to be made that the only reaction occurring in the solution, other than the electrochemical generation of Co(I) from Co(II), is the binding of \( \text{O}_2 \) to the metal center.

From the Nernst equation (Equation 1) an expression can be derived

\[
E = E^0 + \frac{RT}{nF} \ln \left( \frac{[\text{Co(II)}]}{[\text{Co(I)}]} \right)
\]

Equation 1

to relate the equilibrium binding constant of the \([\text{Co(I)}(\text{py})_2\text{DAP}](\text{BF}_4)\) complex with \( \text{O}_2 \) to the shift of the Co(II)/Co(I) redox couple in the presence and absence of \( \text{O}_2 \). In Equation 1, \( R \) is the gas constant, \( T \)
is temperature in degrees Kelvin, \( n \) is the number of electrons in the process, and \( F \) is a Faraday.

With the assumption stated above that the only two reactions occurring in the solution [other than electrochemical generation of Co(I) from Co(II)] are

\[
\text{Co(II)L} + O_2 \rightleftharpoons \text{Co(II)LO}_2 \\
\text{Equation 2}
\]

and

\[
\text{Co(I)L} + O_2 \rightleftharpoons \text{Co(I)LO}_2 \\
\text{Equation 3}
\]

the equilibrium constants, \( K^{\text{II}} \) and \( K^{\text{I}} \), are

\[
K^{\text{II}} = \frac{[\text{Co(II)LO}_2]}{[\text{Co(II)L}][O_2]} \\
\text{Equation 4}
\]

and

\[
K^{\text{I}} = \frac{[\text{Co(I)LO}_2]}{[\text{Co(I)L}][O_2]} \\
\text{Equation 5}
\]

where \( L \) is the ligand \([(py)_2DAP]\). Manometric studies support the 1:1 ratio of Co:O\(_2\). Although there is probably an oxidative addition occurring upon binding of the O\(_2\) to the cobalt center, the metal centers are not depicted as oxidized, as the assumptions used here are that the only reaction occurring is the binding of O\(_2\) to the metal center, with no electron transfer involved.

In the cobalt(II) state all of the cobalt present is represented by

\[
[\text{Co(II)}_{\text{total}}] = [\text{Co(II)L}] + [\text{Co(II)LO}_2] \\
\text{Equation 6}
\]
and for the cobalt(I) state

$$[\text{Co(I)}_{\text{total}}] = [\text{Co(I)I}] + [\text{Co(I)LO}_2]$$  \hspace{1cm} \text{Equation 7}$$

Since the total cobalt in the Co(I) state is the same as in the cobalt(II) state at the electrode surface

$$[\text{Co(II)I}] + [\text{Co(II)LO}_2] = [\text{Co(I)I}] + [\text{Co(I)LO}_2]$$  \hspace{1cm} \text{Equation 8}$$

but from Equation 4 and Equation 5

$$[\text{Co(II)LO}_2] = K^{II}[\text{Co(II)I}]O_2$$  \hspace{1cm} \text{Equation 9}$$

and

$$[\text{Co(I)LO}_2] = K^{I}[\text{Co(I)I}]O_2$$  \hspace{1cm} \text{Equation 10}$$

so

$$[\text{Co(II)I}] + K^{II}[\text{Co(II)I}]O_2 = [\text{Co(I)I}] + K^{I}[\text{Co(I)I}]O_2$$  \hspace{1cm} \text{Equation 11}$$

and

$$[\text{Co(II)I}][1 + K^{II}[O_2]] = [\text{Co(I)I}][1 + K^{I}[O_2]]$$  \hspace{1cm} \text{Equation 12}$$

or

$$\frac{[\text{Co(II)I}]}{[\text{Co(I)I}]} = \frac{1 + K^{I}[O_2]}{1 + K^{II}[O_2]}$$  \hspace{1cm} \text{Equation 13}$$
which can be used in Equation 1 to give

\[
E_{1/2}^{(O_2)} = E_{1/2} + \frac{RT}{nF} \ln \frac{1 + K^I[O_2]}{1 + K^{II}[O_2]}
\]

Equation 14

or

\[
\Delta E_{1/2} = E_{1/2}^{(O_2)} - E_{1/2} = \frac{RT}{nF} \ln \frac{1 + K^I[O_2]}{1 + K^{II}[O_2]}
\]

Equation 15

where \( E_{1/2}^{(O_2)} \) is the \( E_{1/2} \) in the presence of \( O_2 \) and \( E_{1/2} \) is the \( E_{1/2} \) in the absence of \( O_2 \). Therefore

\[
\Delta E \frac{nF}{RT} = \ln \frac{1 + K^I[O_2]}{1 + K^{II}[O_2]}
\]

Equation 16

It is known from manometry results that \([\text{Co(II)(py)}_2\text{DAP}](\text{BF}_4)_2\) does not bind \( O_2 \); therefore \( K^{II} = 0 \) and Equation 16 can be simplified to

\[
\Delta E \frac{nF}{RT} = \ln[1 + K^I[O_2]]
\]

Equation 17

or

\[
\Delta E \frac{nF}{RT} e^{-1} = K^I[O_2]
\]

Equation 18

Therefore, one only needs to determine the concentration of \( O_2 \) in a solution of \( \text{CH}_3\text{CN} \) saturated with \( O_2 \) in order to determine the equilibrium binding constant. If the solubility of \( O_2 \) in \( \text{CH}_3\text{CN} \) is taken to be 1.1 mM, \(^{97} K^I \) is found to be \( 2 \times 10^5 \text{ M}^{-1} \).
If indeed the [Co(I)(py)\textsubscript{2}DAP] complex is unique from the [Co(II)-(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} parent complex, the electronic spectra for the two complexes should substantiate this fact. Also, the electronic spectra of the O\textsubscript{2} active species in the absence and presence of O\textsubscript{2} should be different, if indeed there is a reaction between the metal centers and O\textsubscript{2}.

It can be seen that the intensity of the peaks in the electronic absorption spectra of [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) are of much greater intensity than in the [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} spectra (Figures 63-67), with the [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) complex exhibiting a band around 750 nm (ε = 1262), characteristic of other [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) complexes.\textsuperscript{65} The reactivity of the [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) complex with O\textsubscript{2} can also be verified by examination of Figures 66 and 67 which show the spectra of the [Co(I)-(py)\textsubscript{2}DAP](BF\textsubscript{4}) complex in the absence and presence of O\textsubscript{2}. Upon addition of O\textsubscript{2} to a solution of the [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) complex, there is a change noticeable to the eye, from a burnt orange color to a brown color. In the electronic spectra there is a loss of the 750 nm band, along with a dramatic reduction in intensity of the rest of the spectra, thus spectral evidence for the reaction with O\textsubscript{2}. The absence of change in the spectra of the [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} derivative upon exposure to O\textsubscript{2} is supporting evidence for other data which indicate that there is no reaction with O\textsubscript{2}. The spectra of both [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} and [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) were also shown to be solvent independent.

In contrast to the [Co(II)(py)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} and [Co(I)(py)\textsubscript{2}DAP](BF\textsubscript{4}) derivatives, the spectra for the [Co(II)(imidH)\textsubscript{2}DAP](BF\textsubscript{4})\textsubscript{2} complex is
Figure 63

Electronic Absorption Spectra of

\[ \text{[Co(II)(py)_2DAP](BF}_4\text{)}_2 \text{ and [Co(I)(py)_2DAP](BF}_4\text{)} \]

in DMSO at $10^{-4}$ M at Room Temperature

(A) \[ \text{[Co(I)(py)_2DAP](BF}_4\text{)} \]

(B) \[ \text{[Co(II)(py)_2DAP](BF}_4\text{)}_2 \]
Figure 64

Electronic Absorption Spectrum of $[\text{Co(II)}(\text{py})_2\text{DAP}]\text{(BF}_4\text{)}_2$

in CH$_3$CN at $10^{-4}$ M
Figure 65

Electronic Absorption Spectrum of [Co(II)(py)$_2$DAP](BF$_4$)$_2$

in DMSO at $10^{-4}$ M
Figure 66

Electronic Absorption Spectra of $[\text{Co}(I)(\text{py})_2\text{DAP}](\text{BF}_4)$

in CH$_3$CN at 10$^{-4}$ M at Room Temperature

(A) In deoxygenated CH$_3$CN.

(B) Solution (A) bubbled with O$_2$ for 15 minutes.
Figure 67

Electronic Absorption Spectra of $[\text{Co(I)(py)}_2\text{DAP}](\text{BF}_4)$ in DMSO at $10^{-4}$ M at Room Temperature

(A) In deoxygenated DMSO.

(B) Solution (A) bubbled with $O_2$ for 15 minutes.
found to be solvent dependent, indicative of an interaction between the cobalt complex and the solvent (Figures 68 and 69). It is of interest to note that the spectra of the unoxygenated complex and the freshly oxygenated complex are very similar, showing very little change with the addition of oxygen, although manometric results show there to be an uptake of $O_2$, although very slowly. The spectra of the isolated cobalt oxygen complex is indeed different from the unoxygenated and freshly oxygenated derivative, lending support to the theory that the reaction time is very slow, and perhaps not completed at the time the spectra was taken. It is known from manometric studies that the reaction with $O_2$ takes several hours to complete. Electronic spectral data is given in Table 19.

**Conclusions**

Since the ligand [(imidH)$_2$DAP] in conjunction with copper(I) has been found to result in a system capable of reversible oxygenation, this ligand and its derivative [(py)$_2$DAP] were investigated for the properties of a reversible $O_2$-carrier when complexed with cobalt(II) and cobalt(I). The [Co(I)(py)$_2$DAP](BF$_4$) complex was investigated in particular due to its $E_{1/2}$ for Co(I) $\rightleftharpoons$ Co(II) being $-0.32$ V, which is very close to the $E_{1/2}$ for the [Cu(I)(imidH)$_2$DAP](BF$_4$) ($E_{1/2} = -0.3$ V) system, which reacts reversibly with $O_2$. It was hoped to see if there was a correlation between $E_{1/2}$ and $O_2$ reactivity for two different metals, copper and cobalt. It was found that [Co(II)(imidH)$_2$DAP](BF$_4$)$_2$ reacted irreversibly with $O_2$ to form initially an isolatable and characterizable monomeric cobalt-$O_2$ complex, [Co(imidH)$_2$DAP](BF$_4$)$_2$.$O_2$.,
Figure 68

Electronic Absorption Spectra of [Co(II)(imidH)₂DAP](BF₄)₂ and Its Isolated Oxygenation Product in CH₃CN at 10⁻⁴ M at Room Temperature

(A) [Co(II)(imidH)₂DAP](BF₄)₂, unoxygenated.

(B) Solution (A) bubbled with O₂ for 15 minutes.

(C) [Co(imidH)₂DAP](BF₄)₂·O₂.
Figure 69

Electronic Absorption Spectra of $[\text{Co(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2$ and Its Isolated Oxygenation Product in DMSO at $10^{-4}$ M at Room Temperature

(A) $[\text{Cl(II)(imidH)}_2\text{DAP}](\text{BF}_4)_2$, unoxygenated.

(B) Solution (A) bubbled with $O_2$ for 15 minutes.

(C) $[\text{Co(imidH)}_2\text{DAP}](\text{BF}_4)_2\cdot O_2$. 
<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}, \text{nm}$</th>
<th>$e, \text{M}^{-1} \text{cm}^{-1}$</th>
</tr>
</thead>
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<tr>
<td>$<a href="%5Ctext%7BBF%7D_4">\text{Co}^{II} (\text{imidH})_2 \text{DAP}</a>_2$</td>
<td>DMSO</td>
<td>400</td>
<td>834 (sh)</td>
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<td></td>
<td>300</td>
<td>5249</td>
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<tr>
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<td></td>
<td>360</td>
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<td></td>
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<td>360</td>
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<td>330</td>
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<td>6000 (sh)</td>
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(Table 19 Continued)
(Table 19 Continued)

<table>
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<tr>
<th>Complex</th>
<th>Solvent</th>
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<th>$\epsilon$, M$^{-1}$ cm$^{-1}$</th>
</tr>
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<td>$<a href="%5Ctext%7BBF%7D_4">\text{Co(I)(py)}_2\text{DAP}</a>$</td>
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<td></td>
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<td>450</td>
<td>4000</td>
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<td></td>
<td></td>
<td>295</td>
<td>9000 (sh)</td>
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<tr>
<td>$<a href="%5Ctext%7BBF%7D_4">\text{Co(I)(py)}_2\text{DAP}</a>$</td>
<td>CH$_3$CN</td>
<td>760</td>
<td>132 (sh)</td>
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<td>420</td>
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<td></td>
<td></td>
<td>240</td>
<td>31000 (sh)</td>
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</tbody>
</table>

*a* There are many ill-defined shoulders which may not be included here.

*b* sh = shoulder

*c* This refers to the isolated oxygenated complex.
which decomposed within a few days, while the [Co(II)(py)$_2$DAP](BF$_4$)$_2$ complex was found to be unreactive towards O$_2$. This difference in O$_2$ reactivity shown by these complexes is consistent with results obtained for the copper(I) derivatives,$^{36,37}$ and as in the case for the copper may be correlated to the potential of the redox couple involved in the oxidative addition, where a more positive $E_{1/2}$ would tend to stabilize the cobalt(II) form, thus preventing reaction with the O$_2$.

The [Co(I)(py)$_2$DAP](BF$_4$) complex was synthesized and characterized, and was found to irreversibly react with O$_2$ in the ratio of one O$_2$ per cobalt center, although no oxygenation product could be isolated from a reaction mixture. It should be noted that it is unique to study a Co(I) system as an O$_2$-carrier, as almost all other cobalt(II) O$_2$-carriers are based on cobalt(II) systems. By the use of electrochemical techniques, a rough estimate for the binding constant, K, of the [Co(I)(py)$_2$DAP](BF$_4$) complex with O$_2$ was obtained and found to be $2 \times 10^5$ M$^{-1}$. Based upon IR spectral data for the reaction of the solid [Co(I)(py)$_2$DAP](BF$_4$) complex with O$_2$, an explanation for the irreversible oxygenation is proposed to involve oxidation of the ligand system, with oxidation occurring at the methylene carbons to yield an ethylene group, thus preventing reversible oxidation due to irreversible oxidation of the ligand framework, in the manner described by Burrett.$^{33}$ This same sort of irreversible ligand oxidation has also been proposed to account for the irreversible oxidation of the copper(I) complexes studied by Simmons$^{36}$ and Merrill$^{37}$ and in this work.
REFERENCES


21. The following reviews cover known O2 carriers to date:
   (a) J. W. Buchler, Angew. Chem. Internat. Edn., 17, 407 (1978);
   (b) R. G. Wilkins, in "Bioinorganic Chemistry," Adv. Chem. Ser., 100, 111 (1971);
   (c) J. S. Valentine, Chem. Rev., 13, 235 (1973);
   (d) F. Basolo, B. M. Hoffman, and J. A. Ibers, Acc. Chem. Res., 8, 384 (1975);
   (e) G. McLendon and A. E. Martell, Coord. Chem. Rev., 19, 1 (1976);
   (f) L. Vaska, Acc. Chem. Res., 9, 175 (1976);


70. B. A. Averill, private communication, 1980.


75. \( \chi'_M \) for [Zn(imidH)\(_2\)DAP](BF\(_4\))\(_2\) and [Zn(py)\(_2\)DAP](BF\(_4\))\(_2\) obtained from C. L. Merrill, private communication.


92. C. L. Merrill, private communication.


97. As no literature value was found for the solubility of O₂ in CH₃CN, the value was taken to be close to that found for other solvents: (a) DMSO, 1.1 mM, determined experimentally in the manometry measurements; (b) alcohol, 1.1 mM, "Handbook of Chemistry and Physics," Chemical Rubber Co., 53rd Ed., 1972.
## APPENDIX A

### Table 1

Solid State Magnetic Susceptibility Data for \([\text{Fe(II)(py)}_2\text{DAP}](\text{BF}_4)_2\)

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>(\chi_g(10^3))</th>
<th>(\chi_M(10^3))</th>
<th>(\chi_M'(10^3))</th>
<th>(\mu_{\text{eff}}(\mu_B))</th>
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Table 2
Solid State Magnetic Susceptibility Data for \([\text{Fe(II)}(\text{imidH})_2\text{DAP}](\text{BF}_4)_2\)

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<th>Temperature K</th>
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<th>(\chi_m'(10^3))</th>
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Table 3
Solid State Magnetic Susceptibility Data for [Co(II)(py)$_2$DAP](BF$_4$)$_2$

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<th>$\chi_g(10^6)$</th>
<th>$\chi_M(10^3)$</th>
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Solid State Magnetic Susceptibility Data for [Co(I)(py)_2DAP](BF_4)

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