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PART I: MAGNETIC AND SPIN LIFETIME STUDIES OF DELTA S=1 SPIN EQUILIBRIUM PROCESS FOR SOME 3D('7) COBALT(II) COMPLEXES. PART II: MODELING THE ACTIVE SITE IN HEMOCYANIN: A SYNTHETIC COPPER(I) COMPLEX HAVING IMIDAZOLE LIGANDS AND EXHIBITING REVERSIBLE REACTIVITY WITH MOLECULAR OXYGEN.

RICE UNIVERSITY, PH.D., 1979
RICE UNIVERSITY

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by

MIRIAM GREINER SIMMONS

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

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

Lon J. Wilson, Associate Professor of Chemistry, Chairman
Ronald L. Sass, Professor of Chemistry and Biology
John S. Olson, Associate Professor of Biochemistry

HOUSTON, TEXAS

MAY 1979
ABSTRACT

PART I: MAGNETIC AND SPIN LIFETIME STUDIES OF ΔS=1 SPIN EQUILIBRIUM PROCESS FOR SOME 3d⁷ COBALT(II) COMPLEXES.

PART II: MODELING THE ACTIVE SITE IN HEMOCYANIN: A SYNTHETIC COPPER(I) COMPLEX HAVING IMIDAZOLE LIGANDS AND EXHIBITING REVERSIBLE ReactIVITY WITH MOLECULAR OXYGEN.

by Miriam Greiner Simmons

PART I: Five pseudo-octahedral $^2E$ (low-spin) $\leftrightarrow ^4T$ (high-spin) spin-equilibrium bis(N-R-2,6-pyridinedicarboxaldimine)cobalt(II) complexes with R = C(CH₃)₃, CH(CH₃)₂, NHCH₃, PhCH₃, and CH₂Ph have been synthesized as PF₆⁻ salts and studied in both the solid and the solution states. Voltammetric data for four of the complexes are reported. Although an apparent correlation between spin state population and $E_{1/2}$ is observed, other evidence supports the contention that spin state is unrelated to redox potentials. Variable-temperature magnetic susceptibility measurements (solid, 77-300 K; solution, 200-300 K) reveal considerable differences in behavior of the $^2E$ (ls) $\leftrightarrow ^4T$ (hs) processes in the two environments. In solution the rates of

$$^2E\text{ (ls)} \xrightarrow{k_1} ^4T\text{ (hs)} \xrightarrow{k_{-1}} ^2E\text{ (ls)}$$

intersystem crossing for the R = NH(CH₃) derivative have been measured by laser Raman temperature-jump kinetics. First-order rate constants in CH₃CN/CH₃OH for the forward ($k_1$) and reverse ($k_{-1}$) steps are 3.2 x 10⁶ and 9.1 x 10⁶ s⁻¹. Rate constants and spin lifetimes for this one-electron spin change (ΔS=1) have been compared to available data characterizing ΔS=2 processes in several pseudo-octahedral iron(II) and iron(III) complexes.

PART II: A unique Cu(I) complex, derived from a pentadentate ligand with two imidazole moieties, has been synthesized and found to re-
versibly bind $O_2$ in solution ($CH_3CN$, DMF, $Me_2SO$, pyridine) at room temperature. This is the first well defined Cu(I) species to accurately mimic the active site in hemocyanin, the copper containing respiratory protein. Like hemocyanin, the model compound $\{Bis-2,6[1-(2-imidazol-4-yl-ethylimino)ethyl]pyridine\}Cu(II)$ Perchlorate $\{abbreviated [Cu(I)(imidH)$_2$DAP](ClO$_4$)$\}$ has been observed by manometric techniques to bind one mole of $O_2$ per two copper centers, suggesting a $[Cu-O_2-Cu]$ bridging structure for the oxygenated site. Data from esr measurements indicate that the Cu centers are strongly coupled as is the case for hemocyanin. The green oxy form of the complex can be reconverted to the red deoxy form by application of a vacuum. A 20% decrease in the volume of $O_2$ absorption per oxy/deoxy cycle is observed. The Cu(II) and Zn(II) analog compounds have also been synthesized and characterized. The $[Cu(II)(imidH)$_2$DAP]^{+2}$ cation undergoes a reversible one electron reduction at Pt electrodes at -0.30 V vs. SCE in $Me_2SO$. The electrochemically generated $[Cu(I)(imidH)$_2$DAP]^{+}$ is observed to react reversibly with $O_2$. The analogous $[Cu(I)(py)$_2$DAP](ClO$_4$)$ species (in which pyridines replace the imidazole moieties of the parent compound) exhibits a reversible one electron reduction at -0.17 V vs. SCE in $Me_2SO$. Thus, the $(py)$_2$DAP ligand environment affords greater stabilization for Cu(I) than does the $(imidH)$_2$DAP ligand, as reflected by the lack of reactivity of $[Cu(I)(py)$_2$DAP]^{+}$ with $O_2$. The analogous Cu(II) and Zn(II) complexes have also been synthesized and characterized. X-ray structural determinations verify the pentacoordinate nature of these species. None of these complexes exhibit reactivity with CO.
DEDICATION

To my parents,
and Johnny, and Michele

and to Jim,
who was a member of my
family too.
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I would like to acknowledge Lon J. Wilson, my research advisor and friend. I would like to express to him my profound appreciation and thanks for the last four years of unbelievably exciting research. My respect and admiration for him as a man and as a chemist are unsurpassed.

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And to Mike, for his inexhaustible supply of confidence in me and for teaching me the inherent beauty of this chemistry.

Finally, to Tony, for his unfailing confidence, support, and affection that made this last, and most difficult, year enjoyable.
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PART I

MAGNETIC AND SPIN LIFETIME STUDIES OF $\Delta S=1$ SPIN EQUILIBRIUM
PROCESS FOR SOME $3d^7$ COBALT(II) COMPLEXES
INTRODUCTION

The unusual magnetic and electronic properties that first row transition metal complexes exhibit are due to the partially filled metal d orbitals. For the free ion all five d orbitals are degenerate. When the ion is placed in an idealized octahedral crystal field, this degeneracy is removed, producing a doublet \( (d_{x^2-y^2}, d_{z^2}) \) of \( e_g^* \) symmetry which is higher in energy than a triplet \( (d_{xy}, d_{yz}, d_{xz}) \) of \( t_{2g} \) symmetry. The energy separation between the \( e_g^* \) and \( t_{2g} \) orbital sets is measured by the crystal field energy parameter, \( \Delta_{\text{oct}} \). In molecular orbital terminology, \( \Delta_{\text{oct}} \) separates the strongly anti-bonding \( e_g^* \) orbitals and the non-bonding or slightly \( \pi \) bonding \( t_{2g} \) orbitals. For 3d metal ions a weak ligand field produces a weak perturbation of the d orbitals so that \( \Delta_{\text{oct}} \) is relatively small. Thus, for the ground state, the electron occupancy is expected to follow Hund's rule of maximum multiplicity, producing the high-spin (or spin-free) case. In most octahedral 3d metal complexes the high-spin case persists because the electron repulsion or spin pairing energy, \( P \), is greater than the energy (\( \Delta_{\text{oct}} \)) separating the \( e_g^* \) and \( t_{2g} \) orbitals. For very strong ligand fields, however, \( \Delta_{\text{oct}} \) can become large enough to produce spin pairing, i.e., the low-spin case, where \( \Delta_{\text{oct}} \gg P \). Thus, for 3d\(^4-7\) metal complexes, two possible electronic configurations exist: a low-spin or a high-spin case. Of course, the 3d\(^1-3\) and 3d\(^8-10\) octahedral complexes have only one possible electronic arrangement for their ground states, and all octahedral 4d and 5d metal complexes are only of the low-spin configuration because \( \Delta_{\text{oct}} \) is always much greater than \( P \) for second and third row ions.
Most six-coordinate $3d^4 - 3d^7$ transition metal complexes are either high-spin or low-spin, and for any one compound this configuration is usually invariant. However, in a few such complexes the two electronic states are nearly equi-energetic and may coexist in thermal equilibrium with one another when $(E_{\text{hs}} - E_{\text{ls}}) = kT \approx 200 \text{ cm}^{-1}$. Since this phenomenon is exhibited by relatively few transition metal complexes, including some interesting biological molecules,\textsuperscript{1,2} it has been extensively investigated whenever found. For complexes in which the coordination number is constant and the donor atom set remains intact, this phenomenon has come to be known as a "spin state equilibrium," with the state of lesser multiplicity being the low-spin (ls) state and that of higher multiplicity being the high-spin (hs) state. Figure 1 summarizes the spin state situation for octahedral Co(II) and illustrates the spin equilibrium case between the two possible spin states. The ligand field term symbol terminology used in the figure is for the idealized case of the metal ion in an octahedral ligand field. The actual symmetry of the complexes reported herein is no doubt quite distorted from the ideal; however, the nomenclature for octahedral symmetry will be employed in this work.

Inspection of the Tanabe-Sugano diagram for Co(II) (Figure 2) indicates that there exists a critical value of $\Delta_{\text{oct}}$ for which the high-spin and low-spin electronic states cross. If the ligand field about the metal ion is very close to this "crossover point," external perturbations such as slight ligand modification or temperature and pressure changes which would induce $M$-(ligand) bond length changes can influence the ground state of the metal ion. From the diagram one observes that at low values of $\Delta/B$, the ground state is $^4T$, the high-
FIGURE 1

Crystal Field Diagrams and Spin State Nomenclature for the $3d^7$ Case of Cobalt(II) in an Octahedral Field.

**Cobalt(II), $3d^7$**

Low-spin Case:

$\Delta_{\text{oct}} > P$

\[ \begin{array}{c}
\begin{array}{c}
\uparrow \\
\downarrow
\end{array}
\begin{array}{c}
\downarrow \\
\uparrow
\end{array}
\begin{array}{c}
\uparrow \\
\downarrow
\end{array}
\end{array} e_g^{*}
\]

\[ ^2E_g \]

\[ ^1T_{1g} \]

High-spin Case:

$\Delta_{\text{oct}} < P$

\[ \begin{array}{c}
\begin{array}{c}
\uparrow \\
\downarrow
\end{array}
\begin{array}{c}
\downarrow \\
\uparrow
\end{array}
\end{array} e_g^{*}
\]

\[ ^4T_{1g} \]

Spin Equilibrium Case:

$\Delta_{\text{oct}} \approx P$

\[ \begin{array}{c}
\begin{array}{c}
\uparrow \\
\downarrow
\end{array}
\begin{array}{c}
\downarrow \\
\uparrow
\end{array}
\end{array} e_g
\]

\[ ^2E_g \]

\[ ^4T_{1g} \]
FIGURE 2

spin case, and at higher $\Delta/B$ values, the $^2E$ low-spin state becomes the ground state. The empirical observation is that most Co(II) octahedral species are high-spin, implying that only the strongest field ligands will produce the relatively rare low-spin case, with an expected magnetic moment ($\mu_{\text{eff}}$) of $\approx 1.73 \mu_B$ (the spin-only value for one unpaired electron). The spin-only magnetic moment for the high-spin $^4T$ state with three unpaired electrons is $3.89 \mu_B$; however, there is usually a considerable positive contribution to the moment from spin-orbit coupling so that the commonly observed moments for pseudo-octahedral high-spin cobalt(II) centers are ca. $5.2 \mu_B$. A thermally dependent spin equilibrium for Co(II) is thus easily monitored in both the solid and solution states by variable temperature magnetic susceptibility studies because the two states are of different spin multiplicity.

The utility in studying unusual compounds of the spin equilibrium type is that data from such studies can be uniquely suited to determine important bonding parameters as $E_{\text{hs}} - E_{\text{ls}}$, spin orbit coupling constants, and the degree of distortion from octahedral symmetry. In addition, a measure of $\Delta_{\text{oct}}$ for a spin equilibrium complex is approximately equivalent to a measure of $P$, thus spin equilibrium compounds offer the unique possibility of experimentally determining $3d$ mean pairing energies; for example, in one such recent study for a family of spin equilibrium Fe(II) complexes ($3d^6$), $P$ was determined to be $\approx 12,800$ cm$^{-1}$. Only first-row octahedral transition metal complexes with electronic configurations $3d^{4-7}$ can possess two different spin states. Thus, possible species are Cr(II), Mn(II,III), Fe(II,III), Co(II,III),
and Ni(III). Of these, only Fe(II), Fe(III), and Co(II) have been reported to exhibit the spin equilibrium phenomena in the solution or solid states. Figure 3 depicts the situation for these three metal ions, wherein the two electronic states coexist in thermal equilibrium. Figure 3 also summarizes the ligand field notation for the various spin states. Basically, there are two main differences between the cobalt and the two iron spin equilibrium cases: 1) the cobalt(II) case involves a single electron spin change (ΔS=1) as opposed to a ΔS=2 change for iron, implying that spin interconversion is less "spin forbidden" for the cobalt than for the iron, and 2) in both the high-spin and low-spin states for cobalt, there is electron density in the e^* antibonding orbitals, whereas the low-spin states of the iron complexes possess no e^* electron density. This result implies that (1s) ⇔ (hs) interconversion is accompanied by greater M–(ligand) bond distance changes in the iron complexes than in the cobalt ones, since removal of all antibonding electron density would be consistent with shorter, stronger M–(ligand) bonding in the iron low-spin forms as compared to the low-spin cobalt case. These two factors are potentially of great significance in comparing and understanding the rates of spin interconversion (or intersystem crossing) Fe(II), Fe(III), and the Co(II) systems undergoing spin equilibrium.

The spin equilibrium phenomenon was first observed in 1931 by Cambi, Siego, and Cagnasso.11 A number of pseudo-octahedral systems of Fe(II), Fe(III), and Co(II) have been studied since that time, with the main emphasis being on the solid state magnetic peculiarities that such complexes exhibit. There has recently been a shift in emphasis to the solution state,7 where unpredictable solid state effects such as
FIGURE 3

d - Electronic Configurations and Spin State Nomenclature
for Co(II), Fe(II), and Fe(III) in an Octahedral Field.

Co(II), d⁷
Low-spin (S=1/2)

\[ 4↑ 4↑ \]
\[ 4↑ 1↑ 1↓ \]
\[ ^2E_g \]

High-spin (S=3/2)

\[ 4↑ 4↑ \]
\[ 4↑ 1↑ 1↓ \]
\[ ^4T_{1g} \]

Fe(II), d⁶
Low-spin (S=0)

\[ 4↑ 1↑ \]
\[ 4↑ 1↓ 1↓ \]
\[ ^1A_{1g} \]

High-spin (S=2)

\[ 4↑ 1↑ \]
\[ 4↑ 1↓ 1↓ \]
\[ ^5T_{2g} \]

Fe(III), d⁵
Low-spin (S=1/2)

\[ 4↑ 1↑ \]
\[ 4↑ 1↓ 1↓ \]
\[ ^2T_{2g} \]

High-spin (S=5/2)

\[ 4↑ 1↑ \]
\[ 4↑ 1↓ 1↓ \]
\[ ^6A_{1g} \]
lattice forces, phase changes, and metal-metal interactions may be factored out, or at least minimized. Furthermore, solution studies virtually assure the presence of a "dynamic" equilibrium process, so that the first order rate constants for intersystem crossing can be measured directly by rapid perturbation kinetics such as laser Raman temperature-jump\(^{12,13}\) or ultrasonic relaxation techniques.\(^{14}\) Such rate constants and spin state lifetime data \([\tau_{\text{spin state}} = 1/k]\) studies can then be used to understand intersystem crossing phenomena in photochemical excited states and to lay the groundwork for directly investigating the role of spin multiplicity changes on electron transfer rates in both variable spin inorganic and metalloprotein systems.\(^{15}\) Several proteins, such as hemoglobin,\(^1\) myoglobin,\(^1\) cytochrome P-450\(^{\text{camphor}}\),\(^2\) and cytochrome c oxidase,\(^{16}\) exhibit a spin state change concomitant with electron transfer, and thus studies of synthetic models could ultimately aid in the elucidation of some electron transport pathways in biological systems.

To date, extensive solution state studies have been performed on spin equilibrium complexes of Fe(II) \([^1\text{A}(1s) \rightleftharpoons ^5\text{T}(hs)]\)\(^\text{7,8,9,17,18}\) and Fe(III) \([^2\text{T}(1s) \rightleftharpoons ^6\text{A}(hs)]\).\(^\text{19,20,21,22}\) Representative examples of well characterized iron spin equilibrium compounds are summarized in Table I and included here for comparative purposes. No complete solution characterization of Co(II) spin equilibrium compounds has, as yet, been performed, thus the comprehensive study of a family of Co(II) spin equilibrium compounds (in Figure 4) is the subject of this
### TABLE I

Representative Examples of Iron Spin Equilibrium Complexes.*

<table>
<thead>
<tr>
<th>Complex</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II) [Fe(R$_2$-1,10-phenanthroline)$_2$$X_2$]</td>
<td>18</td>
</tr>
<tr>
<td>[Fe(6Mepy)$_m$(py)$_n$tren]$^{+2}$</td>
<td>7,8</td>
</tr>
<tr>
<td>[Fe(poly(1-pyrazolyl)borate)$_2$]</td>
<td>9</td>
</tr>
<tr>
<td>[Fe(2-(2-pyridyl)imidazole)$_3$]$^{+2}$</td>
<td>17</td>
</tr>
<tr>
<td>Fe(III) [Fe(R$_2$-dithiocarbamate)$_3$]</td>
<td>11</td>
</tr>
<tr>
<td>[Fe(R$_2$-monothiocarbamate)$_3$]</td>
<td>21</td>
</tr>
<tr>
<td>[Fe(myoglobin)OH]</td>
<td>1,40,42</td>
</tr>
<tr>
<td>[Fe(X-Sal$_2$trien)]$^+$</td>
<td>19</td>
</tr>
<tr>
<td>[Fe(acac$_2$trien)]$^+$</td>
<td>20</td>
</tr>
<tr>
<td>[Fe(X-Salmeen)$_2$]$^+$</td>
<td>22</td>
</tr>
</tbody>
</table>

*A more complete listing can be found in the Ph.D. dissertation of M. F. Tweedle, Rice University, p. 9, 1978.*
FIGURE 4

Synthetic Scheme for the Bis(N-R-2,6-pyridine-
dicarboxaldimine)cobalt(II) Complexes.

\[
\text{H}_2\text{CO} + 2\text{(H}_2\text{N-R)} \\
\text{CH}_3\text{OH} \\
\text{R-N} = \text{N-R} \\
1) \text{CoCl}_2 \cdot \text{6H}_2\text{O} \\
2) \text{KPF}_6 \\
\left[ \text{R-N} = \text{N-R} \right]_{\text{Co(II)}} \left( \text{PF}_6 \right)_2
\]
work. Virtually any report of a low [below spin only value of 3.89 $\mu_B$ for high-spin Co(II)] magnetic moment for pseudo-octahedral Co(II) complexes has generated considerable study due to the rarity of low-spin Co(II).$^{3,4}$ The first report of an anomalous magnetic moment for a pseudo-octahedral Co(II) compound appeared in 1956$^{23}$ but no variable temperature studies were performed. A slightly more complete study followed in 1959$^5$ with the room temperature magnetic study of various Co(II) salts and complexes with sulfur and nitrogen containing ligands. In 1960 the first bis-tridentate Co(II) complexes were reported as spin equilibrium compounds, where biacetyl-bis-methylimine, 2-pyridinal-methylimine, and 2,6-pyridinal-bis-methylimine were used as ligands.$^{24,25,26,27}$ Other pyridinal and substituted hydrazones of 2,6-diacetylpyridine have been reported.$^{28,29,30}$ Various salts of Co(II) bis-terpyridyl complexes exhibit anomalous magnetic behavior with temperature but these complexes have been studied only in the solid state.$^{31,32,33,34}$ Two cobalt complexes with sulfur and nitrogen containing ligands, [6-methylpyrid-2-yl-N-(2'-methylthiophenyl)methyleneimine] and [2-pyridyl-N-(2'-methylthiophenyl)methyleneimine]$^{35}$ are spin equilibrium in the solid state. Evidence for spin equilibrium exists for the Co(II) complexes of tri-2-pyridylamine,$^{36}$ for [bis(1,10-phenanthroline-2-carbothioamide)Co(II)](ClO$_4$)$_2$,$^{37}$ and for [2,4,6-tris(2-pyridyl)-1,3,5-triazine]Co(II)]$^{4+}$. Co(II) complexes of (1-2(pyridylazo)-2-phenanthrol) have been investigated with a view toward their unusual magnetic behavior.$^{39}$ A list of these complexes with ligand structure and abbreviation (where applicable) appears in Table II.
### TABLE II

Examples of Six-Coordinate Cobalt(II) Spin Equilibrium Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tris(biacetylhydrazone)Co(II) (I)$_2$</td>
<td>23</td>
</tr>
<tr>
<td>Ligand abbreviation: BdH</td>
<td></td>
</tr>
<tr>
<td><img src="image1.png" alt="Chemical Structure" /></td>
<td></td>
</tr>
<tr>
<td>Tris(biacetylbis-methylimine)Co(II) (I)$_2$</td>
<td>24</td>
</tr>
<tr>
<td>Ligand abbreviation: BMI</td>
<td></td>
</tr>
<tr>
<td><img src="image2.png" alt="Chemical Structure" /></td>
<td></td>
</tr>
<tr>
<td>Tris(2-pyridinal-methylimine)Co(II) (BF$_4$)$_2$</td>
<td>24</td>
</tr>
<tr>
<td>Ligand abbreviation: PMI</td>
<td></td>
</tr>
<tr>
<td><img src="image3.png" alt="Chemical Structure" /></td>
<td></td>
</tr>
</tbody>
</table>
TABLE II (continued)

Bis(2,6-pyridinal-bis-methylimine)Co(II) (I)$_2$  
Ligand abbreviation: PdMI

Bis(2,6-pyridindialhydrazone)Co(II) (I)$_2$  
Ligand abbreviation: PdAdH

Bis(2,2',2''-terpyridine)Co(II) (Cl)$_2$  
Ligand abbreviation: terpy

Bis[6-methylpyrid-2-yl-N-(2'methyl-thiophenyl)-methyleneimine]Co(II) (ClO$_4$)$_2$  
Ligand abbreviation: SNNMe

\[ R = \text{Me, H} \]
TABLE II (continued)

Bis[tri-(2-pyridyl)amine]Co(II) (ClO$_4$)$_2$

![Chemical Structure 1](image1)

Bis[N-(1,10-phenanthrolin-2-ylmethylene)alkyl (or aryl)-amines]Co(II) (BF$_4$)$_2$

![Chemical Structure 2](image2)

Bis[1-(2-Pyridylazo)-2-phenanthrol]Co(II)

![Chemical Structure 3](image3)
This work reports the first complete solution characterization of the spin equilibrium phenomenon of six-coordinate, pseudo-octahedral complexes of Co(II) derived from the condensation of 2,6-pyridinedialdehyde with various primary amines and hydrazines. The synthetic scheme is shown in Figure 4, where \( R = \text{t-buty1, i-propyl, NHCH}_3, \text{p-tolyl, and benzyl.} \) Systematic investigation of these complexes includes variable temperature magnetic susceptibility measurements in both the solution and solid states, variable temperature uv-vis spectra, contact shift pmr spectral studies, electrochemical studies by cyclic voltammetry, and measurement of the kinetics for spin interconversion of a \( \Delta S=1 \) process in solution. The laser Raman temperature-jump technique developed at Brookhaven\(^{12,40,41,42}\) has been used to determine the forward \((k_1)\) and reverse \((k_{-1})\) rate constants where

\[
  ^2E(1s) \xrightarrow{k_1} 4T(1s) \xrightarrow{k_{-1}} ^2E(1s)
\]

spin lifetimes \( \tau_{1s} = (k_1)^{-1} \) and \( \tau_{hs} = (k_{-1})^{-1} \). Previously reported rate constant data for several Fe(II) and Fe(III) (both \( \Delta S=2 \) cases) systems are compared with the information on these new \( \Delta S=1 \) Co(II) systems to better understand the factors influencing spin interconversion (or intersystem crossing) rates in general.
EXPERIMENTAL

Physical Measurements. Solid state magnetic susceptibilities were measured by the Faraday method using a Cahn Model 6600-1 Research Magnetic Susceptibility System. The cryogenics consisted of an Air Products Faraday Interface Model DMX-19 Vacuum Shroud, an LT-3-110B Heli-tran System, and an APD-TL Digital Temperature Readout monitoring an iron-doped gold vs. chromel thermocouple. Hg[Co(NCS)₄] was used as the calibrant. Pascal's constants were used to correct for ligand and PF₆⁻ diamagnetism in 10⁻⁶ cgs units: C(CH₃)₃ compound, -417; CH(CH₃)₂ compound, -392; NHCH₃ compound, -331; p-PhCH₃ compound, -505; CH₂Ph compound, -500; PF₆⁻, -64. Solution magnetic moments were determined by the Evans method with methanol and ethylene glycol being used for temperature calibration. The measurements were corrected for sample concentration and solvent density changes with temperature. For these studies CHCl₃ was used as a reference compound in acetone solutions. The position of the reference compound's signal in solvent alone is different from that when it is in solution with the paramagnetic complex, and the difference between these two signal positions is proportional to χ₂. Since χ₂ = (χ₁ x M.W.) - (diamag. corr.), μ_eff can be calculated by μ_eff = 2.83(χ₂ MU)¹/² in units of μ_B.

Solid state infrared spectra were obtained in the region 4000-600 cm⁻¹ using NaCl plates and Nujol mulls. A Model 31 YSI conductivity bridge was used to obtain solution conductivities. Pmr spectra were run at 60 MHz on a Varian A 56/60A spectrometer modified for isotropic shift studies, or a Perkin-Elmer R12 spectrometer. Uv-vis spectra were run on a Cary 17 using jacketed quartz
cells; the temperature was monitored with a thermistor and are ±.5°C.

Electrochemical measurements were obtained in CH₃CN solutions at room temperature under a constant flow of dry N₂ saturated with CH₃CN. A PAR Model 174 Polarographic Analyzer was used. The electrolysis cell was a Princeton Applied Research (PAR) Polarographic Model K60. A three electrode circuit was employed; the working and auxiliary electrodes were platinum button electrodes and a commercial saturated calomel electrode (SCE) was used as the reference. The reference electrode was partially separated from the bulk solution by a bridge containing supporting electrolyte solution. The supporting electrolyte was .1 M tetrabutylammonium perchlorate (TBAP). The maximum potential range in CH₃CN was checked by running a blank before each run. Cyclic voltammograms were recorded at scan rates of 50 to 500 mV/sec in order to check reversibility. The electrodes were pre-treated before use by soaking them for 5 minutes in 6M HNO₃, rinsing well with distilled water, drying with cellulose tissue, and then placing them in the cell filled with supporting electrolyte solution. The voltage was set at -0.20 volts and the cell current switched on. Current was passed through the cell until a constant reading was obtained on a 2 μA scale. Reported potentials are uncorrected for junction potentials.

The Raman laser temperature-jump instrument has been described in detail elsewhere. The 1.06μ radiation from a Q-switched Nd-glass laser (20J/25 nsec pulse) is Raman shifted to 1.41μ (2J/25 nsec pulse) in liquid N₂. Water and alcohols absorb at 1.41μ and these solvents can be directly heated by this technique. Bubble formation in
the liquid N\textsubscript{2} is suppressed by saturating the liquid N\textsubscript{2} with helium gas. The temperature-jump produces changes in the absorbance of the solution (typically in the region of the intense charge-transfer bands of the complexes) associated with changes in the temperature-dependent populations of the two spin states. These absorbance changes were monitored using a Xe lamp-monochromator-photomultiplier (RCA 1P28) system. The combined bandwidth of the photomultiplier preamplifier detection system is in excess of 30 MHz. The experimentally observed relaxations were displayed on an oscilloscope and photographed. The first-order relaxation time constant, \( \tau \) in nsec, was determined from linear log \( (I_\infty - I) \) vs. time plots, where \( I \) is the intensity of the light passing through the solution at time \( t \) and \( I_\infty \) is the limiting value of the intensity at long times. For the small intensity changes measured in these experiments, this is equivalent to plotting the log of the absorbance or concentration changes. Equilibrium constants for the \( (1s) \rightarrow (hs) \) processes \( [K_{eq} = (hs)/(1s)] \) were obtained from solution magnetic susceptibility data using the NMR method of Evans.\textsuperscript{43,44} Rate constants \( k_1 \) and \( k_{-1} \), and the lifetimes of the spin states, \( \tau(1s) = (k_1)^{-1} \) and \( \tau(hs) = (k_{-1})^{-1} \), were calculated from the measured values of \( K_{eq} \) and \( \tau \) by solving equations 1 and 2 simultaneously. First-order relaxation

\[
K_{eq} = \frac{k_1}{k_{-1}}
\]

(1)

\[
\tau^{-1} = k_1 + k_{-1} = [\tau(1s)]^{-1} + [\tau(hs)]^{-1}
\]

(2)

times are reported as the average of at least six determinations. For these experiments a CH\textsubscript{3}CN/CH\textsubscript{3}OH solution (1:4 by volume) was used and data were obtained at 25°C in a thermostated (±1°C) cell using path
lengths of 0.020-0.081 mm. The final 83 nsec value for the R = NHCH₃ derivative resulted from eight separate lasing experiments on the same sample; the estimated error is 23 nsec. The equilibrium constant $K_{eq} = k_1/k_\cdot_1$ was obtained from the solution magnetic susceptibility measurements, with the value used being 0.35 at 25°C. Fundamental limitations on the resolution obtainable in the temperature-jump experiment arise from the finite duration of the heating pulse (~25 nsec), the enthalpy change ($\Delta H^°$) of the spin multiplicity transition, and the differences in the molar absorptivities of the high-spin and low-spin complexes ($\Delta \varepsilon$). Although small $\Delta H^°$ and $\Delta \varepsilon$ values decrease the signal-to-noise ratio, it was possible to optimize the detection system so that these were not limiting factors and, in practice, only the heating pulse width of ~25 nsec proved to be a fundamental limitation.

**Materials and Syntheses.** The reagent grade primary amines were purchased from Aldrich Chemical. Spectro-quality acetone, CH₃OH, and reagent grade CH₃CN and DMSO, and practical grade CH₃NO₂ were used for the studies. TEAP was purchased from Eastman Chemicals and used without further purification. Elemental chemical analyses were performed by the microanalytical laboratory of the School of Chemical Sciences, University of Illinois.

The 2,6-pyridinedicarboxaldehyde was prepared by MnO₂ oxidation of 2,6-pyridinedimethanol (Aldrich Chemicals) as previously reported:⁴⁵ 1 g of 2,6-pyridinedimethanol was refluxed for 12 h with 10 g of MnO₂ in 80 mL of CHCl₃. The solution was taken to dryness and the light yellow solid was recrystallized from ethyl ether/heptane.
A troublesome part of the synthesis involved the preparation of the MnO₂, since oxidation will not occur unless the MnO₂ is correctly prepared. To prepare sufficient MnO₂, 75 g KMnO₄ was dissolved with the aid of mild (ca. 65°C) heating in about 500 mL H₂O and 80 g of MnSO₄ was dissolved in about 300 mL H₂O and heated to 90°C in a large beaker. The KMnO₄ solution was added slowly, with stirring. Brown MnO₂ formed immediately and the solution was heated at 90°C and stirred for 15 min, then filtered through at least two pieces of filter paper on a large Buchner funnel and rinsed with hot (at least 90°C) water until the filtrate was colorless. The dark brown MnO₂ was dried in an oven at 110-115°C for 6 hr. MnO₂ prepared in this manner will remain active for months if placed in a well-stoppered bottle. The 2,6-pyridinedicarboxaldehyde was obtained in 20% yield. M.P.: 121°C (lit., 125°C). Predominant ir peaks (Nujol mull): 1730 cm⁻¹, 1310 cm⁻¹, 1210 cm⁻¹, 810 cm⁻¹, and 780 cm⁻¹.

The cobalt(II) compounds were prepared, as their PF₆⁻ salts, by the same general method: to 2 mmol of 2,6-pyridinedicarboxaldehyde dissolved in 25 mL CH₃OH, 4 mmol of the appropriate amine were added dropwise, except for p-toluidine which is added directly as the solid. A yellow colored solution resulted immediately. One mmol of CoCl₂·6H₂O was then added as a crystalline solid, yielding an intensely colored solution in all cases. To this solution 5 mmol of KPF₆ dissolved in 50 mL of warm CH₃OH was then added with filtration. After addition of the KPF₆, which usually initiated precipitation, the solution was taken to dryness at room temperature under reduced pressure. The resulting solid was extracted into 50 mL of dry acetone to remove inorganic salts and crystallization of the [Co(N-R-2,6-pyridinedialdimine)₂]PF₆₂
compound from the acetone solution was induced by cooling and the slow addition of anhydrous ether. The products were recrystallized from an acetone-ether mixture, collected by filtration, and dried in vacuum over P₂O₅ at 1 torr for a minimum of 12 hours.

The R = C(CH₃)₃ compound was obtained as a light green solid in 87% yield. Anal. calcd for CoC₃₀H₄₆N₆P₂F₁₂: Co, 7.03%; C, 42.91%; H, 5.53%; N, 10.01%. Found: Co, 6.91%; C, 42.87%; H, 5.52%; N, 9.80%. Λ_c = 268 ohm⁻¹ cm⁻¹ for a 10⁻³ M acetone solution at 30°C. Electronic spectrum in CH₃OH: peak maximum at 305 nm (ε ~ 16,000) with shoulder at 360 nm (ε ~ 2,000).

The R = CH(CH₃)₂ compound was obtained as a brick red solid in 75% yield. Anal. calcd. for CoC₂₆H₃₈N₆P₂F₁₂: Co, 7.52%; C, 39.85%; H, 4.90%; N, 10.73%. Found: Co, 7.49%; C, 39.79%; H, 4.86%; N, 10.56%. Λ_c = 266 ohm⁻¹ cm⁻¹ for a 10⁻³ M acetone solution at 30°C. Electronic spectrum in CH₃OH: peak maximum at 295 nm (ε ~ 16,000) with a shoulder at 375 nm (ε ~ 2,000).

The R = NH(CH₃) compound was obtained as a light brown powder in 80% yield. Anal. calcd. for CoC₁₈H₂₆N₁₀P₂F₁₂: Co, 8.07%; C, 29.55%; H, 3.56%; N, 19.15%. Found: Co, 8.07%; C, 29.64%; H, 3.38%; N, 19.24%. Λ_c = 265 ohm⁻¹ cm⁻¹ for a 10⁻³ M acetone solution at 30°C. Electronic spectrum in CH₃OH: peak maximum at 290 nm (ε ~ 51,000) with a shoulder at 365 nm (ε ~ 12,000).

The R = p-PhCH₃ compound was obtained as a rust-red solid in 60% yield. Anal. calcd. for Co₄₂H₃₈N₆P₂F₁₂: Co, 6.05%; C, 51.69%; H, 3.90%; N, 8.61%. Found: Co, 6.08%; C, 51.68%; N, 8.60%. Λ_c = 273 ohm⁻¹ cm⁻¹ for a 10⁻³ M acetone solution at 30°C. Electronic spectrum in CH₃OH: peak maximum at 335 nm (ε ~ 20,000) with a
shoulder at 560 nm (ε ~ 750).

The R = CH₂Ph compound was obtained as a light red solid in 71% yield. Anal. calcd. for CoC₄₂H₃₈N₆P₂F₁₂: Co, 6.05%; C, 51.69%; H, 3.90%; N, 8.61%. Found: Co, 6.28%; C, 50.95%; H, 3.88%; N, 8.39%. 

Λₐ = 250 ohm⁻¹ cm⁻¹ for a 10⁻³ M acetone solution at 30°C. Electronic spectrum in CH₃CN: peak maximum at 285 nm (ε ~ 10,500) with shoulders at 380 nm (ε ~ 1900) and 560 nm (ε ~ 950).

Variable Temperature Susceptibility Data. (T in K, χₚ in 10⁻⁶ cgau mol⁻¹, μeff in μₜ. B.) R = C(CH₃)₃ compound (solid): 304.0, 11,218, 5.24; 252.2, 13,122, 5.17; 208.9, 14,742, 4.98; 155.7, 18,853, 4.87; 101.1, 25,268, 4.54; 78.3, 32,328, 4.52; 6.1, 139,528, 2.68.

R = C(CH₃)₃ compound (acetone): 334.2, 9,798, 5.14; 310.2, 10,143, 5.04; 304.2, 10,470, 5.07; 285.2, 10,553, 4.93; 263.7, 11,644, 4.98; 249.7, 12,126, 4.94; 238.2, 12,629, 4.93; 217.7, 14,056, 4.96; 208.2, 14,926, 5.01.

R = CH(CH₃)₂ compound (solid): 297.8, 6,631, 3.99; 280.0, 6,245, 3.76; 265.0, 6,042, 3.59; 251.2, 5,687, 3.39; 240.0, 5,483, 3.26; 227.6, 5,226, 3.10; 210.0, 4,764, 2.84; 182.5, 4,236, 2.50; 150.0, 3,865, 2.16; 130.3, 4,151, 2.09; 111.3, 4,451, 2.00; 91.7, 5,065, 2.00; 77.7, 6,204, 2.00.

R = CH(CH₃)₂ compound (acetone): 332.2, 7,600, 4.52; 312.2, 7,450, 4.33; 303.2, 7,056, 4.15; 273.2, 6,815, 3.88; 255.7, 6,494, 3.66; 236.7, 5,953, 3.37; 224.7, 5,640, 3.20; 208.2, 4,860, 2.87; 200.7, 4,947, 2.83; 192.2, 4,441, 2.62.
\[ R = \text{NH}(\text{CH}_3) \text{ compound (solid)}: \ 269.0, 1,988, 2.18; 231.2, 2,217, 2.03; \]
\[ 182.5, 2,824, 2.04; 117.3, 4,672, 2.00; 79.2, 5,993, 2.00. \]

\[ R = \text{NH}(\text{CH}_3) \text{ compound (acetone)}: \ 333.2, 4,549, 3.50; 298.7, 4,029, \]
\[ 3.12; 285.2, 3,955, 3.02; 273.2, 3,955, 2.93; 255.7, 3,587, 2.72; \]
\[ 236.7, 3,291, 2.51; 224.7, 3,104, 2.37; 208.2, 3,043, 2.26; 200.7, \]
\[ 2,951, 2.10. \]

\[ R = \text{NH}(\text{CH}_3) \text{ compound (CH}_3\text{CN):} \ 334.2, 4,694, 3.56; 308.2, 4,397, 3.31; \]
\[ 295.7, 4,057, 3.11; 277.2, 3,963, 2.98; 259.7, 3,750, 2.80; 246.2, \]
\[ 3,438, 2.61; 241.2, 3,384, 2.56; 224.7, 3,169, 2.40. \]

\[ R = \text{NH}(\text{CH}_3) \text{ compound (CH}_3\text{OH):} \ 319.2, 4,444, 3.38; 310.2, 4,390, 3.31; \]
\[ 302.7, 3,968, 3.11; 272.2, 3,522, 2.78; 248.2, 2,993, 2.45; 223.7, \]
\[ 2,737, 2.22; 188.2, 2,827, 2.07. \]

\[ R = \text{NH}(\text{CH}_3) \text{ compound (CH}_3\text{NO}_2): \ 319.2, 4,064, 3.23; 310.2, 4,068, 3.19; \]
\[ 302.7, 3,680, 3.00; 272.2, 3,597, 2.81; 248.2, 2,924, 2.42. \]

\[ R = \text{p-PhCH}_3 \text{ compound (solid)}: \ 296.9, 9,634, 4.99; 275.0, 9,856, \]
\[ 4.67; 242.0, 10,368, 4.52; 227.4, 10,948, 4.50; 185.5, 13,251, 4.47; \]
\[ 138.5, 16,298, 4.20; 101.5, 20,111, 4.12; 78.5, 25,128, 3.99. \]

\[ R = \text{p-PhCH}_3 \text{ compound (acetone):} \ 333.2, 7,311, 4.43; 309.2, 7,084, \]
\[ 4.20; 292.7, 6,684, 3.97; 271.2, 6,387, 3.74; 248.2, 5,907, 3.44; \]
\[ 229.7, 5,305, 3.13; 213.2, 4,924, 2.91. \]

\[ R = \text{p-PhCH}_3 \text{ compound (CH}_3\text{OH):} \ 311.2, 4,816, 3.48; 271.5, 4,355, 3.09; \]
\[ 249.7, 4,543, 3.02; 234.7, 4,029, 2.88; 183.15, 4,031, 2.46. \]
R = p-PhCH₃ compound (CH₃CN): 315.2, 7,923, 4.49; 295.7, 7,756, 4.30; 267.2, 7,262, 3.96; 249.7, 6.77, 3.69; 228.2, 6,037, 3.33.

R = p-PhCH₃ compound (CH₃NO₂): 315.2, 7,149, 4.25; 295.7, 6,974, 4.08; 267.2, 6,750, 3.81; 255.7, 6,512, 3.66.

R = CH₂Ph compound (solid): 297.4, 7,681, 4.29; 272.4, 7,837, 4.14; 255.2, 7,704, 3.98; 196.5, 7,699, 3.49; 153.7, 7,763, 3.10; 127.7, 7,888, 2.85; 106.5, 8,128, 2.64; 82.3, 8,961, 2.44.

R = CH₂Ph compound (CH₃CN): 334.2, 5,275, 3.77; 306.2, 4,739, 3.42; 295.7, 4,669, 3.34; 285.2, 4,445, 3.20; 277.2, 4,637, 3.22; 263.2, 4,318, 3.05; 248.2, 4,122, 2.87; 241.2, 3,896, 2.75; 236.2, 3,872, 2.72; 232.2, 4,003, 2.74; 224.7, 3,743, 2.61.
RESULTS AND DISCUSSION

Characterization of the Complexes. All the bis(N-R-2,6-pyridinedialdimine)cobalt(II) complexes synthesized and studied in this work as their PF$_6^-$ salts are new except for a R = CH$_2$Ph iodide salt$^{32}$ derivative which has previously been reported to be a $^2E \leftrightarrow ^4T$ spin equilibrium compound in the solid state. In addition, several other R derivatives, not reported here, such as the R = CH$_3$,$^{24}$ NH$_2$,$^{23}$ and C$_2$H$_5$ and C$_6$H$_5$ compounds$^{28}$ have been synthesized, but of these only the R = NH$_2$ compound has been studied for its anomalous spin equilibrium magnetic behavior in the solid.$^{32}$ However, no systematic studies of these Co(II) $^2E \leftrightarrow ^4T$ spin equilibria in solution have previously appeared, although a solution state spin equilibrium has been documented for the structurally similar [Co(terpy)$_2$]$^{2+}$ complex.$^{12,33}$ Available analytical and solution conductivity data, as reported in the experimental section, are consistent with the bis(tridentate) monomeric nature of the bis(N-R-2,6-pyridinedialdimine)cobalt(II) cations as shown in Figure 5.

Solid State Considerations. The $\mu_{\text{eff}}$ vs. T curves (77 - 300 K) for the series in the solid are shown in Figure 6 as a function of the R substituent. Depending on the R substituent, the Co(II) centers at room temperature exhibit $\mu_{\text{eff}}$ values spanning the entire $^2E$ low-spin (1.9 - 2.0 $\mu_B$) to $^4T$ high-spin (4.7 - 5.2 $\mu_B$) range with the R = C(CH$_3$)$_3$ (5.24 $\mu_B$ at 304 K) and R = NHCH$_3$ (2.18 $\mu_B$ at 296 K) derivatives being near the limiting high-spin and low-spin values, respectively. The remaining three derivatives, R = CH(CH$_3$)$_2$, CH$_2$Ph, and p-PhCH$_3$, exhibit intermediate magnetic moments at room temperature which display
FIGURE 5

The $^{2}E \not\Rightarrow ^{4}T$ Bis(N-R-2,6-pyridinedicarboxaldimine)cobalt(II)

Compounds with $R = C(CH_{3})_{3}, CH(CH_{3})_{2}, NHCH_{3}, PhCH_{3}$, and $CH_{2}Ph$. 

\[
\begin{align*}
\text{[} & \begin{array}{c}
\text{H} \quad \text{C} \quad \text{N} \quad \text{H} \\
\text{C} \quad \text{N} \quad \text{C} \quad \text{H} \\
\text{R} \quad \text{N} \quad \text{R}
\end{array} \\
\text{Co(II)} & \text{[} \begin{array}{c}
\text{N} \quad \text{N} \\
\text{2}
\end{array} \text{]}^{-2}
\end{align*}
\]
\( \mu_{\text{eff}} (\mu_B) \) vs. Temperature Curves for the
Bis(N-R-2,6-pyridinedicarboxaldimine)Co(II) (PF_6)_2
Salts as Solids.

a) \( R = \text{C(CH}_3\text{)}_3 \)
b) \( R = \text{CH(CH}_3\text{)}_2 \)
c) \( R = \text{NHCH}_3 \)
d) \( R = \text{CH}_2-\text{CH}_3 \)
e) \( R = \text{CH}_2-\text{C} \)
the anomalous non-Curie temperature dependency characteristically associated with Co(II) $^2E \rightarrow ^4T$ spin equilibria, having the spin crossover region around room temperature. All the $\mu_{\text{eff}}$ vs. $T$ curves appear continuous and are devoid of the sharp discontinuities that are known to sometimes accompany spin equilibrium processes in the solid phase.\textsuperscript{7,47}

Solution State Considerations. Variable temperature solution magnetic data (200 - 300 K) for the series in acetone are shown in Figure 7 where it is seen that all the derivatives, except for the R = C(CH$_3$)$_3$ species, exhibit a pattern of decreasing $\mu_{\text{eff}}$ values with temperature which is consistent with the preservation of the spin equilibrium phenomenon in the solution state. While these magnetic data demonstrate the existence of the $^2E \rightarrow ^4T$ spin equilibrium phenomenon in solution, they also serve to emphasize that solid state magnetic data can not be used \textit{a priori} to infer solution behavior since, as shown in Figure 2, 1) the C(CH$_3$)$_3$ derivative is a $^2E \rightarrow ^4T$ compound in the solid but not in solution, 2) the NHCH$_3$ derivative is a $^2E \rightarrow ^4T$ compound in solution but essentially only low-spin in the solid, and 3) the relative "ordering" of the CH(CH$_3$)$_2$, p-PhCH$_3$, and CH$_2$Ph compounds differ in the two environments. Such solution vs. solid discrepancies are not, however, particularly surprising in view of the fact that it has been recently shown\textsuperscript{19,20} that subtle effects such as [(metal complex)...solvent] hydrogen bonding interactions can drastically influence the equilibrium position of (ls) $\rightleftharpoons$ (hs) solution processes. The present Co(II) $^2E \rightleftharpoons ^4T$ processes are also solution dependent with the high-spin state for the NHCH$_3$ compound being favored according to the solvent sequence: DMSO > CH$_2$CN ~ acetone > CH$_3$OH >
FIGURE 7

$\mu_{\text{eff}} (\mu_B)$ vs. Temperature Curves
for the Complexes in Acetone.
Concentration is $10^{-2}$ M in complex.
(1) $R = C(CH_3)_3$

(2) $R = CH(CH_3)_2$

(3) $R = NHCH_3$

(4) $R = -\text{CH}_3$

(5) $R = CH_2=\text{CH}$
CH₃NO₂ as shown in Figure 8. The p-PhCH₃ compound has a different ordering of solvents which favor the high-spin state and a wider range for μ eff: DMSO > CH₃CN > CH₃NO₂ > acetone > CH₃OH. The μ eff (μB) vs. temperature plots for this compound are shown in Figure 8. Only for the R = NHCH₃ compound is any [solvent....HN] hydrogen bonding interaction with the ligand itself possible, so only with this derivative should such an influence be expected. However, investigation of the N-H stretching frequency by infrared spectroscopy of this complex in each solvent revealed no correlation between the changing bond strength and the magnetic moment (ν N-H in DMSO, 3480 cm⁻¹; ν N-H in CH₃CN, 3370 cm⁻¹; ν N-H in acetone, 3410 cm⁻¹; ν N-H in CH₃NO₂, 3410 cm⁻¹) of the nature recently reported for an Fe(III) spin equilibrium system. Furthermore, the differences in moment with solvent for the R = p-PhCH₃ derivative precludes a hydrogen bonding mechanism as a primary cause of the changing moment.

In MeOH solution the percent high-spin character for the present spin equilibrium series increases according to the R group ordering: C(CH₃)₃ > CH(CH₃)₂ > p-PhCH₃ > CH₂Ph > NHCH₃. This ordering is undoubtedly a composite reflection of both R group electronic and steric consequences. However, space-filling molecular models indicate that steric considerations play a dominant role in these complexes. For the most sterically demanding R = C(CH₃)₃ group, space-filling models show that the greater high-spin character of this compound is promoted by intra-molecular nonbonding interactions between the R group hydrogens of one pyridinedialdimine ligand and the pyridine π network of the second ligand. Increasing Co-N bond distances minimizes these steric interactions and apparently decrease Δoct sufficiently to
Variable Temperature Magnetic Moment Data

Obtained for the Compounds in Various Solvents.

Complex concentration is $10^{-2}$ M.

1) $R = \text{NHCH}_3$
2) $R = \text{p-PhCH}_3$
stabilize the high-spin $^4T$ state as the ground state for these compounds. On the other hand, less sterically demanding R substituents presumably permit shorter Co–N bond distances with sufficiently strong ligand fields to produce the $^2E(1s)$ state as the ground state and the thermally accessible $^4T(hs)$ state.

Comparison of the pmr isotropic shift resonances for each of the compounds, as listed in Table III and shown in Figure 9, lends credence to the presence of a steric mechanism in determining the spin equilibrium property in these $^2E \rightleftharpoons ^4T$ complexes. Resonances occur over a wide range as expected for these Co(II) species, where a large dipolar shift contribution to the observed isotropic shift is expected because of anisotropy associated with the high-spin $^4T$ state. At room temperature the $R = C(CH_3)_3$ and $R = CH(CH_3)_2$ compounds in CD$_3$CN yield ten signals ranging from -200 ppm to +125 ppm from external TMS. The intermediate spin compound, $R = PhCH_3$, also gives ten signals ranging from -211 to +105 ppm. Assuming three of the observed resonances of these complexes must be due to the methine and pyridine meta and para protons, the remaining resonances must be assigned to the stereochemically nonequivalent methyl (for compounds a and b) or phenyl (compound d) rotationally "locked" groups resulting from rather severe steric contact interactions. Such steric restraints undoubtedly impose considerable asymmetry on the molecules, which would result in greater than expected multiplicity in their pmr spectra. The remaining two derivatives ($c$, $R = NHCH_3$, and $e$, $R = CH_2Ph$) show fewer resonances, which is consistent with a smaller degree of steric hindrance expected for these two complexes. Indeed, both $c$ and $e$ have fairly low solution magnetic moments, which is in agreement with shorter Co–N
TABLE III

PMR Contact Shift Spectra for the Bis(N-R-2,6-pyridinedicarboxaldimine) Cobalt(II) Complexes in CD$_3$CN Relative to External TMS at 34°C.

<table>
<thead>
<tr>
<th></th>
<th>R = C(CH$_3$)$_3$</th>
<th>R = CH(CH$_3$)$_2$</th>
<th>R = NHCH$_3$</th>
<th>R = p-PhCH$_3$</th>
<th>R = CH$_2$Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>-200.5</td>
<td>-202.5</td>
<td>-201.0</td>
<td>-211.5</td>
<td>-201.5</td>
<td></td>
</tr>
<tr>
<td>-178.5</td>
<td>-190.5</td>
<td>-197.5</td>
<td>-208.5</td>
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<tr>
<td>-128.0</td>
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<td>-197.5</td>
<td></td>
<td>-201.5</td>
<td>-100.0</td>
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<td>-96.5</td>
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</tr>
<tr>
<td>-87.5</td>
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<td></td>
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<tr>
<td>-77.5</td>
<td>-55.5</td>
<td></td>
<td>-12.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-27.5</td>
<td>-24.0</td>
<td>-27.0</td>
<td>-8.5</td>
<td>-5.5</td>
<td></td>
</tr>
<tr>
<td>+18.5</td>
<td>+11.0</td>
<td>+3.0</td>
<td>+17.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+105.0</td>
<td>+103.5</td>
<td>+105.0</td>
<td>+97.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+124.5</td>
<td>+115.5</td>
<td>+109.0</td>
<td>+104.5</td>
<td></td>
<td>+105.0</td>
</tr>
</tbody>
</table>
FIGURE 9

PMR Spectra for the Cobalt(II) Complexes at Room Temperature in CD₃CN. Peak positions are references relative to external TMS. The CD₃CN solvent peak is denoted with an asterisk.
bond distances, arising from sterically less crowded molecules. Obviously, the NHCH$_3$ derivative is the least sterically hindered molecule in this series of complexes, but considerable molecular asymmetry would lead to greater than expected spectrum multiplicity. For the $R = \text{CH}_2\text{Ph}$ derivative, the relatively low multiplicity could be due to the virtual equivalence of the phenyl protons, which would arise if the phenyl groups were freely rotating. Space-filling molecular models of this complex indicate that the phenyl rings are adequately separated from the ligand backbone (i.e., direct interaction with the pyridine $\pi$ network) to avoid the severe steric problems which arise for the other derivatives.

Temperature dependent pmr studies (202 - 317 K) were performed on two of the complexes and data are tabulated in Table IV. Variation of the temperature for the $R = \text{C(CH}_3)_3$ compound did not produce any change in spectrum multiplicity and a $\Delta \nu$ vs. $T$ plot of the -27.0 ppm (RT) signal was found to be linear (see Figure 10) and thus Curie in behavior, ($\chi = \frac{1}{T}$), having increasing shifts from TMS with decreasing temperature. In contrast, a similar plot of the -27.5 ppm (RT) signal for the $R = \text{NHCH}_3$ compound deviated from a Curie pattern, exhibiting decreasing shifts from TMS with decreasing temperature. This behavior is consistent with the expected non-Curie behavior accompanying the $^2\text{E} \xrightarrow{\delta} ^4\text{T}$ process, in which the $^4\text{T}$ state population is steadily decreased with decreasing temperature. This behavior has previously been noted for Fe(II) spin equilibrium complexes$^{51}$ and these results further verify and characterize the spin equilibrium nature of the $R = \text{NHCH}_3$ derivative in solution.
**TABLE IV**

Variable Temperature PMR Shift Data for One Resonance in the High-Spin $R = C(CH_3)_3$ and in the Spin Equilibrium $R = NHCH_3$ Cobalt(II) Complexes.*

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$\Delta \nu$, $R = C(CH_3)_3$</th>
<th>$\Delta \nu$, $R = NHCH_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>316.6</td>
<td>-27.5</td>
<td>-27.0</td>
</tr>
<tr>
<td>306.1</td>
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</tr>
<tr>
<td>285.6</td>
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</tr>
<tr>
<td>280.6</td>
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<td>259.1</td>
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<td>234.6</td>
<td>-36.3</td>
<td>-12.6</td>
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<tr>
<td>219.6</td>
<td>-39.2</td>
<td>-9.1</td>
</tr>
<tr>
<td>202.6</td>
<td>-42.5</td>
<td>-6.1</td>
</tr>
</tbody>
</table>

* Saturated CD$_3$CN solutions. Position reported relative to external TMS.
FIGURE 10

Change in Signal Position with Temperature for the High-Spin \( R = \text{C}(\text{CH}_3)_3 \) and Spin Equilibrium \( R = \text{NHCH}_3 \) Cobalt(II) Complexes in CD$_3$CN.
Thermodynamic Parameters for the Spin Equilibrium Processes. The $\Delta H^o$ and $\Delta S^o$ thermodynamic parameters for the $^2E(1s) \rightarrow ^4T(hs)$ processes as calculated from their temperature dependent equilibrium constants, are shown in Table V. $K_{eq} (=[hs][ls])$ for each compound is calculated at a given temperature from the expression 
\[
\frac{\mu^2 - \mu_{ls}^2}{\mu_{hs}^2 - \mu^2}
\]
using a magnetic moment of 2.0 $\mu_B$ for the $^2E(1s)$ state and a moment of 5.2 $\mu_B$ for the $^4T(hs)$ state which are the limiting low- and high-spin values found for this series of complexes. $\Delta H^o$ is obtained from a plot of $\ln K$ vs. $1/T$, and since $\Delta G^o = -RT\ln K$, and $\Delta G^o = H^o - T\Delta S^o$, $\Delta S^o$ can be calculated. In general, the parameters obtained from the variable temperature solution magnetic measurements are judged to be the more useful for discussion purposes, since, in the solid, unpredictable lattice effects (phase changes, anion dependence, hysteresis) are known to sometimes obscure the true electronic structure within the spin crossover region; this view is further supported by the data in the table where the parameters for a given compound, as derived from solid and solution state data, usually differ to a much larger degree than those obtained in solution where only the solvent is varied.

The calculated $\Delta H^o$(solution) values in Table V range from 1.53 - 3.26 kcal mol$^{-1}$ with the major contribution to $\Delta H^o$ likely arising from the changing Co-N bond distances and energies which are known to accompany spin conversion processes. The positive $\Delta H^o$'s demonstrate the $^2E(1s)$ state to be the lower energy state in these complexes. Although no structural data, viz., variable temperature crystallography, is yet available for these or any other $^2E \leftrightarrow ^4T$ one electron interconversion ($\Delta S=1$) spin equilibrium compounds, it is reasonable that
the low-spin \( ^2E \) (\( t^{6g}e^* \)) form will possess shorter Co-N distances, and therefore greater Co-N bond strengths, than the high-spin \( ^4T \) (\( t^{5g}e^*2 \)) form. In cases where variable temperature structural data are available, as for the two \( \Delta S=2 \) Fe(II) species, \([\text{Fe}(6\text{Mepy})_3\text{tren}]^{2+7}\) and \([\text{Fe}(\text{Bipy})_2(\text{NCS})_2]^{53}\) the average Fe-N distances have been found to decrease by \( \geq 0.12\text{Å} \) upon a high-spin \( ^5T(t^{4g}e^*2) \rightarrow \) low-spin \( ^1A(t^{6g}) \) spin conversion. Similarly, for the \( \Delta S=2 \) Fe(III) complex, \([\text{Fe}(\text{Et}_2\text{dtc})_3]^{54}\) the six Fe-S bond distances have also been shown to decrease, but by only \( \sim 0.05\text{Å} \) for a partial high-spin \( ^6A(t^{3g}e^*2) \rightarrow \) low-spin \( ^2T(t^{5g}) \) spin transition process. The average Fe-donor atom bond distance in two other Fe(III) complexes, \([\text{Fe}(\text{Sal}_2\text{trien})]^+\) and \([\text{Fe}(\text{acac}_2\text{trien})]^+\), have been observed to change by about \( 0.13\text{Å} \) in a recent study of the crystal structures of several variable spin Fe(III) complexes.\(^{55}\) Thus, available data indicate that primary coordination sphere reorganization for spin equilibrium \( \Delta S=2 \) processes involve changes in the average M-ligand bond distances of \( \sim 0.05 - 0.15\text{Å} \). For the Co(II) \( \Delta S=1 \) case, the corresponding (high-spin) \( \rightarrow \) (low-spin) geometry change is predicted to be smaller, since the spin transition involves only a single, rather than a two electron, depopulation of the \( e^* \) orbital set. Of course, other factors, such as intramolecular ligand-ligand nonbonding stereochemical interactions, could serve to modify the extent of such structural alterations so that geometry changes for \( \Delta S=1 \) and \( \Delta S=2 \) processes might actually be more similar than predicted on these electronic grounds alone. Only detailed crystallographic studies on these and other variable-spin systems hold some hope of unraveling the relative importance of these electronic and stereochemical contributions to the geometry changes accompanying
\[ \text{TABLE V} \]

Thermodynamic Parameters for the Co(II) \(^2\text{E} \rightarrow \text{^4T}\) Spin Equilibrium Processes in the Solid and Solution States.

<table>
<thead>
<tr>
<th>R</th>
<th>(\Delta H^o) (kcal mol(^{-1}))(^{a,b})</th>
<th>(\Delta S^o) (eu)(^{a,b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C((\text{CH}_3))(_3) (solid)</td>
<td>1.38 ± .65</td>
<td>13.80 ± 3.24</td>
</tr>
<tr>
<td>CH((\text{CH}_3))(_2) (solid)</td>
<td>2.43 ± .20</td>
<td>8.29 ± .90</td>
</tr>
<tr>
<td>(acetone)</td>
<td>2.37 ± .10</td>
<td>8.45 ± .37</td>
</tr>
<tr>
<td>NHCH(_3) (acetone)</td>
<td>2.70 ± .06</td>
<td>6.95 ± .25</td>
</tr>
<tr>
<td>(MeOH)</td>
<td>3.26 ± .14</td>
<td>8.64 ± .53</td>
</tr>
<tr>
<td>((\text{CH}_3)CN)</td>
<td>2.61 ± .08</td>
<td>6.71 ± .29</td>
</tr>
<tr>
<td>((\text{CH}_3)NO(_2))</td>
<td>3.23 ± .35</td>
<td>8.32 ± 1.18</td>
</tr>
<tr>
<td>(\text{p-PhCH}_3) (solid)</td>
<td>0.34 ± .10</td>
<td>3.55 ± .44</td>
</tr>
<tr>
<td>(acetone)</td>
<td>2.85 ± .18</td>
<td>9.15 ± .71</td>
</tr>
<tr>
<td>(MeOH)</td>
<td>1.53 ± .10</td>
<td>3.54 ± .41</td>
</tr>
<tr>
<td>((\text{CH}_3)CN)</td>
<td>2.69 ± .06</td>
<td>10.07 ± .20</td>
</tr>
<tr>
<td>((\text{CH}_3)NO(_2))</td>
<td>2.16 ± .07</td>
<td>7.67 ± .26</td>
</tr>
<tr>
<td>(\text{CH}_2)Ph (solid)</td>
<td>0.79 ± .08</td>
<td>3.20 ± .38</td>
</tr>
<tr>
<td>((\text{CH}_3)CN)</td>
<td>2.27 ± .09</td>
<td>6.11 ± .33</td>
</tr>
</tbody>
</table>

\(^{a}\) Determined from magnetic susceptibility data (with standard deviations), assuming \(K_{eq} = \frac{[^4\text{T}]/[^2\text{E}]}{[^2\text{E}]/[^4\text{T}]}\), and \(\mu_{\text{eff}}\) (\(^4\text{T}\)) = 5.2 \(\mu_B\) and \(\mu_{\text{eff}}\) (\(^2\text{E}\)) = 2.0 \(\mu_B\) as the limiting high-spin and low-spin values, respectively.

\(^{b}\) Temperature intervals used in calculating parameters are as listed in variable temperature susceptibility data section in the Experimental.
spin conversion processes. Such studies, for the present Co(II) compounds, are presently under way in other laboratories.\(^{56}\)

Assuming that \(\Delta H^\circ\) (solution) values for these spin equilibria largely reflect the changing M-ligand bond distances and energies which accompany the spin interconversion process, it was of interest to attempt a comparison of the \(\Delta S=1\) and \(\Delta S=2\) processes by way of this parameter. Relatively few spin equilibria have yet been documented and studied in solution with the only available \(\Delta H^\circ\) (solution) values (i.e., in acetone) being for the \(1^A \rightleftharpoons 5^T\) Fe(II) species, \([\text{Fe(polypyrazolylborate)}_2]^+\) \((\Delta H^\circ = 3.9 \text{ kcal mol}^{-1})\), \(^{10}\)

\([\text{Fe(6Mepy)}(\text{py})_2\text{tren}]^{2+}\) \((\Delta H^\circ = 4.6 \text{ kcal mol}^{-1})\), \(^{7}\)

\([\text{Fe(6Mepy)}_2(\text{py})\text{tren}]^{2+}\) \((\Delta H^\circ = 2.8 \text{ kcal mol}^{-1})\), \(^{7}\)

\([\text{Fe(pyImidH)}_3]^{+2}\) \((\Delta H^\circ = 3.8 \text{ kcal mol}^{-1})\), \(^{17}\)

the \(2^T \rightleftharpoons 6^A\) Fe(III) species, \([\text{Fe(Me}_2\text{dtc)}_3]^+\) \((\Delta H^\circ = 1.6 \text{ kcal mol}^{-1})\), \(^{57}\)

\([\text{Fe(X-Sal}_2\text{trien})]^{+}\) \((\Delta H^\circ = 3.5 - 5.9 \text{ kcal mol}^{-1})\), \(^{19}\)

\([\text{Fe(acac}_2\text{trien})]^{+}\) \((\Delta H^\circ = 2.0 \text{ kcal mol}^{-1})\), \(^{20}\)

\([\text{Fe(acacCl}_2\text{trien})]^{+}\) \((\Delta H^\circ = 2.2 \text{ kcal mol}^{-1})\), \(^{20}\)

\([\text{Fe(bzac}_2\text{trien})]^{+}\) \((\Delta H^\circ = 2.5 \text{ kcal mol}^{-1})\), \(^{20}\)

\([\text{Fe(Salmeen)}_2]^+\)

\((\Delta H^\circ = 3.76 \text{ kcal mol}^{-1})\), \(^{22}\) and the present \(2^E \rightleftharpoons 4^T\) Co(II) species \((\Delta H^\circ = 2.3 - 2.9 \text{ kcal mol}^{-1})\). While the \(\Delta H^\circ\) (solution) values for the \(\Delta S=1\) Co(II) complexes fall near the low end of the range spanned by the available data, they are, however, not otherwise distinguished.

The \(\Delta S^\circ\) parameters in Table V partially reflect the electronic entropy change of spin conversion. The electronic entropy is defined as \(\Delta S^\circ_e = R \ln(g_{\text{hs}}/g_{\text{ls}})\), where \(g\) is the total degeneracy of the state (spin multiplicity times ligand field symmetry degeneracy of 3 for a \(T\) state and 2 for an \(E\) state). Thus, an entropy change of \(R \ln 3\) or \(2.13\) eu is expected for these \(2^E \rightleftharpoons 4^T\) phenomena due solely to a change in spin state. The remaining contributions to the entropy
probably arise from configurational entropy due to solvent-sphere reorganization accompanying the spin-induced geometry changes. The solvent dependency of $\Delta S^\circ$ is, therefore, not unexpected.

**Electrochemical Measurements.** Cyclic voltammograms for four of the complexes are shown in Figure 11. The half-wave potentials, peak potential separations, and current/(scan rate)$^{1/2}$ values are listed in Table VI. Each complex exhibits a two step reduction process with the first wave probably corresponding to a Co(II) $\rightarrow$ Co(I) reduction and a second more negative wave that is likely either Co(I) $\rightarrow$ Co(0) or a ligand centered reduction. For each wave $E_{1/2}$ and $i_p/V^{1/2}$ were constant for each scan rate, consistent with diffusion controlled electron transfers.

The purpose of electrochemical investigations for this series of spin equilibrium complexes was an attempt to correlate half-wave potentials to the high- and low-spin state populations. An apparent correlation has been found between the ease of reduction and the predominant spin state for a series of Fe(III)(dtc)$_3$ spin equilibrium complexes where the high-spin compounds were found to be more easily reduced than the low-spin complexes. In fact, this same trend is observed for the present Co(II) spin equilibrium complexes, where the magnetic moment (indicating the spin state population) and Co(II) $\rightarrow$ Co(I) redox potentials decrease in the order: $R = C(CH_3)_3$ (hs = 92.5%) > $R = CH(CH_3)_2$ (hs = 56.4) > $R = CH_2Ph$ (hs = 30.5%) > $R = NHCH_3$ (hs = 24.2%). However, the second reduction wave also exhibits the same trend, and since this wave represents either Co(I) $\rightarrow$ Co(0) ($3d^8 \rightarrow 3d^9$) or reduction of the ligand, and since in either case the initial spin state
FIGURE 11

Room Temperature Cyclic Voltammograms of the Cobalt(II) Complexes for $10^{-3}$ M CH$_3$CN Solutions, Containing 0.1 M TBAP (scan rate = 200 mV/sec).
**TABLE VI**

Room Temperature Voltammetric Data for the Bis(N-R-2,6-pyridinedicarboxaldimine)cobalt(II) Complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^a$ (volts)</th>
<th>Scan Rate (mV/s)</th>
<th>$i_p/V^{1/2}$ ($\times 10^4$)</th>
<th>$E_{pa}$ - $E_{pc}$ (volts)</th>
<th>$E_{pc}$ - $E_{pc/2}$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{R} = \text{C(CH}_3\text{)}_3$</td>
<td>-0.44</td>
<td>100</td>
<td>6.0</td>
<td>0.060</td>
<td>0.060</td>
</tr>
<tr>
<td>$\mu_{\text{eff}} = 5.07\mu_B$</td>
<td>-0.45</td>
<td>200</td>
<td>7.7</td>
<td>0.080</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td>-0.46</td>
<td>500</td>
<td>6.0</td>
<td>0.080</td>
<td>0.065</td>
</tr>
<tr>
<td>$\text{R} = \text{CH(CH}_3\text{)}_2$</td>
<td>-0.47</td>
<td>50</td>
<td>7.7</td>
<td>0.080</td>
<td>0.050</td>
</tr>
<tr>
<td>$\mu_{\text{eff}} = 4.15\mu_B$</td>
<td>-0.48</td>
<td>100</td>
<td>8.0</td>
<td>0.080</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>-0.47</td>
<td>200</td>
<td>6.0</td>
<td>0.090</td>
<td>0.060</td>
</tr>
<tr>
<td>$\text{R} = \text{NH(CH}_3\text{)}$</td>
<td>-0.77</td>
<td>100</td>
<td>3.0</td>
<td>0.060</td>
<td>0.060</td>
</tr>
<tr>
<td>$\mu_{\text{eff}} = 3.11\mu_B$</td>
<td>-0.75</td>
<td>200</td>
<td>3.0</td>
<td>0.055</td>
<td>0.055</td>
</tr>
<tr>
<td>$\text{R} = \text{CH}_2\text{Ph}$</td>
<td>-0.54</td>
<td>50</td>
<td>5.6</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>$\mu_{\text{eff}} = 3.34\mu_B$</td>
<td>-0.55</td>
<td>100</td>
<td>5.0</td>
<td>0.060</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>-0.55</td>
<td>200</td>
<td>5.6</td>
<td>0.065</td>
<td>0.055</td>
</tr>
</tbody>
</table>

**TABLE VI** (continued)
### TABLE VI (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ a (volts)</th>
<th>Scan Rate (mV/s)</th>
<th>$i_p/v^{1/2}$ ($\times 10^4$)</th>
<th>$E_{p_a} - E_{p_c}$ (volts)</th>
<th>$E_{p_c} - E_{p_c/2}$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = C(CH$_3$)$_3$</td>
<td>-1.32</td>
<td>100</td>
<td>8.0</td>
<td>.065</td>
<td>.060</td>
</tr>
<tr>
<td></td>
<td>-1.32</td>
<td>200</td>
<td>8.0</td>
<td>.080</td>
<td>.065</td>
</tr>
<tr>
<td></td>
<td>-1.31</td>
<td>500</td>
<td>7.0</td>
<td>.075</td>
<td>.060</td>
</tr>
<tr>
<td>R = CH(CH$_3$)$_2$</td>
<td>-1.45</td>
<td>100</td>
<td>7.5</td>
<td>.070</td>
<td>.060</td>
</tr>
<tr>
<td></td>
<td>-1.46</td>
<td>200</td>
<td>7.1</td>
<td>.080</td>
<td>.065</td>
</tr>
<tr>
<td>R = NHCH$_3$</td>
<td>-1.68 b</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R = CH$_2$Ph</td>
<td>-1.47</td>
<td>100</td>
<td>6.0</td>
<td>.070</td>
<td>.065</td>
</tr>
<tr>
<td></td>
<td>-1.47</td>
<td>200</td>
<td>5.6</td>
<td>.060</td>
<td>.060</td>
</tr>
</tbody>
</table>

a $E_{1/2}$'s were obtained in CH$_3$CN solutions, 0.1 M in TBAP, at platinum button electrodes. Potentials are referenced to SCE and uncorrected for junction potential.

b $E_{p_c}$ value, since no oxidation wave was observed.
is invariant, i.e., $t_{2g}^{6}e_{g}^{2}$, this strongly indicates that the spin state is not a primary influence on the redox potentials. In a study of various metals with dithiocarbamate ligands [Cr(III), Mn(III), Co(III), Ni(II), and Cu(II)], all the complexes exhibit a trend of oxidation potential that is substituent dependent, which implies that geometric factors are more important in influencing the half-wave potentials than spin state. It may be that the only effect that variable spin state could have in these systems is on the electron transfer rates. It is possible that only one spin state is selectively oxidized or reduced for spin equilibrium compounds, or that the transition state prior to electron transfer is invariant regardless of the dominating spin state. Indeed, the rapid rate of spin interconversion for these Co(II) complexes (vide infra) would probably allow the electron transfer to occur only at the species possessing the energetically favorable spin state.

In any case, the true test for spin state-redox potential correlation is the electrochemical measurement of a spin equilibrium compound at high and low temperatures, so that only one variable exists: the electronic state of the metal. With our present techniques it is possible only to report the electrochemical data for these complexes and to note the relationship between R group substituent and half-wave potential.

**Measurement of the $^2E$ and $^4T$ Spin State Lifetimes.** The uv-visible electronic absorption spectra for the complexes are shown in Figure 12. The $R = CH(CH_3)_2$, $CH_2Ph$, and $NHCH_3$ exhibit temperature dependent spectra in MeOH. The $R = p-PhCH_3$ and $C(CH_3)_3$ derivatives display very
FIGURE 12

UV-Visible Electronic Absorption Spectra of the Complexes at $10^{-5}$M in CH$_3$OH.

a) $R = C(CH_3)_3$; room temperature spectrum shown. This spectrum exhibits no discernable changes in intensity with decreasing temperature.

b) $R = CH(CH_3)_2$; variable temperature spectrum of the complex showing the band intensity increasing with decreasing temperature.

c) $R = NHCH_3$; variable temperature spectrum of the complex showing the band intensity increasing with decreasing temperature.

d) $R = p$-PhCH$_3$; room temperature spectrum shown. This spectrum exhibits no discernable changes in intensity with decreasing temperature.

e) $R = CH_2$Ph; variable temperature spectrum of the complex showing the band intensity increasing with decreasing temperature.
a) $R = C(CH_3)_3$
b) \( R = \text{CH}(\text{CH}_3)_2 \)

\[ \epsilon \times 10^{-3}, \text{ M}^{-1} \text{ cm}^{-1} \]

\[ \lambda, \text{ nm} \]
c) $R = NHCH_3$
d) \( R = \text{--} \text{CH}_3 \)
\[ e \times 10^{-3}, \text{M}^{-1} \text{cm}^{-1} \]

\[ \lambda, \text{nm} \]

\[ e = \text{CH}_2-\bigcirc \]

\[ T = -39^\circ \text{C} \]

\[ T = 0.0^\circ \text{C} \]

\[ T = 19^\circ \text{C} \]
slight band sharpening only at lower temperatures and so the low
temperature spectra of these two compounds have been omitted from the
figure. The spectral changes with temperature for these spin
equilibrium processes in solution are much less dramatic than that
displayed by some recently reported variable spin Fe(II)\textsuperscript{7,8,12,17,41}
and Fe(III)\textsuperscript{19,20,22} systems and are more reminiscent of the small
temperature effects observed in the spectrum of the \( ^2T \rightleftharpoons ^6A \)
tris(dithiocarbamato)iron(III) complexes.\textsuperscript{65} For this reason the
Fe(dtc)\textsubscript{3}'s and present Co(II) complexes do not exhibit the marked
thermochromism often found to be characteristic of the spin equilibrium
phenomenon.\textsuperscript{7,19} Nevertheless, for these cobalt complexes the origin
of the spectral change with temperature is attributed to changing
low-spin and high-spin populations (see Figure 7), although some of the
observed temperature dependency may simply be due to band sharpening at
low temperatures, since all the complexes appear to display this
tendency. Judging from the band intensities (see Figure 12), all the
bands are of metal → ligand charge transfer in origin, and a careful
search at lower energies revealed no low intensity bands of purely
"d → d" character.

To measure the kinetics of a \( ^2E \xrightleftharpoons[k_1]{k_-1} ^4T \) intersystem crossing
process, the \( R = \text{NHCH}_3 \) compound was chosen as a representative
species and the laser Raman temperature jump technique, developed at
Brookhaven, was employed.\textsuperscript{13} The instrumentation and data collection
are described in the Experimental Section. The solvent medium chosen
for the study was CH\textsubscript{3}CN/CH\textsubscript{3}OH (1:4 by volume) with CH\textsubscript{3}CN being used to
facilitate compound solubility and CH\textsubscript{3}OH to produce effective
stimulated Raman heating of the sample solution. A typical relaxation
curve for the \( R = \text{NHCH}_3 \) compound at 25°C, as monitored at 400 nm, is shown in Figure 13 from which the first-order relaxation time, \( \tau \), has been found to be 83 ± 23 nsec (see Experimental Section).

In order to verify that the observed spectral change corresponded to the spin state change and thus to the observed relaxation trace of Figure 13, the exclusively high-spin \( R = \text{C(CH}_3)_3 \) compound was also examined at several wavelengths by the laser experiment. No relaxation curve was obtained for this derivative, whereas the \( R = \text{NHCH}_3 \) derivative, which is a spin equilibrium species in solution, yielded a relaxation trace. This result strongly implies that the absorbance changes observed in the temperature-jump experiment for the \( R = \text{NHCH}_3 \) compound are indeed spin equilibrium in origin and are due to the intramolecular spin interconversion process between the \( ^2E(1s) \) and \( ^4T(\text{hs}) \) energy levels.

Therefore, the observed relaxation trace in Figure 13 has been analyzed in terms of a first-order exponential time dependence for a \( ^2E \leftrightarrow ^4T \) spin interconversion process. The low signal intensity in Figure 13 is undoubtedly a combined result of the fact that \( \Delta H^0 \) is relatively small (\(-3 \text{ kcal mol}^{-1}\) for this spin interconversion process and that the electronic spectral changes with temperature are also small.

Forward and reverse rate constants, \( k_1 \) and \( k_{-1} \), for the \( \Delta S=1 \)

\[
^2E(1s) \xrightarrow{k_1} \xleftarrow{k_{-1}} ^4T(\text{hs})
\]

spin interconversion process are shown in Table VII, along with similar results which have been reported for several \( \Delta S=2 \) iron processes.
FIGURE 13

Laser Raman Temperature-Jump Relaxation Trace Obtained for the $R = \text{NHCH}_3$
Derivative in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ Solution at $25^\circ\text{C}$; $[\text{complex}] = 10^{-3}$ M.
<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>( K_{eq} )</th>
<th>( \tau ), nsec</th>
<th>( k_1 ), s(^{-1}) ([\tau(s), s])</th>
<th>( k_{-1} ), s(^{-1}) ([\tau(hs), s])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II) ([d^7, 2E \rightleftharpoons ^4T, \Delta S=1])</td>
<td>CH(_3)CN/MeOH ((25^\circ C))</td>
<td>0.35</td>
<td>83(23)</td>
<td>(3.2 \times 10^6)</td>
<td>(9.1 \times 10^6)</td>
</tr>
<tr>
<td><a href="PF(_6)">Co(N-R-2,6-pyAld)(_2)</a>(_2) ((H))</td>
<td>CH(_3)CN/MeOH ((25^\circ C))</td>
<td>0.35</td>
<td>83(23)</td>
<td>(3.1 \times 10^{-7})</td>
<td>(1.1 \times 10^{-7})</td>
</tr>
<tr>
<td><a href="PF(_6)">Co(terpy)(_2)</a>(_2) ((I))</td>
<td>MeOH ((20^\circ C))</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(II) ([d^6, 1A \rightleftharpoons ^5T, \Delta S=2])</td>
<td>MeOH/CH(_2)Cl(_2) ((21^\circ C))</td>
<td>0.47</td>
<td>32(10)</td>
<td>(1 \times 10^7)</td>
<td>(2 \times 10^7)</td>
</tr>
<tr>
<td>[Fe(hydrotris(1-pyrazolyl)borate)(_2)] ((G))</td>
<td>MeOH/CH(_2)Cl(_2) ((21^\circ C))</td>
<td>0.47</td>
<td>32(10)</td>
<td>(1 \times 10^7)</td>
<td>(2 \times 10^7)</td>
</tr>
<tr>
<td><a href="BPh(_4)">Fe(pyImidH)(_3)</a>(_2) ((F))</td>
<td>20% CH(_3)CN/MeOH ((23^\circ C))</td>
<td>1.06</td>
<td>48(8)</td>
<td>(1.1 \times 10^7)</td>
<td>(1.0 \times 10^7)</td>
</tr>
<tr>
<td><a href="PF(_6)">Fe(6-Mepy)(py)tren</a>(_2) ((E))</td>
<td>MeOH, 10% acetone/ H(_2)O ((20^\circ C))</td>
<td>0.05</td>
<td>120(20)</td>
<td>(4 \times 10^5)</td>
<td>(8 \times 10^6)</td>
</tr>
<tr>
<td>System</td>
<td>Conditions</td>
<td>( K_{eq} )</td>
<td>( \tau, \text{nsec} )</td>
<td>( k_1, \text{s}^{-1} ) [( \tau(s), \text{s} )]</td>
<td>( k_{-1}, \text{s}^{-1} ) [( \tau(\text{hs}), \text{s} )]</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>-------------------</td>
<td>---------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Fe(III) ([d^5, 2T \rightleftarrows 6A, \Delta S=2])</td>
<td>MeOH (20°C)</td>
<td>1.03</td>
<td>35(8)</td>
<td>( 1.5 \times 10^7 )</td>
<td>( 1.4 \times 10^7 )</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Fe(Sal₂trien)</a> (B)</td>
<td>MeOH (20°C)</td>
<td>1.31</td>
<td>9</td>
<td>( 7.1 \times 10^7 )</td>
<td>( 5.4 \times 10^7 )</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Fe(Salmeen)₂</a> (C)</td>
<td>MeOH (20°C)</td>
<td>1.03</td>
<td>9</td>
<td>( 1.4 \times 10^8 )</td>
<td>( 1.8 \times 10^8 )</td>
</tr>
<tr>
<td>[Fe(Me₂dtc)₃] (D)</td>
<td>MeOH (20°C)</td>
<td>0.80</td>
<td>&lt;30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Fe(acac₂trien)</a> (A)</td>
<td>10% Acetone/MeOH</td>
<td>2.26</td>
<td>45(10)</td>
<td>( 1.5 \times 10^7 )</td>
<td>( 6.9 \times 10^6 )</td>
</tr>
</tbody>
</table>

[6.7 \times 10^{-8}] [7.1 \times 10^{-8}] [1.4 \times 10^{-8}] [1.8 \times 10^{-8}]
Also shown in the table are the corresponding spin state lifetimes where $\tau(1s) = (k_1)^{-1}$ and $\tau(hs) = (k_{-1})^{-1}$. Figure 14 shows the structural features of the complexes for which rate data is reported in the table. Considering the diverse collection of metal ion electronic structures and ligand types found in the table, the measurable spin state lifetimes span a surprisingly narrow range of $2.5 \times 10^{-6}$ to $9.1 \times 10^{-8}$ sec. Attempts to measure spin interconversion rates for other systems, such as $[\text{Co(terpy)}_2]^{+2}$ (I) and $[\text{Fe(III)(Me}_2\text{dtc})_3]^{0}$ (D) have not been successful because the relaxation times of less than 30 nsec appear shorter than the duration of the laser pulse ($\sim 25 - 30$ nsec), although a "second method of moments" integral deconvolution procedure has been used successfully in a few cases to obtain $\tau$'s $< 30$ nsec.\textsuperscript{42,68,69} More recently, ultrasonic relaxation studies have been used to determine $\tau$'s as short as 20 nsec for some $\Delta S=2$ iron spin equilibrium cases.\textsuperscript{14,70}

For these octahedral complexes the spin interconversions are of three electronic types: iron(III), $d^5$, $2^T \leftrightarrow 6^A$, $\Delta S=2$; iron(II), $d^6$, $1^A \leftrightarrow 5^T$, $\Delta S=2$; and cobalt(II), $d^7$, $2^E \leftrightarrow 4^T$, $\Delta S=1$. Thus, spin interconversion in the cobalt systems would be expected to be less "spin forbidden" than the iron cases. Another important electronic factor is the potential for term mixing through spin-orbit coupling. For the iron(II) case no spin-orbit coupling between the high-spin $5^T$ and low-spin $1^A$ terms can occur. This is also true for the iron(III) $6^A(\text{hs})$ and $2^T(1s)$ terms, but here, when a spin equilibrium situation exists, a low lying $4^T$ state can mix with both the $6^A(\text{hs})$ and $2^T(1s)$ state separately, thus providing an indirect mechanism for mixing. In the cobalt(II) compounds the high-spin $4^T$ state can readily mix with the
FIGURE 14

Structures of the Iron(III) ($d^5$), Iron(II) ($d^6$) and Cobalt(II) ($d^7$) Spin-Equilibrium Metal Complexes.

(A) $[\text{Fe(III)}(\text{acac}_2\text{trien})]^+$ \hspace{1cm} R = \text{CH}_3; \hspace{0.2cm} X = \text{H}

$[\text{Fe(III)}(\text{benzac}_2\text{trien})]^+$ \hspace{0.5cm} R = \text{Ph}; \hspace{0.2cm} X = \text{H}

(B) $[\text{Fe(III)}(\text{X-Sal}_2\text{trien})]^+$ \hspace{0.5cm} X = \text{H}, \text{NO}_2, \text{OCH}_3

(C) $[\text{Fe(III)}(\text{X-Salmeen})_2]^+$ \hspace{0.5cm} X = \text{H}, \text{NO}_2, \text{OCH}_3

(D) $[\text{Fe(III)}(\text{Me}_2\text{dtc})_3]$

(E) $[\text{Fe(II)}(\text{6-Mepy})_n(\text{py})_m\text{tren}]^{2+}$ \hspace{0.2cm} (n = 0,1,2,3; \hspace{0.2cm} m = 3 - n)

(F) $[\text{Fe(II)}(\text{pyImidH})_3]^{2+}$

(G) $[\text{Co(II)}(\text{hydrotris(1-pyrazolyl)borate})_2]$

(H) $[\text{Co(II)}(\text{N-NH(CH}_3)_2-2,6\text{-pyAld})_2]^{2+}$

(I) $[\text{Co(II)}(\text{terpy})_2]^{2+}$
low-spin $^{2}\text{E}$ state. On this basis alone the cobalt(II) complexes might be expected to undergo a more rapid spin interconversion than an analogous iron(II) or iron(III) complex. Furthermore, Co(II) $\Delta S=1$ processes are expected to exhibit smaller coordination sphere reorganization (*vide supra*), and this difference could be manifested in larger $k$ values and shorter $\tau^{(\text{spin state})}'s$ than for any $\Delta S=2$ iron(II) or iron(III) system. However, this is apparently not the case for the present Co(II) $R = \text{NHCH}_3$ (H) derivative, although it may be true for the [Co(terpy)$_2$]$^{2+}$ complex (I). In fact, spin interconversion rates for the $R = \text{NHCH}_3$ $\Delta S=1$ process are among the slowest of the $\Delta S=1$ and $\Delta S=2$ processes listed in Table VII.

In view of these findings, it must be concluded that $\Delta S=1$ vs. $\Delta S=2$ electronic considerations alone are not adequate to explain the existing spin interconversion rate constant data in Table VII. Obviously, nonelectronic factors significantly affect the rates of spin multiplicity changes since, in fact, the largest variation of $\tau$ exists among groups of Fe(II) or Fe(III) complexes. Intraligand steric repulsions are known to be of importance in producing the spin equilibrium phenomenon within the [Fe(6-Mepy)$_m$(py)$_n$tren]$^{1+2}$ series (E)$_7$.$^8$ As an example of the steric effects on the interconversion rate, it is interesting to compare the hexadentate [Fe(Sal$_2$trien)]$^+$ (B) having a $\tau$ of $6.7 \times 10^{-8}$ sec, with a sister compound, the bis-tridentate [Fe(salmeen)$_2$]$^{1+2}$ (C) exhibiting a relaxation trace of less than 30 nsec, which yields a lifetime of $1.4 \times 10^{-8}$ sec by the "method of moments" technique.$^{22}$ The ligand in (C) possesses greater coordinative flexibility, posing fewer geometrical restrictions to spin interconversion than (B). By contrast, crystal structures for several
[Fe(R2dtc)3] complexes (like D)54 and the Co(II) analog of [Fe(hydrotris(1-pyrazolyl)borate)2] (G)71 indicate that intramolecular steric interactions between ligands are not of much significance in determining their characteristic spin state behavior.

It is apparent from the data in Table VII that there is no obvious correlation between metal ion oxidation state and the rate of spin interconversion. The data accumulated on this family of bis(N-N-2,6-pyridinedicarboxylimine)Cobalt(II) complexes indicate that geometrical restraints, mainly intraligand steric repulsions, must be the critical rate determiners in these processes. For example, if the rate determining step in the spin interconversion process involves a primary coordination sphere and secondary solvent sphere reorganization as a prerequisite to the spin transition itself, ΔS=1 and ΔS=2 events could appear kinetically indistinguishable for similar reorganizational processes and [Rate(spín transition)] ≫ [Rate(reorganization)].72 If this interpretation is correct, it might be possible to significantly modify spin interconversion rates and lifetimes by appropriate ligand design or solvent selection. In this manner spin conversion rates might be sufficiently retarded so as to become competitive with fast out-sphere electron exchange reactions, such as for the [Fe(6Mepy)2(py)tren]+2 - [Fe(6Mepy)2(py)tren]+3 or [Fe(bipy)3]+2 - [Fe(bipy)3]+3 couples where $k_{\text{exchange}}$ is likely to be $\geq 10^5$ sec$^{-1}$.73 But, for the present, all available data suggest that intermolecular electron transfer rates will not be determined by intramolecular spin conversion processes in those cases where both events occur.74
REFERENCES AND NOTES


56. Private communication with E. Sinn, University of Virginia.
57. Unpublished results.


63. A recent report provides an explanation for anomalously slow C\textsubscript{2}O \textsubscript{2} \rightarrow Co(III) reaction rates by considering that the oxidation occurs via the C\textsubscript{2}E (low-spin) state of the Co(II) species. See: T. Strekas and G. Schonbuch, Inorg. Nucl. Chem. Lett., 14, 235 (1978).

64. Variable temperature studies on series of spin equilibrium complexes are underway in collaboration with K. M. Kadish and L. A. Bottomley, University of Houston.


67. See Reference 12, footnote 9.


PART II

MODELING THE ACTIVE SITE IN HEMOCYANIN: A SYNTHETIC COPPER(I) COMPLEX HAVING IMIDAZOLE LIGANDS AND EXHIBITING REVERSIBLE REACTIVITY WITH MOLECULAR OXYGEN
INTRODUCTION

Among the O₂-transport proteins, iron and copper are the only transition metals known to be at the O₂ carrying active site. Without direct evidence of the structure of the active sites by X-ray crystallographic techniques, the nature of the O₂-transport center is unclear. Synthetic mimics of the proteins provide one of the best available methods to date for inferring the active site structure. The structures of hemoglobin and myoglobin, the O₂-transport and storage proteins which are widely distributed in nature, have been the subject of intensive study for decades.¹ Both the nature of the Fe-O₂ bond and the stereochemistry of the Fe(heme)-O₂ center have been reasonably well documented by X-ray crystallography²,³ and magnetochemical⁴ measurements, as well as epr,⁵ ORD-CD⁶ and Mössbauer⁷ spectroscopic studies. Other O₂-transport proteins have not been as exhaustively studied, and only incomplete information is available. Erythrocrucouin and chlorocruorin are large heme-containing proteins existing extracellularly in the blood of annelid worms.⁸ Hemerythrin⁹ and hemo- cyanin¹⁰ contain no heme groups despite their names, and are the respiratory proteins of primitive organisms such as mollusks and arthropods. These proteins are seemingly less efficient O₂ carriers than their heme containing counterparts in that they require two (rather than one) metal centers per O₂ in their transport function. Lastly, hemovanadium,¹¹ suspected to be the respiratory enzyme in sea squirts, has recently been studied with renewed interest although the protein itself has yet to be isolated and identified. Table I summarizes some of the information about the known O₂-transport proteins.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Protein</th>
<th>Functional Group</th>
<th>Enzymatic Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Hemoglobin</td>
<td>Heme</td>
<td>$O_2$-transport</td>
</tr>
<tr>
<td></td>
<td>(M.W. $6.7 \times 10^4$)</td>
<td></td>
<td>$1Fe / O_2$</td>
</tr>
<tr>
<td></td>
<td>contained in cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Myoglobin</td>
<td>Heme</td>
<td>$O_2$ storage</td>
</tr>
<tr>
<td></td>
<td>(M.W. $1.7 \times 10^5$)</td>
<td></td>
<td>$1Fe / O_2$</td>
</tr>
<tr>
<td></td>
<td>extracellular</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Erythrocruorin</td>
<td>Heme</td>
<td>$O_2$-transport</td>
</tr>
<tr>
<td></td>
<td>(M.W. $3.1 \times 10^6$)</td>
<td></td>
<td>$1Fe / O_2$</td>
</tr>
<tr>
<td></td>
<td>extracellular</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chlorocruorin</td>
<td>Heme</td>
<td>$O_2$-transport</td>
</tr>
<tr>
<td></td>
<td>(M.W. $2.7 \times 10^6$)</td>
<td></td>
<td>$1Fe / O_2$</td>
</tr>
<tr>
<td></td>
<td>extracellular</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hemerythrin</td>
<td>unknown</td>
<td>$O_2$-transport</td>
</tr>
<tr>
<td></td>
<td>(M.W. $1 \times 10^5$)</td>
<td>coordination</td>
<td>$2Fe / O_2$</td>
</tr>
<tr>
<td></td>
<td>contained in cells</td>
<td>environment</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Hemocyanin</td>
<td>unknown</td>
<td>$O_2$-transport</td>
</tr>
<tr>
<td></td>
<td>(M.W. $9 \times 10^6$)</td>
<td>coordination</td>
<td>$2Cu / O_2$</td>
</tr>
<tr>
<td></td>
<td>extracellular</td>
<td>environment</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Hemovanadium</td>
<td>unknown</td>
<td>$O_2$-transport</td>
</tr>
<tr>
<td></td>
<td>(M.W. $2.4 \times 10^5$)</td>
<td>coordination</td>
<td>$O_2$?</td>
</tr>
<tr>
<td></td>
<td></td>
<td>environment</td>
<td></td>
</tr>
</tbody>
</table>
While there is little direct structural information about the metal atom active site in these proteins, there is considerable indirect evidence from ORD-CD, esr, and resonance Raman spectroscopic measurements suggesting possible active site structures. The ultimate goal of such experiments is to elucidate the composition of the primary coordination sphere about the metal center in the protein and, thus, to learn more about the ligand requirements for the \( \text{O}_2 \)-transport center.

The alternative to directly determining active site structure in large proteins is the synthesis of small molecules which act as functional mimics of the protein. Collman's elegant "picket fence" porphyrin model for the iron center in myoglobin and hemoglobin represents the most notable achievement to date of this approach.\(^{12}\) However, for non-heme \( \text{O}_2 \)-transport proteins like hemerythrin and hemocyanin where it has not yet been possible to draw analogies to well understood protein structures, the modeling approach is even more challenging. Of the non-heme proteins, hemocyanin is particularly interesting and unique in that it is the only copper containing respiratory enzyme.

Hemocyanin is found in only two animal phyla, mollusks and arthropods. It is one of hundreds of physiologically important copper containing proteins but it is unlike the majority of these proteins since most of them exhibit electron transport or various catalytic functions.\(^{13}\) Hemocyanin (Hc) is of variable size and composition, depending on the species from which it was isolated. The most common sources of Hc for biochemical studies and a summary of most of the known properties of the protein are listed in Table II. The largest of the hemocyanins is derived from *Helix pomatia*, and has a molecular weight
**TABLE II**

Hemocyanin.

The Oxygen Carrying Protein in the Blood
of Some Molluscs and Arthropods.

<table>
<thead>
<tr>
<th>Prevalent Sources</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Helix pomatia (snail)</td>
<td>M.W. = 8.9 \times 10^6</td>
</tr>
<tr>
<td>Busycon canaliculatum (whelk)</td>
<td>M.W. = 6.8 \times 10^6</td>
</tr>
<tr>
<td>Cancer Magister (crab)</td>
<td>M.W. = 0.95 \times 10^6</td>
</tr>
</tbody>
</table>

**Properties**

<table>
<thead>
<tr>
<th>Deoxyhemocyanin</th>
<th>Oxyhemocyanin</th>
</tr>
</thead>
<tbody>
<tr>
<td>No esr signal</td>
<td>No esr signal</td>
</tr>
<tr>
<td>No visible absorption spectrum</td>
<td>Visible absorption spectrum characteristic of Cu(II)</td>
</tr>
<tr>
<td>Protein reconstitution occurs only with Cu(I)</td>
<td>Oxygen uptake corresponds to 2Cu/O_2. O_2 is in the form of a peroxide.</td>
</tr>
</tbody>
</table>

**Copper Environment**

The number and type of ligands around the copper have not been definitely identified, but sulfur has been ruled out by spectrophotometric and titrimetric methods.

The imidazole of a histidine residue has been postulated as a likely ligand.
of $9 \times 10^6$, containing about 300 coppers. The large size of these proteins partly accounts for the difficulty of crystallizing Hc, and explains why no crystal structure data are yet available. The huge size of Hc may be related to $O_2$-transport efficiency, since the protein backbone serves to protect the Cu(I) center of deoxy-Hc from irreversible oxidation by $O_2$ to Cu(II) during the reversible oxygenation processes. The protein is known to function in a similar manner in hemoglobin, where the Fe(II) center is likewise protected in a hydrophobic "pocket."  

The $O_2$ uptake stoichiometry in hemocyanin (yielding oxy-Hc) corresponds to two coppers per $O_2$ molecule, a ratio which suggests that the oxygenated active site is binuclear, as shown in Figure 1. Neither deoxy-Hc nor oxy-Hc exhibit an esr signal, i.e., both forms are diamagnetic. Since Cu(II) is known to exist in oxy-Hc, this result was initially surprising but led to the suggestion of an antiferromagnetically coupled binuclear unit, formally $[Cu^{2+} - O_2^{-2} - Cu^{2+}]$, as the form of the oxygen adduct in the protein. Magnetic measurements have since verified the presence of antiferromagnetic exchange in oxy-Hc, with $-J \geq 625 \text{ cm}^{-1}$. 

Reactions of hemocyanin with a variety of small molecules have been studied in order to understand the binding site structure, but these studies have not yet yielded definitive information. Hemocyanin reacts with CO, in a ratio of 2Cu:1CO, but the nature of the binding unit is not well understood. Adducts of Hc with NO, cyanide, and thiocyanate have also been reported.

There are no heme groups in hemocyanin, thus the copper is bound directly to the protein. The formal oxidation state of the copper in
A proposed model for hemocyanin
oxy- and deoxy-Hc was not established until recently. A 1978 EXAFS study\textsuperscript{22} has determined that all the copper in deoxy-Hc is in the +1 oxidation state. This substantiates early experiments which indicated that the apoprotein can be reconstituted only with Cu(I)\textsuperscript{24}. The EXAFS experiments further showed that all the copper in the light blue oxy-Hc is in the +2 oxidation state. This finding is in agreement with the absorption spectrum of oxy-Hc, which displays a visible band characteristic of Cu(II), with $\varepsilon_{570\text{nm}} = 500 \text{ M}^{-1} \text{ cm}^{-1}\textsuperscript{25}$.

Attempts at identifying the copper ligands in hemocyanin began in early studies. Because of the similarities between the absorption spectra of Hc and known sulfur containing proteins, sulfur was proposed as a likely ligand as early as 1955\textsuperscript{26}. However, this suggestion has now been discarded on the basis of numerous studies designed to prove that sulfur is not a donor atom in hemocyanin. In particular, the EXAFS experiments have established unequivocally that sulfur is absent. Instead, the EXAFS study indicated that copper is ligated by 4-5 nitrogen and/or oxygen atoms. Unfortunately, the study yielded no data on the specific type of donor atom or on the coordination geometry.

Hemocyanin has ample sources for oxygen and nitrogen donor atoms. Oxygen donors would be readily available from the carboxyl functions of the protein or from tyrosine residues, and nitrogen donors would be available from lysine, arginine, tryptophan\textsuperscript{10h} or histidine residues.\textsuperscript{10a} The imidazole from histidine residues is a particularly attractive ligand because imidazole appears to be ubiquitously distributed in proteins,\textsuperscript{28,29} and because of the significant number of histidine residues in Hc.\textsuperscript{10a} The presence of at least two imidazoles per copper in Hc has been suggested by a resonance Raman study.\textsuperscript{30} In 1974,
Ghiretti$^{31}$ reported results of potentiometric and spectrophotometric studies which indicated that the copper is bound to four non-carboxyl and probably imidazole groups. Despite extensive efforts, however, research on this protein has not yet elucidated the detailed structure of the copper center in hemocyanin.

A Cu(I) model for hemocyanin behavior has eluded chemists for 30 years. Appropriate hemocyanin models are difficult to generate due to the paucity of information on Cu(I) chemistry, particularly Cu(I) complexes with nitrogen ligands.$^{32}$ Air sensitivity and kinetic lability of Cu(I) compounds have exacerbated the problem. This contrasts markedly with the existence of several well-characterized synthetic systems with other metals such as iron and cobalt.$^{33}$

There have been only a few reports of Cu(I) complexes forming adducts with small molecules such as CO or O$_2$. Of these, only the Cu(I)–CO compounds have been satisfactorily documented. There are only five known compounds of this type,$^{34,35}$ and only three of these contain nitrogen donor atoms.$^{36-38}$ The existence of copper complexes which apparently exhibit reversible reactivity with O$_2$ has, to date, been poorly substantiated in the literature. In 1964, a [Cu(I)(cysteine)] complex was reported to add O$_2$ reversibly, but the species was inadequately characterized.$^{39}$ In 1973, a binuclear species was isolated from Cu(II) acetate which was formulated as a μ-peroxo bridged species.$^{40}$ In 1974, Ibers reported the apparent reaction of O$_2$ with {Bis[hydrotris(1-pyrazolyl)borato]}copper(I) yielding a product corresponding to a reaction stoichiometry of 2Cu:1O$_2$.$^{41}$ In 1975, a Cu(I) compound with pyridine ligands forming a binuclear peroxo-bridged species was reported.$^{42}$ A report of a reversible Cu(I)–O$_2$
adduct appeared in the literature in 1977 where a [NOS₂] donor set was chosen as a reasonable model for the copper environment in hemocyanin. Only solid state reactivity was reported, however, and products were identified by esr spectroscopy, with no information being given about the Cu:O₂ stoichiometry. In addition, color changes were interpreted as indicating O₂ reversibility, but such criteria are unreliable, as shown for one of the first "reversible" O₂ carriers of iron.

The initial objective of this work was to synthesize an O₂ carrying Cu(I) complex with the expectation that it would serve where other models have failed to reasonably mimic the active site in hemocyanin. Since overwhelming evidence points to imidazole as a ligand in hemocyanin, a "good" model demanded imidazole-containing ligands. It was anticipated that imidazole, which is both a moderate σ donor and a moderate π acceptor, would stabilize Cu in both the +1 and +2 oxidation states. One necessary feature of reversible O₂ carriers appears to be facile and reversible metal centered oxidation/reduction. Therefore, if the first step of an oxygenation reaction for Cu(I) is formally viewed as an oxidative addition reaction,

\[ \text{Cu(I)} + \text{O}_2 \rightarrow \text{Cu(II)} - \text{O}_2^- \]

then the reaction must be readily reversed,

\[ \text{Cu(II)} - \text{O}_2^- \rightarrow \text{Cu(I)} + \text{O}_2 \]

if the system is to function as an O₂ carrier. An appropriate ligand donor set and a coordination geometry stabilizing both states are thus required. Cu(I) would be stabilized by any ligands capable of extensive metal – ligand π back-bonding which would provide a mechanism
for delocalization of electron density for the electron rich Cu(I) center. Generally, imine nitrogen donor atoms provide excellent \( \pi \) back-bonding capability.\(^{45}\) Various imine ligands would then be expected to form stable Cu(I) compounds. Such donors are also well known to stabilize Cu(II).\(^{46}\) Had sulfur donor atoms been found to exist in hemocyanin, they would have served as excellent choices for Cu(I) donor atoms in model compounds since they also fulfill \( \pi \) back-bonding requirements.

The coordination geometry is the second consideration in construction of a model compound. For example, inflexible square planar macrocyclic ligands are known to stabilize Cu(II), yet they significantly destabilize Cu(I).\(^{47}\) Therefore, a flexible, imine-containing multidentate ligand was reasoned to be an appropriate choice for stabilizing both Cu(I) and Cu(II). Moreover, such a ligand would have a greater likelihood of incorporating some of the proposed geometrical features of the copper in hemocyanin.\(^{48}\) A multidentate species would provide a well defined coordination environment for the metal, obviating the problems of ligand exchange known to occur in Cu(I) compounds. In addition, a high degree of coordinative flexibility is surely required for a facile Cu(I) \( \Leftrightarrow \) Cu(II) interconversion and this could be provided by an appropriate multidentate ligand.

Our search for a model of the active site in hemocyanin has yielded the Cu(I) species shown in Figure 2A, the \{Bis-2,6\[1-(2-imidazol-4-ylethylimino)ethyl\]pyridine)copper(I) cation (hereafter [Cu(I)(imidH)\(_2\)DAP\(^+\)]. The parent compound has been characterized as a novel five coordinate species which exhibits reversible \( \text{O}_2 \) binding in solution with a reaction stoichiometry of \( 2 \text{Cu} : \text{O}_2 \). To our knowledge,
A. The \{\text{Bis-2,6}[1-(2\text{-imidazol-4-ylethylimino})\text{ethyl}]\text{pyridine}}\text{copper(1)} \text{Cation.}

B. The \{\text{Bis-2,6}[1-(2\text{-pyrid-2-ylethylimino})\text{ethyl}]\text{pyridine}}\text{copper(1)} \text{Cation.}
this is the first well characterized synthetic Cu(I) O₂ carrier to be reported. The degree of reversibility for O₂ uptake is greater than 80% per oxy/deoxy cycle in solution at room temperature. The Cu(II) and Zn(II) analogs have also been synthesized and characterized for purposes of comparison. Furthermore, the solution behavior and reactivity of [Cu(I)(imidH)₂DAP]⁺ with O₂ has been compared with that exhibited by the {Bis-2,6[1-(2-pyrid-2-ylethyl)iminomethyl]pyridine}-copper(I) ion (hereafter [Cu(I)(py)₂DAP]⁺) as shown in Figure 2B, in an effort to understand the role that imidazole plays in the O₂ carrying capability of the complex. Although the [Cu(I)(py)₂DAP]⁺ complex is geometrically very similar to [Cu(I)(imidH)₂DAP]⁺, the [Cu(I)(py)₂DAP]⁺ species does not react reversibly with O₂. Finally, Cu(II) and Zn(II) complexes of the [(py)₂DAP] ligand have also been synthesized and characterized.
**EXPERIMENTAL**

**Physical Measurements.** Solid state infrared spectra were obtained as Nujol mulls using NaCl plates and a Beckman IR-20 spectrometer. The samples were prepared under dry N\textsubscript{2} and the spectra are shown in Appendix II. Solution conductivities were obtained using a Model 31 YSI conductivity bridge; the Cu(I) compounds were loaded into the conductivity cell under a stream of dry N\textsubscript{2}. PMR spectra of the Zn(II) and Cu(I) complexes were run at 90 mHz on a Varian EM390 spectrometer at room temperature. The samples were dissolved in CD\textsubscript{3}CN until the solution was saturated, and then 1 drop of TMS was added. UV-VIS spectra were run on a Cary 17 Recording Spectrophotometer using matched quartz cells with 1 cm path lengths; O\textsubscript{2} sensitive Cu(I) solutions were syringed into N\textsubscript{2}-filled cells through septum caps.

Electrochemical measurements were obtained in CH\textsubscript{3}CN, Me\textsubscript{2}SO, DMF, and pyridine solutions at room temperature under a constant flow of N\textsubscript{2} using a PAR Model 174A Polarographic Analyzer or a Model 173 potentiostat/galvanostat driven by a Model 175 universal programmer. The current voltage curves were recorded on a Houston Omnigraphic 2000 X - Y recorder at scan rates between 0.02 and 0.50 V/s and a Tektronix Model 5111 storage oscilloscope at scan rates between 0.10 and 50.0 V/s. The electrolysis cell was a PAR Polarographic Model K60. A three electrode geometry was employed with a platinum button serving as the working electrode, a platinum wire as the counter electrode. A Metrohm K901 saturated calomel electrode (SCE) was used as the reference electrode. The reference electrode was partially separated from the bulk solution by means of a fritted-glass bridge containing supporting
electrolyte solution. Solutions in the bridge were changed periodical-
ly to prevent aqueous contamination from entering the cell. The over-
all number of electrons transferred was determined by controlled
potential electrolysis in a standard H cell. Two platinum gauze
electrodes of approximately equal surface area served as the cathode
and the anode. The reference electrode (SCE) was placed as close as
possible to the cathode without shorting the circuit. Stirring of the
solution was accomplished by bubbling N₂ through the solutions during
electrolysis. Electronic integration of the current-time curve was
achieved by means of a PAR Model 179 coulometer and displayed as
coulombs vs. time with the aid of a strip chart recorder. A Labchron
digital timer was used to monitor all time measurements. All solutions
were 0.1 M in tetrabutylammonium perchlorate (TBAP) and 10⁻³ M in com-
plex. The maximum potential range in each solvent was checked by run-
ning a supporting electrolyte blank prior to each run. Nitrogen and
argon gas were used interchangeably as deoxygenating agents. The inert
gas was presaturated with solvent for measurements in CH₃CN in order to
avoid evaporation. All potentials are reported vs. SCE and are uncor-
rected for junction potentials. The electrodes were pretreated before
use by soaking them for 5 minutes in 6M HNO₃, rinsing well with dis-
tilled water, drying with cellulose tissue, then placing them in the
cell filled with blank solution. The voltage was set at -0.20 V and
cell current switched on. Current was passed through the cell until a
constant current reading on a 2 μA scale was obtained.

The Warburg Manometers used to monitor O₂ and CO uptake for
1 - 5 x 10⁻³ M solutions of sample were purchased from Precision
Scientific (Model #66662). The manometer flasks were placed in a constant temperature bath to achieve temperature control over the time of a measurement (maximum of 30 min). The flasks were paired with a manometer and the flask constants were determined in the usual manner using triply distilled mercury as the calibrant.\textsuperscript{49,50} \( \text{Me}_2\text{SO} \), DMF, and pyridine were used in the uptake studies. For each solvent, a blank was measured to determine absorption due only to the solvent and this value was subtracted from the uptake of a solution containing the complex. The complex was weighed into the sidearm of the manometer flask, and 2.6 - 3.0 mL of deoxygenated solvent was placed into the flask. After equilibration to constant temperature under flowing \( \text{N}_2 \), the manometer was flushed with pre-purified \( \text{O}_2 \) for 1 minute and adjusted to atmospheric pressure. The entire apparatus was then "tilted" to mix the solid sample and solvent. A typical uptake measurement required approximately 20 minutes. For the recycling runs, 10 mL of 1 - 5 mM solutions were oxygenated, then deoxygenated under vacuum with vigorous stirring. \( \text{N}_2 \) gas was then bubbled through this solution for 5 minutes, then 3 mL of this solution was transferred with a syringe into the manometer flask under flowing \( \text{N}_2 \). The apparatus was flushed with \( \text{N}_2 \) and allowed to equilibrate, and then flushed with pre-purified \( \text{O}_2 \) for exactly 30 seconds. A blank was treated in exactly the same manner and its uptake volume subtracted from the uptake for the sample. The apparatus was checked using Vaska's iodide complex which forms a 1:1 Ir:O\textsubscript{2} adduct with O\textsubscript{2} in solution.\textsuperscript{51} For oxygenation of solid samples, the complex was finely powdered and placed into the Warburg flask under one atmosphere O\textsubscript{2}. To promote oxygenation, approximately 0.5 mL H\textsubscript{2}O was placed in the flask sidearm. A complete description of
the use of the manometer appears in Appendix I.

A Finnigan 9500 Automated Gas Chromatograph/Mass Spectrometer System was used to monitor $O_2$ evolution from solid samples of oxygenated $[\text{Cu(I)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)$

The solid was ground into a fine powder and oxygenated in the Warburg apparatus immediately before a run. The green solid was placed in the spectrometer probe under a vacuum of ca. $10^{-6}$ torr. The probe was slowly heated so that one scan (ca. 2 s) corresponded to 3°C. Ion current vs. scan number traces were recorded for selected m/e values.

Magnetic susceptibilities in the solid state were measured by the Faraday technique using Hg[Co(NCS)$_4$] as the calibrant. A Cahn Model 6600-1 Research Magnetic Susceptibility System was used; all measurements were recorded at room temperature under 1 atmosphere He. The molar susceptibilities of the Zn(II) complexes were used to correct for ligand and anion diamagnetism: $[\text{Zn(II)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)_2$: $X'_M = -2.9795 \times 10^{-4}$ cgsu mol$^{-1}$ and $[\text{Zn(II)}(\text{py})_2\text{DAP}](\text{ClO}_4)_2$: $-1.702 \times 10^{-4}$ cgsu mol$^{-1}$.

Electron spin resonance (esr) spectra were obtained on a Varian E-line spectrometer at ca. 100 K and X-band frequencies using standard quartz tubes. Field positions are referenced relative to DPPH. The copper content of the samples was determined using known concentrations of CuSO$_4$ as the calibrant. The $[\text{Cu(I)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)$ samples were prepared under $N_2$ and the sample tubes filled under flowing $N_2$. Solutions of the Cu(I) compound were oxygenated, excess $O_2$ removed by bubbling $N_2$ through the solution, and the solution then transferred to a sample tube. Deoxygenation was accomplished by vigorously stirring the solution with the application of a vacuum, after which the solution
was transferred to the esr tube with a syringe under flowing N₂. Me₂SO was the solvent of choice for the esr studies because of the greater solubility of [Cu(I)(imidH)₂DAP](ClO₄) in Me₂SO, and because this solvent formed the best glass.

Chemical analyses were performed by the microanalytical laboratory at the University of Illinois.

**Materials.** All solvents used were reagent grade. CH₃CN was distilled from KMnO₄ and Na₂CO₃. Me₂SO was distilled from BaO under high vacuum. The CD₃CN for the PMR studies was obtained from Stohler Isotope Chemicals. Histamine, free base (Grade B), was obtained from Calbiochem. 2,6-Diacetylpuridine and 2-(2-Aminoethyl)pyridine were obtained from Aldrich Chemicals. Tetrabutylammonium perchlorate (TBAP) was purchased from G. Frederick Smith Chemical Company or Eastman Chemicals and used without further purification. Cu(II)(ClO₄)₂·6H₂O and Zn(II)(ClO₄)₂·6H₂O were from Alpha Products. Industrial grade N₂ from Big Three Industries was used and the gas dried by passing it through a column packed with CaSO₄ and CaCl₂. Pre-purified O₂ and CO for the manometric measurements were obtained from Matheson Gas Products.

**Syntheses.** [Cu(I)(CH₃CN)₄](ClO₄) was prepared by the method of Hemmerich and Sigwart. 1.43 g of Cu₂O was added to a degassed solution of 100 mL 0.2 M HClO₄ and 25 mL CH₃CN, then heated and stirred under N₂ until the Cu₂O dissolved. Upon cooling, the white crystals which precipitated were collected by suction filtration under flowing N₂. The crystals were washed with deoxygenated H₂O and dried under vacuum at 80°C for 12 h.
[Cu(I)\(\text{CH}_3\text{CN})_4\](BF\(_4\))\(_{53}\) was prepared by adding 1.43 g Cu\(_2\)O to 100 mL H\(_2\)O and 25 mL CH\(_3\)CN and then adding dropwise 3 mL BF\(_3\)·Et\(_2\)O. The solution was heated and stirred under N\(_2\) until the Cu\(_2\)O dissolved. Upon cooling, the white needles which precipitated were collected under N\(_2\), washed with deoxygenated H\(_2\)O, and dried under vacuum at 80°C for 12 h.

\{Bis-2,6\([\text{1-(2-imidazol-4-yethylimino)ethyl]pyridine}\}\text{copper(I)}\}

Perchlorate, abbreviated: [Cu(I)(imidH)\(_2\)DAP](ClO\(_4\)). A ligand solution was prepared by dissolving 1 mmol of 2,6-diacetylpyridine and 2 mmol of histamine (free base) in 25 mL MeOH. The solution was stirred and refluxed for 1 h, producing a solution which was light yellow in color. To approximately 30 mL of deoxygenated CH\(_3\)CN, 1 mmol of [Cu(I)(CH\(_3\)CN)\(_4\)]\(-(\text{ClO}_4)\) was added. The ligand solution was flushed with N\(_2\) for 15 min, and then the [Cu(I)(CH\(_3\)CN)\(_4\)](ClO\(_4\)) solution was quickly added, producing an intense red-purple colored solution. This solution was reduced to dryness by application of a vacuum. The resulting solid was removed from the flask, dried at 80°C under vacuum for 12 h, washed (under N\(_2\)) with carefully degassed distilled water, and then with degassed CH\(_2\)Cl\(_2\). The compound was dissolved in CH\(_3\)CN, filtered, transferred to a flask and the solution again reduced to dryness under vacuum. This solid was removed from the flask, and again dried under vacuum at 80°C for 12 h. (Note: decomposition was observed to occur if P\(_2\)O\(_5\) was used as a drying agent.) The Cu(I) complex prepared in such a manner was obtained as a very dark red shiny solid in 60% yield.

\(A_c = 177 \ \Omega^{-1} \ cm^{-1}\) for a 10\(^{-3}\) M CH\(_3\)CN solution at 30°C. \(\mu_{\text{eff}}\text{(solid, 298) = 0.85 } \mu_B\). Anal. calcd. for CuC\(_{19}\)H\(_{23}\)N\(_7\)ClO\(_4\): C, 44.53; H, 4.53;
N, 19.13; Cu, 12.40. Found: C, 44.16; H, 4.61; N, 19.24; Cu, 12.24.

\([\text{Cu}(\text{imidH})_2\text{DAP}](\text{BF}_4)\) was prepared as for the \(\text{ClO}_4\) salt, except that \([\text{Cu}(\text{imidH})_2\text{DAP}](\text{BF}_4)\) was used as the source of Cu(I). The \(\text{BF}_4\) salt is considerably more hygroscopic than the \(\text{ClO}_4\) salt. Yield: 60%.

\(\Lambda^\text{C} = 150 \, \Omega^{-1}\text{cm}^{-1}\) for a \(10^{-3}\) M \(\text{CH}_3\text{CN}\) solution at 30°C. \(\mu_{\text{eff}}\)(solid, 298) = 0.50 \(\mu_\text{B}\). Anal. calcd. for \(\text{CuC}_{19}\text{H}_{23}\text{N}_7\text{BF}_4\cdot 1.5\text{H}_2\text{O}\): C, 43.32; H, 4.97; N, 18.61; Cu, 12.06. Found: C, 43.16; H, 4.46; N, 18.66; Cu, 12.93.

**{Bis-2,6[1-(2-imidazol-4-ylethylimino)ethyl]pyridine}copper(I)**

Perchlorate, abbreviated: \([\text{Cu}(\text{II})(\text{imidH})_2\text{DAP}](\text{ClO}_4)_2\). A ligand solution was prepared as above for the Cu(I) complex. After the ligand solution had cooled, 1 mmol of \(\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}\) was added as a solid. A dark green solution resulted after several minutes of stirring. This solution was taken to dryness under vacuum, and the solid was removed from the flask and dried under vacuum at 80°C for 12 h. This green solid was washed with distilled water, then with \(\text{CH}_2\text{Cl}_2\). The compound was dissolved in \(\text{CH}_3\text{CN}\), the solution filtered and taken to dryness under vacuum and the resulting solid again removed from the flask and dried at 80°C for 12 h. Yield: 70%. \(\Lambda^\text{C} = 346 \, \Omega^{-1}\text{cm}^{-1}\) for a \(10^{-3}\) M \(\text{CH}_3\text{CN}\) solution at 30°C. \(\mu_{\text{eff}}\)(solid, 298) = 1.8 \(\mu_\text{B}\). Anal. calcd. for \(\text{CuC}_{19}\text{H}_{23}\text{N}_7\text{Cl}_2\text{O}_3\): C, 37.29; H, 3.80; N, 16.03; Cu, 10.38. Found: C, 38.24; H, 3.82; N, 15.36; Cu, 10.26.

**{Bis-2,6[1-(2-imidazol-4-ylethylimino)ethyl]pyridine}Zinc(II)**

Perchlorate, abbreviated: \([\text{Zn}(\text{II})(\text{imidH})_2\text{DAP}](\text{ClO}_4)_2\) was prepared and treated identically as the above Cu(II) compound. The light orange solid was obtained in 70% yield. \(\Lambda^\text{C} = 350 \, \Omega^{-1}\text{cm}^{-1}\) for a \(10^{-3}\) M
CH₃CN solution at 30°C. Anal. calcd. for ZnC₁₉H₂₃N₇Cl₂O₈: C, 37.19; H, 3.78; N, 15.98; Zn, 10.65. Found: C, 37.00, H, 4.10; N, 15.76; Zn, 9.77.

**[Bis-2,6[1-(2-pyrid-2-ylethylamino)ethyl]pyridine]copper(I) Perchlorate**, abbreviated: [Cu(I)(py)₂DAP](ClO₄). A ligand solution was prepared by dissolving 1 mmol of diacetylpyridine in 25 mL MeOH and then adding, dropwise, 2 mmol of 2-(2-Aminoethyl)pyridine. This solution was stirred and gently heated for about 1 h, after which it appeared yellow in color. One mmol of [Cu(I)(CH₃CN)₄](ClO₄) was added to ca. 30 mL deoxygenated CH₃CN, allowed to dissolve, and then added, under N₂, to the deoxygenated ligand solution. The cherry red colored solution was taken to dryness under vacuum and the resulting solid recrystallized from deoxygenated CH₃CN/Et₂O with cooling. The red solid was collected by filtration under flowing N₂ and washed with Et₂O. The compound was dried under vacuum at 80°C for 12 h. Yield: 50%.

νₐ = 147.4 cm⁻¹ for a 10⁻³ M CH₃CN solution at 30°C. νₑ_ff(solid, 298) = 0.2 μ_B. Anal. calcd. for CuC₂₃H₂₅N₅ClO₄: C, 51.68; H, 4.72; N, 13.10; Cu, 11.89. Found: C, 52.45; H, 4.73; N, 13.86; Cu, 11.67.

**[Bis-2,6[1-(2-pyrid-2-ylethylamino)ethyl]pyridine]copper(II) Perchlorate**, abbreviated [Cu(II)(py)₂DAP](ClO₄)₂. A ligand solution was prepared as above for the Cu(I) complex. After the ligand solution had cooled, 1 mmol of Cu(ClO₄)₂·6H₂O was added as a solid. The blue solution which immediately resulted was reduced in volume to about 15 mL and cooled to induce crystallization. This solution was further cooled and the solid collected by filtration, and washed with a small amount of cold MeOH. The resulting blue-green powder was dried under
vacuum at 80°C for 12 h. Yield: 50%. $\Lambda_c = 339 \ \Omega^{-1} \ cm^{-1}$ for a $10^{-3} \ M$ CH$_3$CN solution at 30°C. $\nu_{\text{eff}}$(solid, 298) = 2.1 $\nu_B$. Anal. calcd. for CuC$_{23}$H$_{25}$N$_5$Cl$_2$O$_8$: C, 43.57; H, 3.98; N, 11.05; Cu, 10.02. Found: C, 43.06; H, 3.91; N, 10.54; Cu, 9.84.

{Bis-2,6[1-(2-pyrid-2-ylethylamino)ethyl]pyridine}zinc(II) Perchlorate, abbreviated: [Zn(II)(imidH)$_2$DAP](ClO$_4$)$_2$. The compound was prepared in exactly the same manner as above for the Cu(I) compound, with the light yellow solid being produced in 80% yield. $\Lambda_c = 305 \ \Omega^{-1} \ cm^{-1}$ for a $10^{-3} \ M$ CH$_3$CN solution at 30°C. Anal. calcd. for ZnC$_{23}$H$_{25}$N$_5$Cl$_2$O$_8$: C, 43.45; H, 3.97; N, 11.02; Zn, 10.28. Found: C, 44.29; H, 3.81; N, 11.73; Zn, 10.68.
RESULTS AND DISCUSSION

Synthesis and Characterization of the Complexes. The synthetic scheme for \([\text{Cu(I)}(\text{imidH})_2\text{DAP})(\text{ClO}_4)]\) is shown in Figure 3, where the (imidH)_2DAP ligand is generated by the Schiff base condensation of free base histamine with 2,6-diacetylpyridine. Addition of \([\text{Cu(I)}(\text{CH}_3\text{CN})_4]\text{ClO}_4) under N_2 results in an intensely red colored solution from which \([\text{Cu(I)}(\text{imidH})_2\text{DAP})(\text{ClO}_4)]\) is isolated as a dark red solid. Substitution of \(\text{Cu(ClO}_4)_2\cdot6\text{H}_2\text{O}\) or \(\text{Zn(ClO}_4)_2\cdot6\text{H}_2\text{O}\) in the synthesis yields the dark green Cu(II) analog or the light orange Zn(II) species, respectively. If 2-(2-Aminoethyl)pyridine is substituted for histamine in the synthesis, addition of \([\text{Cu(I)}(\text{CH}_3\text{CN})_4]\text{ClO}_4) under N_2 yields a cherry red colored solution from which \([\text{Cu(I)}(\text{py})_2\text{DAP})(\text{ClO}_4)]\) can be isolated, also as a dark red solid. The yellow Zn(II) and blue-green Cu(II) analogs of this complex have also been synthesized by substitution of the appropriate metal salt. As indicated in Figure 2, both ligands are assumed to serve in a fully pentacoordinate fashion, with the complexes being monomeric in solution as indicated by available analytical and solution conductivity and pmr data, as reported in the Experimental Section, and discussed below. Furthermore, in the solid state both the \([\text{Zn(II)}(\text{imidH})_2\text{DAP}]^{2+}\) and \([\text{Cu(II)}(\text{imidH})_2\text{DAP}]^{2+}\) cations have been established to be pentacoordinate species by single crystal X-ray structural determinations,\(^{54}\) where the coordination geometries are best described as intermediate between the idealized trigonal bipyramid and the square planar structures. For the Zn(II) complex, the preliminary Zn-N bond distances are 2.00Å for the Zn-N(py) and Zn-N(imidH) bonds and 2.19Å for the two Zn-N(imine) bonds.
FIGURE 3

Synthetic Scheme for the \{\text{Bis-2,6}[1-(2-imidazol-4-ylethyl-imino)ethyl]pyridine copper(I)}\ Perchlorate Complex.
However, a question arises concerning the pentacoordinate nature of the Cu(I) complexes because five coordinate Cu(I) is exceedingly rare, though there seems to be no inherent reason why pentacoordinate Cu(I) should be unstable. The alternative to the ligands realizing their fully pentadentate capability for Cu(I) would most likely be formation of a four coordinate species, where, for example, one of the imidazole or pyridine nitrogens might remain uncoordinated. The pmr spectra of the two Zn(II) complexes in CD$_3$CN at room temperature are shown in Figure 4a and 4b and are consistent with the proposed formulation of these complexes as pentadentate species, since there appears to be no additional multiplicity of the nature expected for uncoordinated ligand "arms." Proposed assignments for the resonances are indicated on the figures. A somewhat broadened pmr spectrum was obtained for [Cu(I)(py)$_2$DAP](ClO$_4$) as shown in Figure 4c. This broadening is likely due to a small amount of Cu(II) contaminate, since the compound exhibits slow and irreversible reactivity with O$_2$ (vide infra) to presumably produce some Cu(II) species. Alternatively, the broadening may be due to some solvent promoted decomposition, although this seems less likely since the compound can be recrystallized from CH$_3$CN without apparent damage. Nevertheless, the multiplicity and general features of the spectrum appear the same as for the analogous Zn(II) complex. A pmr spectrum of the [Cu(I)(imidH)$_2$DAP](ClO$_4$) compound could not be obtained by the present methods of sample handling. The lack of any resonances for this compound is undoubtedly due to the severe line broadening from Cu(II) impurities which arise from the extreme O$_2$ sensitivity of the complex in solution (see esr discussion below). The available proton resonance positions and assignments
Proton Magnetic Resonance Spectra for Several of the Complexes at Room Temperature, as Saturated Solutions in CD₃CN. Signals are referenced to internal TMS. Proposed assignments of the resonances are shown on the figures. (*) indicates a CD₃CN contaminant.

a) [Zn(II)(imidH)₂DAP](ClO₄)₂
b) [Zn(II)(py)₂DAP](ClO₄)₂
c) [Cu(I)(py)₂DAP](ClO₄)
are summarized in Table III.

The [Cu(II)(imidH)$_2$DAP](ClO$_4$)$_2$ compound exhibits a low intensity d-d absorption band (with at least two components) centered at ca. 850 nm, with $\varepsilon_{850\text{nm}} = 100 \text{ M}^{-1} \text{ cm}^{-1}$. A variable solvent study of the complex yielded the same absorption band in CH$_3$CN, DMF, Me$_2$SO, pyridine, and 2,6-lutidine as shown in Figure 5a. This behavior indicates that the ligand remains intact for Cu(II) in each of these solvents, and that the complex is inert toward potentially ligating solvent molecules since changes in shape or shifts in position of d-d bands are usually a good criteria for changes in coordination environment. Moreover, the shape of this absorption envelope is similar to known Cu(II) five coordinate complexes, such as [Cu(II)(tren)NCS](SCN)$_2$, [Cu(II)(Me$_6$tren)ClO$_4$](ClO$_4$)$_2$, and [Cu(II)(bipy)$_2$Cl]Cl. For the [Cu(II)(py)$_2$DAP](ClO$_4$)$_2$ complex, different absorption spectra were observed in pyridine and 2,6-lutidine than in DMF, Me$_2$SO, or CH$_3$CN as shown in Figure 5b. This suggests possible coordination of pyridine and 2,6-lutidine, or ligand dissociation in these solvents. In Me$_2$SO, DMF, and CH$_3$CN, however, there is little doubt that the complex remains pentacoordinate, with a spectrum similar to that of [Cu(II)(imidH)$_2$DAP]$_2$.

The Cu(I) complexes also exhibit absorptions in the visible region, which account for their intense red colors. The high intensity of these bands indicate that they are due to metal $\rightarrow$ ligand charge transfer (CT). Since these bands should also be sensitive to solvent coordination or ligand dissociative processes, a variable solvent study was performed on both of the Cu(I) complexes. The [Cu(I)(imidH)$_2$DAP](ClO$_4$)$_2$ compound exhibits a CT band centered at 529 nm
**TABLE III**

Proton Magnetic Resonance Data for the Complexes as Saturated Solutions in CD$_3$CN. Positions are referenced to internal TMS.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Position (ppm)</th>
<th>Assignment*</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Zn(II)}(\text{imidH})_2\text{DAP})(\text{ClO}_4)_2])</td>
<td>2.54</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>3.18</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>3.97</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>7.20</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>8.37</td>
<td>f</td>
</tr>
<tr>
<td>([\text{Zn(II)}(\text{py})_2\text{DAP})(\text{ClO}_4)_2])</td>
<td>2.57</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>3.45</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>4.19</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>7.62 - 8.08</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>8.45</td>
<td>e</td>
</tr>
<tr>
<td>([\text{Cu(I)}(\text{py})_2\text{DAP})(\text{ClO}_4))</td>
<td>2.27</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>3.56</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>4.13</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>7.0 - 8.5</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>e</td>
</tr>
</tbody>
</table>

* As shown in Figure 4.
FIGURE 5

Room Temperature Electronic Absorption Spectra for the Complexes in the Near-ir and Visible Regions for $2 \times 10^{-3}$ M Solutions.

a) $[\text{Cu(II)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)_2$ in $\text{Me}_2\text{SO}$, $\text{DMF}$, $\text{CH}_3\text{CN}$, pyridine and 2,6-lutidine.

b) $[\text{Cu(II)}(\text{py})_2\text{DAP}](\text{ClO}_4)_2$ in various solvents.
FIGURE 6

Room Temperature Electronic Absorption Spectrum of

a) $[\text{Cu(I)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)$ in deoxy-
genated Me$_2$SO at $5 \times 10^{-4}$ M.

b) Solution A upon oxygenation, i.e.,
absorption of 0.5 moles of O$_2$ per
available Cu.

c) Solution B deoxygenated by applica-
tion of a vacuum with vigorous
stirring, i.e., after one oxy-deoxy
cycle.
(see Figure 6A). The absorption band displays the same shape and position in $\text{Me}_2\text{SO}$, DMF, $\text{CH}_3\text{CN}$, pyridine, and 2,6-lutidine, though a slight broadening is observed in 2,6-lutidine. For $[\text{Cu(I)(py)}_2\text{DAP}]^{-}(\text{ClO}_4)$, the spectra were found to differ somewhat in $\text{Me}_2\text{SO}$, DMF, and $\text{CH}_3\text{CN}$, as shown in Figure 7, with the CT band maximum at ca. 500 nm. However, in pyridine, the 500 nm band is completely absent, which is assumed to be a result of compound decomposition in that solvent. Thus, only in pyridine and only for the case of the $[\text{Cu(I)(py)}_2\text{DAP}]^+$ compound, does the electronic spectral data suggest significant compound decomposition, although both the Cu(I) and Cu(II) complexes of (py)$_2$DAP show indication of solvent "involvement" in their solution chemistries. The $[\text{Cu(I)(imidH)}_2\text{DAP}]^+$ species, on the other hand, shows little or no such tendency, implying that the species remain penta-coordinate in all the solvents studied. The spectral data for the complexes are summarized in Table IV.

Reactivity of the Cu(I) Complexes with $\text{O}_2$. The most striking property observed for $[\text{Cu(I)(imidH)}_2\text{DAP}]^{-}(\text{ClO}_4)$ was the change in color from red to green for a $\text{CH}_3\text{CN}$ solution upon exposure to $\text{O}_2$ and the reverse color change when the solution was degassed with $\text{N}_2$ and gently heated. The absorption spectra of this complex, shown in Figures 6 and 8-10, quantify this observation. In deoxygenated $\text{Me}_2\text{SO}$, DMF, or pyridine solutions, the complex exhibits a CT band at 520 nm, $\varepsilon_{\text{max}} = 1400 \text{ M}^{-1} \text{ cm}^{-1}$, which is shown as spectrum A in the figures. If the solution is exposed to $\text{O}_2$, a light green color is produced, and spectrum B results. If this solution is deoxygenated by gentle warming and bubbling through with $\text{N}_2$, or vigorously stirred under high vacuum
Figure 7

Room Temperature Electronic Absorption Spectrum of \([\text{Cu(I)}(\text{py})_2\text{DAP}](\text{ClO}_4)\) at 5 x 10\(^{-4}\) M in Various Deoxygenated Solvents.
### TABLE IV

Electronic Spectral Data for the Copper Complexes in Various Solvents at Room Temperature.*

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\nu_{max}$ (cm$^{-1}$)</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="ClO$_4$">Cu(II)(imidH)$_2$DAP</a>$_2$</td>
<td>Me$_2$SO</td>
<td>670</td>
<td>14930</td>
<td>136 (70)</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>1000 (sh)</td>
<td>(10000)</td>
<td>(70)</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pyridine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,6-lut</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="ClO$_4$">Cu(I)(imidH)$_2$DAP</a></td>
<td>Me$_2$SO</td>
<td>520</td>
<td>19230</td>
<td>1415</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td></td>
<td></td>
<td>1415</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td></td>
<td></td>
<td>1190</td>
</tr>
<tr>
<td></td>
<td>pyridine</td>
<td>510</td>
<td>19610</td>
<td>975</td>
</tr>
<tr>
<td></td>
<td>2,6-lut</td>
<td>520</td>
<td>19230</td>
<td>800</td>
</tr>
<tr>
<td><a href="ClO$_4$">Cu(II)(py)$_2$DAP</a>$_2$</td>
<td>Me$_2$SO</td>
<td>750</td>
<td>13330</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>pyridine</td>
<td>660</td>
<td>15150</td>
<td>172 (145)</td>
</tr>
<tr>
<td></td>
<td>875 (sh)</td>
<td>(11430)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,6-lut</td>
<td>650</td>
<td>15380</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>900 (sh)</td>
<td>(11110)</td>
<td></td>
<td>(120)</td>
</tr>
<tr>
<td><a href="ClO$_4$">Cu(I)(py)$_2$DAP</a></td>
<td>Me$_2$SO</td>
<td>420</td>
<td>23810</td>
<td>2340</td>
</tr>
<tr>
<td></td>
<td>480 (sh)</td>
<td>(20830)</td>
<td></td>
<td>(2360)</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>470</td>
<td>21280</td>
<td>2180</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>470</td>
<td>21280</td>
<td>2500</td>
</tr>
<tr>
<td></td>
<td>pyridine</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Data taken from Figures 5-10. In the case of the shoulders (sh), band positions are estimated, with no attempt at deconvolution.
FIGURE 8

Room Temperature Electronic Absorption Spectrum of

a) $[\text{Cu(I)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)$ in deoxygenated Me$_2$SO at $5 \times 10^{-4}$ M.

b) Solution A upon oxygenation, i.e., absorption of 0.5 moles of O$_2$ per available Cu.

c) Solution B deoxygenated with mild heating and bubbling N$_2$.

d) $[\text{Cu(II)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)_2$ in Me$_2$SO at $5 \times 10^{-3}$ M. (Shown to illustrate its intensity in comparison to the Cu(I) species.)
FIGURE 9

Room Temperature Electronic Absorption Spectrum of

a) $[\text{Cu(I)(imidH)}_2\text{DAP}](\text{ClO}_4)$ in
deoxygenated DMF at $5 \times 10^{-4}$ M.

b) Solution A upon oxygenation.

c) Solution B deoxygenated by mild
heating and bubbling $\text{N}_2$. 
FIGURE 10

Room Temperature Electronic Absorption Spectrum of $[\text{Cu(I)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)$ in pyridine.

a) A $5 \times 10^{-4}$ M solution in deoxygenated pyridine.

b) Solution A upon exposure to atmospheric $O_2$ for 2 minutes.

c) Solution B upon exposure to atmospheric $O_2$ for 15 minutes.

d) Solution C upon exposure to atmospheric $O_2$ for 30 minutes.
\begin{align*}
\epsilon \times 10^3, \text{ M}^{-1} \text{ cm}^{-1} \\
\lambda, \text{ nm}
\end{align*}
for several minutes, the solution appears to return to its original red color and spectrum C results. Undoubtedly, the extinction coefficients for the absorption band in A are rather low and somewhat variable from one determination to another due to contamination with \( \text{O}_2 \) that inevitably occurs during sample handling. Figures 6 and 8 depict the spectra which result when the solutions are deoxygenated in various ways, where the percent reversibility of oxygenation appears to be greater using the vacuum/stirring technique. Figure 9 indicates the good reversibility found for DMF solutions of the complex. In pyridine, the complex exhibits the slowest rate of oxygenation with, for example, 15 minutes at ambient \( \text{O}_2 \) pressure being required to significantly diminish the \( \text{Cu(I)} \) parent species band intensity, as shown in Figure 10. The pyridine solutions also exhibited good oxygenation reversibility, but the spectra are omitted from the figure for clarity. Once deoxygenated, any of the solutions again absorbs \( \text{O}_2 \), turns green and produces spectrum B of Figures 6, 8, and 9. The solution can again be deoxygenated, yielding a red solution of diminished intensity as compared to the original solution and again yielding a spectrum resembling C. By comparing the extinction coefficients for recycled solutions (spectrum C) with those of unoxygenated \( \text{Cu(I)} \) solutions (spectrum A), it appears that the reversibility per oxy/deoxy cycle is greater than 80%. This is a crude estimate due to spectral broadening upon recycling, but, interestingly enough, this value is in good agreement with the manometric \( \text{O}_2 \) uptake results discussed below.

The reactivity of [\( \text{Cu(I)(imidH)}_2\text{DAP}]\text{(ClO}_4\text{)} \) with \( \text{O}_2 \) has been verified by manometric methods (see Experimental Section). In all cases, the uptake of \( \text{O}_2 \) corresponded to one mole of \( \text{O}_2 \) per two moles of avail-
able copper. The O\textsubscript{2} uptake in 2 - 5 mM solutions of the complex was found to be solvent dependent, but complete in 2 - 5 minutes under 1 atmosphere O\textsubscript{2}, after which no further absorption was observed. The manometric data for [Cu(I)(imidH)\textsubscript{2}DAP](ClO\textsubscript{4}) are listed in Table V and, within experimental error, the data correspond to 2Cu:O\textsubscript{2}. Various solvents were used primarily to verify that oxygenation was not some artifact of solvent system, and the BF\textsubscript{4}\textsuperscript{-} salt was checked to ensure that the counterion did not alter the oxygenation stoichiometry (Table VI). Me\textsubscript{2}SO solutions were used in the majority of the uptake measurements because the low volatility of that solvent yields more accurate manometric data by the Warburg technique. If the Me\textsubscript{2}SO solutions are deoxygenated by application of a vacuum accompanied by vigorous stirring, the solutions again absorb O\textsubscript{2}, in a ratio of ca. 2Cu:0.8 O\textsubscript{2}. Such data for oxy/deoxy cycles are shown in Table VI, where the first cycle represents a solution which has been oxygenated, deoxygenated, and then the uptake measured. The volume of O\textsubscript{2} absorbed upon recycling is somewhat time dependent, in that an oxy/deoxy solution absorbs less O\textsubscript{2} the longer one waits to measure the uptake. The total time for the measurements listed in Table VI (i.e., for 2 cycles), is about one hour. After three hours no O\textsubscript{2} absorption was observed in solutions that had been exposed to O\textsubscript{2} and then deoxygenated and kept under vacuum. From this observation, it is inferred that oxygenated by-products which form with time inhibit the reversible O\textsubscript{2} reactivity of the complex. Over a short time interval, the oxy/deoxy cycling process is observed for each solvent system examined, but it was difficult to obtain such data for DMF or CH\textsubscript{3}CN, due to the high sensitivity of the complex to O\textsubscript{2} once in solution (see Experimental Section).
### TABLE V

Manometric Data for the [Cu(I)(imidH)$_2$DAP](ClO$_4$)$_2$

Complex in Various Solvents at 22°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Exp. No.</th>
<th>Moles of Complex (x 10$^5$)</th>
<th>Moles of O$_2$ (x 10$^5$)</th>
<th>O$_2$/Cu Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_2$SO*</td>
<td>1</td>
<td>11.0</td>
<td>4.92</td>
<td>.447</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.66</td>
<td>2.64</td>
<td>.466</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5.85</td>
<td>3.04</td>
<td>.519</td>
</tr>
<tr>
<td>DMF</td>
<td>1</td>
<td>4.88</td>
<td>2.50</td>
<td>.512</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.07</td>
<td>2.09</td>
<td>.412</td>
</tr>
<tr>
<td>Pyridine</td>
<td>1</td>
<td>16.98</td>
<td>7.27</td>
<td>.428</td>
</tr>
</tbody>
</table>

* A complete listing of the Me$_2$SO data appears in Appendix I.
TABLE VI
Oxygenation/Deoxygenation Manometric Measurements for the Copper(I) Complexes in Me₂SO at 23°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th># Cycle *</th>
<th>Moles of Complex (x 10⁶)</th>
<th>Moles of O₂ (x 10⁶)</th>
<th>O₂/Cu Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="ClO%E2%82%84">Cu(I)(imidH)₂DAP</a></td>
<td>1</td>
<td>5.85</td>
<td>2.38</td>
<td>.407</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.85</td>
<td>1.36</td>
<td>.232</td>
</tr>
<tr>
<td><a href="BF%E2%82%84">Cu(I)(imidH)₂DAP</a></td>
<td>1</td>
<td>10.0</td>
<td>4.4</td>
<td>.443</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.0</td>
<td>3.59</td>
<td>.350</td>
</tr>
</tbody>
</table>

* The cycle number refers to the number of times a solution was oxygenated and deoxygenated. Thus, #1 refers to a solution that has been oxygenated one and deoxygenated once.
The same approximate degree of reversibility is observed in all the solvents, although qualitatively, the rate of \( \text{O}_2 \) uptake is solvent dependent, decreasing in the order: \( \text{CH}_3\text{CN} \simeq \text{DMF} > \text{Me}_2\text{SO} > \text{pyridine} = 2,6\)-lutidine.

After multiple oxy/deoxy cycling, dark brown colored solutions eventually result, and though the brown product has not been identified, it is clearly not simply the oxidized form of the complex, i.e., the green \([\text{Cu(II)}(\text{imidH})_2\text{DAP}]^{+2}\). The \([\text{Cu(II)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)_2\) and \([\text{Zn(II)}(\text{imidH})_2\text{DAP}](\text{ClO}_4)_2\) complexes exhibit no reactivity with \( \text{O}_2 \) in any solvent or as solids. Furthermore, none of the complexes react with CO (at one atmosphere pressure). The Cu(I) species is "consumed" by NO, producing a bright green colored solution, but the compound does not appear to exhibit any reactivity toward \( \text{CN}^- \) or 1-methylimidazole, i.e., no adduct could be isolated.

The \([\text{M(py)}_2\text{DAP}]^{+n}\) \([\text{M} = \text{Cu(I)}, \text{Cu(II)}, \text{Zn(II)}]\) complexes were synthesized in order to investigate close geometric and electronic analogs of the \( \text{O}_2 \) reactive \([\text{Cu(I)}(\text{imidH})_2\text{DAP}]^{+}\) species. The \([\text{Cu(I)}(\text{py})_2\text{DAP}](\text{ClO}_4)\) complex does not react with \( \text{O}_2 \) within 2 - 5 minutes exposure to one atmosphere \( \text{O}_2 \), although over longer periods of time (ca. one hour) the complex exhibits a slow and continuous uptake of \( \text{O}_2 \). Eventually the uptake reaches a stoichiometry of less than 1:1 (Cu:O\(_2\)); the products of this irreversible oxygenation are as yet unidentified. As a solid, \([\text{Cu(I)}(\text{py})_2\text{DAP}](\text{ClO}_4)\) does not react with \( \text{O}_2 \) even over very long exposure times (hours). Furthermore, neither the Zn(II) nor the Cu(II) complexes react with \( \text{O}_2 \), as observed manometrically, and none of these complexes react with CO in the solid or solution state.
The Warburg manometric technique does not lend itself well to measurement of O₂ uptake for [Cu(I)(imidH)₂DAP](ClO₄) as a solid due to the long time required for oxygenation. In addition, O₂ absorption in the solid state appears to be dependent upon the presence of protic solvents. Typically, two hours are required for a finely ground solid sample of [Cu(I)(imidH)₂DAP](ClO₄) to turn green under 1 atm of water saturated O₂. There was no perceptible difference in the infrared spectrum of this complex as compared to the unoxygenated Cu(I). An uptake measurement performed by Professor R. R. Gagné tentatively indicates 0.15 moles of O₂ per mole of available copper is absorbed over a 20 hour period. Absorption was observed only in an H₂O saturated atmosphere of O₂. The low value of the uptake could be an effect of the surface area of the powder, but in any case, the behavior of the solid toward O₂ is not clear. An attempt to observe O₂ evolution from an oxygenated solid sample was made by a mass spectrometer experiment. Traces of ion current vs. number of scans are shown in Figure II. There is about a 3°C increase in temperature per scan, so that these traces also indicate ion current vs. temperature. As seen in the figure, a sudden intensity increase of m/e 16 at scan number 30 is observed, followed by a decrease in intensity and then again a gradual increase in intensity indicative of sample decomposition. For the m/e 28 peak (N₂⁺) and total ion traces, the current intensity gradually increased until, at about scan #65 (~ 200°C), the sample vaporized. It is inferred that the m/e 16 peak, which maximizes in intensity prior to sample decomposition, is due to the liberation of O⁺ ions from the oxygenated sample, especially since the Zn(II) complex, run as a blank, did not exhibit this behavior, but yielded a trace for m/e 16 similar
FIGURE 11

Ion Current vs. Scan Number Traces (2 sec/scan, 3°C/scan) for an Oxygenated Solid Sample of \([\text{Cu}(1)(\text{imidH})_2\text{DAP}](\text{ClO}_4)\).

a) m/e 16

b) m/e 32

c) m/e 28

d) total ion trace
SIMMONS 2

MASS 16

100

20  50  100

a)

SIMMONS 2

MASS 32

100

20  50  100

b)
to c) and d) in the figure. Figure 11b shows m/e 32 peak behavior.
The ion current displays constant intensity until scan #65, where the
complex apparently vaporizes. The constant intensity of this ion
current may well indicate evolution of O₂ (and, thus, detection of
O₂⁺) as soon as the sample is placed in the high vacuum.⁵⁸

The [Cu(I)(imidH)₂DAP](ClO₄) complex exhibits a solid state mag-
netic moment of 0.8 μ₀ (R.T.), a high value probably due to some
contamination of Cu(II) impurity. Even this solid exhibits a weak
esr signal, indicating small but significant Cu(II) impurities are
present (vide infra). The oxygenated solid, a green powder, has a
μₑₑₑ(₂R.T.) = 1.5 μ₀/Cu. The moment did not increase with time. If
the green solid is placed under vacuum at 80°C for six hours, the
original red color appeared to be regenerated, yielding a μₑₑₑ(₂R.T.) =
1.2 μ₀/Cu. These results indicate that, indeed, oxygenation/oxidation
processes are occurring in the solid state, but that the behavior is
very ill-defined. The oxygenated solid does not appear stable over
long periods of time, as the green solid turns brown within 48 hours.
This behavior parallels the solution behavior in that oxygenation by-
products appear to aid in sample decomposition.

**Electrochemical Studies.** Electrochemical measurements provide a
very sensitive method for observing the solution behavior of the
complexes with O₂. Especially interesting are the comparative studies
between the [M⁺ⁿ(imidH)₂DAP]+ⁿ and [M⁺ⁿ(py)₂DAP]+ⁿ complexes and
information gathered therefrom as criteria of relative compound
stability. Cyclic voltammograms were obtained for each compound at
platinum button electrodes in a variety of solvents. It would be use-
ful to compare the redox potentials obtained here with other systems, but unfortunately very few electrochemical studies have been performed on Cu(II) compounds, and those available concern only four coordinate copper. The studies on four coordinate copper complexes clearly indicate that distortions from tetragonal symmetry for Cu(II) complexes destabilizes Cu(II), so that Cu(I) stability is enhanced as the geometry becomes more tetrahedral. 47 Electronic factors, like the presence of donor atoms known to stabilized Cu(I), such as sulfur, do not seem to have as dramatic an effect on the potentials as the geometry.

There is no systematic study of pentacoordinate Cu(II) compounds, for which reduction potentials would be expected to be different from four coordinate solely on the basis of geometry. The one well characterized five coordinate Cu(I) species reported thus far has a Cu(II) → Cu(I) reduction potential -1.0 V in CH₃CN solutions at platinum electrodes vs. Ag/AgNO₃ (or -0.6 vs. NHE). There have, as yet, been no reported redox data on hemocyanin, and because of the very slow redox equilibration in this huge protein, such information will probably not be forthcoming. However, many smaller copper proteins display remarkably positive (- +0.5 V vs. NHE) Cu(II)/Cu(I) reduction potentials indicative of Cu(I) stabilization. 59

In the absence of O₂, [Cu(II)(imidH)₂DAP](ClO₄)₂ and [Cu(II)(py)₂DAP](ClO₄)₂ were characterized by reversible one electron transfers. Current function values were independent of scan rate and peak to peak separations were consistent with one electron reduction processes in each solvent. The formation of a Cu(I) species was verified coulometrically, with the green Cu(II) solutions turning red (the characteristic Cu(I) color) under an inert atmosphere by the end
of the electrolysis period. The half-wave potentials and diffusion coefficients are compiled in Table VII. From the data it is possible to unambiguously assign the reversible redox process as

\[
[Cu(II)(L)]^{+2} \rightleftharpoons e^{-} \rightarrow [Cu(I)(L)]^{+1}
\]

The Zn(II) analogs are not reduced until a much more negative potential, supporting the above assignment. The \([Cu(I)(imidH)_2DAP]^+\) cation yielded no oxidation wave in any solvent, and this behavior is attributed to immediate oxidation/oxygenation at the electrode surface. Characteristics of this species, electrochemically generated from the Cu(II) complex, are discussed below. The \([Cu(I)(py)_2DAP]^+\) complex did exhibit a reversible oxidation wave in CH\(_3\)CN under N\(_2\) at -0.18 V (SCE) but the compound is not indefinitely solution stable; for example, after one hour, the cathodic and anodic peak potentials were observed to shift, with a 20 mV increase in peak separation, as shown in Figure 12c.

The electrochemical data for each compound in CH\(_3\)CN are listed in Table VIII. The potential of the Cu(II)/Cu(I) couple for \([Cu(II)(py)_2DAP]^{+2}\) is 120 mV more positive than the \([Cu(II)(imidH)_2DAP]^{+2}\) complex, indicating a possible stabilization of Cu(I) in the former complex. This is not surprising since pyridine should provide superior \(\pi\) back-bonding capability as compared to imidazole, thus stabilizing the Cu(I) state.\(^{45,60,61,62}\)

Only one reduction process was observed for each of the Zn(II) complexes. In CH\(_3\)CN, \([Zn(II)(py)_2DAP](CIO_4)_2\) gave a reversible one electron reduction at -1.08 V (SCE), probably corresponding to a ligand centered reduction. At slow scan rates (less than 2 V/s), the
TABLE VII
Variable Solvent Voltammetric Data for the Complexes at $10^{-3}$ M and 0.1 M in TBAP. Scan Rate = 50 mV/c.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$E_{1/2}$ (V)</th>
<th>$D \times 10^5$ (cm$^2$/s)</th>
<th>$E_{p_a} - E_{p_c}$ (V)</th>
<th>$E_{p_c} - E_{p_c/2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="ClO$_4$">Cu(II)(imidH)$_2$DAP</a>$_2$</td>
<td>CH$_3$CN</td>
<td>-0.30</td>
<td>0.50</td>
<td>.102</td>
<td>.065</td>
</tr>
<tr>
<td>DMF</td>
<td>-0.27</td>
<td>0.30</td>
<td>.089</td>
<td>.066</td>
<td></td>
</tr>
<tr>
<td>Me$_2$SO</td>
<td>-0.27</td>
<td>0.12</td>
<td>.107</td>
<td>.072</td>
<td></td>
</tr>
<tr>
<td>pyridine</td>
<td>-0.20</td>
<td>0.25</td>
<td>.089</td>
<td>.079</td>
<td></td>
</tr>
<tr>
<td><a href="ClO$_4$">Cu(II)(py)$_2$DAP</a>$_2$</td>
<td>CH$_3$CN</td>
<td>-0.17</td>
<td>1.08</td>
<td>.073</td>
<td>.063</td>
</tr>
<tr>
<td>DMF</td>
<td>-0.13</td>
<td>0.41</td>
<td>.070</td>
<td>.060</td>
<td></td>
</tr>
<tr>
<td>Me$_2$SO</td>
<td>-0.15</td>
<td>0.16</td>
<td>.070</td>
<td>.064</td>
<td></td>
</tr>
<tr>
<td>pyridine</td>
<td>-0.63*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* Unobtainable at platinum electrodes; obtained at DME, reported vs. SCE. $E$ vs. log$[i/(i - i_d)] = 70$ mV.
FIGURE 12

Cyclic Voltammograms of the Copper Complexes in
Deoxygenated CH$_3$CN at $10^{-3}$ M and 0.1 M TBAP.
Scan Rate = 200 mV/s.

a) [Cu(II)(py)$_2$DAP](ClO$_4$)$_2$

b) [Cu(I)(py)$_2$DAP](ClO$_4$)

c) [Cu(I)(py)$_2$DAP](ClO$_4$) solution
after 1 h under N$_2$.
TABLE VIII
Voltammetric Data for the ClO₄⁻ Complexes in CH₃CN
at 10⁻³ M and 0.1 M in TBAP, at Room Temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Scan Rate (V/s)</th>
<th>E₁/₂ (V)</th>
<th>Eₚa - Eₚc (V)</th>
<th>Eₚc - Eₚc/2 (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(II)(imidH)₂DAP]²⁺</td>
<td>.05</td>
<td>-0.30</td>
<td>0.102</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>.10</td>
<td>-0.30</td>
<td>0.108</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>.20</td>
<td>-0.30</td>
<td>0.115</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>-0.31</td>
<td>0.138</td>
<td>0.086</td>
</tr>
<tr>
<td>[Cu(II)(py)₂DAP]²⁺</td>
<td>.05</td>
<td>-0.17</td>
<td>0.080</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>.10</td>
<td>-0.17</td>
<td>0.080</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>.20</td>
<td>-0.17</td>
<td>0.080</td>
<td>0.060</td>
</tr>
<tr>
<td>[Cu(I)(py)₂DAP]⁺</td>
<td>.05</td>
<td>-0.18</td>
<td>0.100</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>.10</td>
<td>-0.18</td>
<td>0.090</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>.20</td>
<td>-0.18</td>
<td>0.120</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>-0.19</td>
<td>0.140</td>
<td>0.070</td>
</tr>
<tr>
<td>[Zn(II)(imidH)₂DAP]²⁺</td>
<td>.20</td>
<td>-1.21*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>-1.17</td>
<td>.140</td>
<td>.050</td>
</tr>
<tr>
<td>[Zn(II)(py)₂DAP]²⁺</td>
<td>.05</td>
<td>-1.08</td>
<td>0.080</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>.10</td>
<td>-1.08</td>
<td>0.110</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>.20</td>
<td>-1.10</td>
<td>0.150</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>-1.10</td>
<td>.150</td>
<td>.050</td>
</tr>
</tbody>
</table>

* No anodic wave obtained at this sweep rate; Eₚc reported.
[Zn(II)(imidH)$_2$DAP]$^{+2}$ complex did not yield an anodic wave. The cathodic peak gave constant $i_p/V^{1/2}$ values and the peak geometry was consistent with the formulation of this process as a one electron transfer. The cyclic voltammograms at slow scan rates are shown in Figure 13. As the scan rate was increased to 50 V/s, a coupled anodic process began to appear ca. 130 mV anodic of the reduction peak. At fast scans of 10 V/s, shown in Figure 14, [Zn(II)(imidH)$_2$DAP](ClO$_4$)$_2$ yielded a $E_{1/2} = -1.10$ V. $i_p/i_c$ ratios for this process began to approach unity as the scan rate increased. Thus, an EC mechanism was indicated in which a reversible charge transfer is followed by an irreversible chemical reaction at the electrode surface.$^{63}$ No attempt was made to identify the reduction products of either zinc complex.

It is tempting to rationalize the EC process in the [Zn(II)(imidH)$_2$DAP]$^{+2}$ complex and not in the [Zn(II)(py)$_2$DAP]$^{+2}$ complex, as due to the presence of the imidazole proton, which may provide a mechanism for fast chemical reaction subsequent to electron transfer.$^{64}$

Cyclic voltammetry provides an elegant method of observing the oxygenation process for [Cu(I)(imidH)$_2$DAP]$^+$, formed electrochemically from the Cu(II) compound. Figure 15 shows the behavior of the complex in Me$_2$SO (1.6 mM) at platinum electrodes and at sweep rates of 200 mV/s. Table IX summarizes the data for each scan where (a) is under N$_2$ and (b) through (d) are under O$_2$ at varying conditions. At a scan rate of 200 mV/s, the voltammograms (a) and (b) of the figure are identical for the entire potential range. The potential sweep was terminated in these runs at -0.60 V in order not to reduce any dissolved O$_2$ to O$_2^-$. If the potential were held at -0.60 V for 9 s (c), no reverse oxidation of the Cu(II) reduction product was observed, indicating the species
FIGURE 13

Cyclic Voltammograms of the Complexes in Deoxygenated CH$_3$CN at 10$^{-3}$ M and 0.1 M TBAP. Scan Rate: 100 mV/s.

a) [Zn(II)(imidH)$_2$DAP](ClO$_4$)$_2$

b) [Zn(II)(py)$_2$DAP](ClO$_4$)$_2$
FIGURE 14

Photographic Traces of the Fast (10 V/s) Scans for the Zinc(II) Complexes in Deoxygenated CH₃CN at 1.5 mM and 0.1 M in TBAP.

a) [Zn(II)(imidH₂DAP)](ClO₄)₂

b) [Zn(II)(py)₂DAP](ClO₄)₂
FIGURE 15

Cyclic Voltammograms of [Cu(II)(imidH)₂DAP](ClO₄)₂ in Me₂SO at 1.6 mM and 0.1 M in TBAP. Scan Rate = 200 mV/sec.

a) Under N₂.

b) Under O₂.

c) Under O₂, and the potential held after the cathodic sweep at -0.60 V for 9 s, then scanned back (→ →).

d) Under O₂, and the potential held after the cathodic sweep at -0.60 V for 27 s, then scanned back (→ →).
TABLE IX
Cyclic Voltammetric Data for [Cu(II)(imidH)₂DAP](ClO₄)₂ at 1.6 mM and 0.1 M in TBAP, under N₂ or O₂. Scan Rate = 200 mV/sec. Description of Figure 15.

<table>
<thead>
<tr>
<th>Description</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Under N₂.</td>
<td>( E_{pc} = -0.32 \text{ V} )</td>
</tr>
<tr>
<td></td>
<td>( E_{pa} = -0.22 )</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2} = 0.27 )</td>
</tr>
<tr>
<td></td>
<td>( E_{pc} - E_{pc/2} = 0.065 )</td>
</tr>
<tr>
<td>b) Under O₂</td>
<td>Identical to (a)</td>
</tr>
<tr>
<td>c) Under O₂, held at (-0.60 \text{ V}) for 9 s.</td>
<td>( E_{pc} = -0.33 \text{ V} )</td>
</tr>
<tr>
<td></td>
<td>First Scan:</td>
</tr>
<tr>
<td></td>
<td>Second Scan:</td>
</tr>
<tr>
<td></td>
<td>( E_{pc} = -0.44 )</td>
</tr>
<tr>
<td></td>
<td>( E_{pa} = -0.20 )</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2} = -0.32 )</td>
</tr>
<tr>
<td></td>
<td>( E_{pc} - E_{pc/2} = 0.065 )</td>
</tr>
<tr>
<td>d) Under O₂, held at (-0.60 \text{ V}) for 27 s.</td>
<td>( E_{pc} = 0.33 \text{ V} )</td>
</tr>
<tr>
<td></td>
<td>First Scan:</td>
</tr>
<tr>
<td></td>
<td>Second Scan:</td>
</tr>
<tr>
<td></td>
<td>( E_{pc} = -0.46 )</td>
</tr>
<tr>
<td></td>
<td>( E_{pa} = -0.20 )</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2} = -0.33 )</td>
</tr>
<tr>
<td></td>
<td>( E_{pc} - E_{pc/2} = 0.120 )</td>
</tr>
</tbody>
</table>
at the electrode surface had reacted with $O_2$. When the potential was held at -0.60 V with the complex under $N_2$, the reversible wave was obtained, which implies that the observed behavior is due to a reaction of the electrochemically generated species only with $O_2$. The second sweep shown in Figure 15(c) reveals the reformation of $[\text{Cu(II)(imidH}_2\text{DAP}]^{+2}$ and its normal coupled oxidation. After stirring the solution, the cathodic wave was scanned again, and the potential held at -0.60 V for 27 s (Figure 15(d)). Again, no anodic process was observed. The second scan showed reformation of $[\text{Cu(II)(imidH}_2\text{DAP}]^{+2}$ but with a cathodic shift in the reduction potential concomitant with a decrease in peak current and a broadening of peak shape. This behavior clearly indicates a chemical reaction subsequent to the electron transfer at longer exposure times to $O_2$ (i.e., longer hold times). A cathodic peak could be observed on any re-scan only if the potential were swept back to +0.80 V. No cathodic peak could be observed if the potential were held at less than +0.80 V on the anodic scan. Therefore, the reappearance of the Cu(II) reduction is due to an oxidative process at ca. +0.80 V, and not to diffusion of the Cu(II) species to the electrode. The oxidation process is obscured by the Me$_2$SO solvent edge, however.

Reappearance of the Cu(II) species by an oxidation mechanism could be due to (1) oxidation of the solvent and subsequent fast reaction with the oxygenated species so that Cu(II) is produced, or (2) direct oxidation of the oxygenated Cu(I) complex so that the original Cu(II) is reformed. The latter possibility is most consistent with the behavior of this species since the shape and characteristics of the wave on a successive re-scan are variable depending on reaction
time (or hold time) with \( O_2 \). Figure 16 provides a summary of the events consistent with the observed behavior of the oxygenation process. In these \( O_2 \) saturated solutions, almost all of the Cu(I) species produced at the electrode reacts with \( O_2 \) within 9 seconds, as shown in Figure 15(c). It is now generally accepted, largely on the basis of Co(II) - \( O_2 \) work, that \( O_2 \) adds to a metal center via an "internal oxidative addition reaction," i.e.,

\[
M^{+n} + O_2 \rightarrow M^{+(n+1)} - O_2^-
\]

in which the metal is formally oxidized and the \( O_2 \) formally reduced. If this formalism is accurate, then an electron transfer from the Cu(I) center is surely concomitant with \( O_2 \) adduct formation, so that the species to be oxidized on an anodic scan formally contains Cu(II).

The immediate product of oxygenation would be expected to be monomeric, i.e., \([\text{Cu(II)}(L) - O_2^-]\), which would be the first step in the formation of a binuclear species, \([\text{Cu(II)}(L) - O_2^= - \text{Cu(II)}(L)]\). The binuclear product is consistent with the stoichiometry of the \( O_2 \) uptake in this complex. It is possible that either the monomeric or dimeric (formally a binuclear peroxy bridged) species is readily oxidizable at sufficiently positive potentials, thus permitting observance of a Cu(II) wave on a re-scan as in Figure 15(c). The irreversibility observed on a re-scan [Figure 15(c) and (d)] could be due to decomposition of the oxygenated product into intermediates not readily oxidizable below +0.80 V, for example, species such as \([\text{CuL}]^{2+}\), or \([\text{Cu(II)L-O}_2^=]\) as shown in Figure 16. All oxygenated solutions eventually decompose (within hours), as evidenced by their changing color and the production of brown precipitate. Electrochemical treatment appears to accelerate
FIGURE 16

Proposed Mechanism for Oxygenation of $[\text{Cu}^I(\text{imidH})_2\text{DAP}]^+$.

$[\text{Cu}^{II}\text{L}]^{2+}$ (green) $\xrightarrow{-0.29\text{V}}$ $[\text{Cu}^I\text{L}]^+$ (red)

$(S=1/2)$

$\xrightarrow{+O_2}$ $(S=0)$

$\xleftarrow{-O_2}$

$[\text{LCu}^{II-0^-}]^+$ (green)

$(S=0)$

$[\text{Cu}^I\text{L}]^+$ $\xrightarrow{\downarrow}$ $-\text{[Cu}^I\text{L}]^+$

$[\text{LCu}^{II-0^-} \text{O}^- \text{Cu}^{II}\text{L}]^{2+}$ (green)

$(S=0?)$

$\xrightarrow{\downarrow}$

$[\text{Cu}^{II}\text{L}]^{2+}$ + $[\text{Cu}^{II-0^-}]$ (?)

$(S=1/2)$

$(S=1/2)$

$\xrightarrow{\text{H}^+}$

$[\text{Cu}^{II}\text{L}]^{2+}$ + $\text{HO}_2^-$

Unknown Brown Product(s)
the decomposition process since brown precipitate is observed to form after only a few scans in O₂ saturated solutions (i.e., within minutes). Formation of such reactive species is certainly a viable explanation in view of manometric studies showing complete loss of O₂ reactivity in a multiply cycled solution over long periods of time.

The [Cu(I)(imidH)₂DAP]⁺ complex exhibits the same oxygenation behavior in Me₂SO, CH₃CN, DMF, and pyridine, but the rate is clearly solvent dependent, as noted above: CH₃CN = DMF > Me₂SO > pyridine. In CH₃CN, for example, even a fast (200 mV/s) scan in O₂ saturated solutions did not yield an anodic peak. This cyclic voltammetry result corroborates the above qualitative observations that there is a solvent effect on the oxygenation rate. Since the electrochemical measurements occur in saturated O₂ solutions, it is inferred that the observed rate dependence on solvent is not due to bulk solvent properties, such as rate of O₂ dissolution, but rather to [solvent · · · Cu(L)⁺] interactions of some nature. Since the rates parallel solvent characteristics such as donor number and basicity (Table X), the correlations suggest some kind of solvent promoted inhibition to the site of O₂ coordination at the Cu(I) center. However, since the above electronic spectral data for [Cu(I)(imidH)₂DAP]⁺ give no indication of solvent participation in the primary coordination sphere, it may be that close association of the solvent molecules with the ligand affects the oxygenation rate. Table X shows values of Gutman's Donor Number and Drago's C/E parameters. Both of these parameters are measures of Lewis base character for these solvents. The notable shared characteristic of these solvents is their basic nature, thus an acidic site seems the most likely position for solvent interaction. The only
### TABLE X

Some Solvent Characteristics.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Donor Number $^a$</th>
<th>C/E $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>14.1</td>
<td>1.55</td>
</tr>
<tr>
<td>DMF</td>
<td>26.6</td>
<td>2.02</td>
</tr>
<tr>
<td>Me$_2$SO</td>
<td>29.8</td>
<td>2.13</td>
</tr>
<tr>
<td>pyridine</td>
<td>33.1</td>
<td>5.47</td>
</tr>
</tbody>
</table>

---


acidic proton of the molecule is the imidazole hydrogen, and this may be the site susceptible to solvent interactions such as hydrogen bonding. An equilibrium between the imidazole and its deprotonated form seems unlikely, as no shift in electronic absorption band position was observed upon the addition of small increments of acid. Substitution of the imidazole proton would allow better understanding of the function of this hydrogen in the oxygenation process. Unfortunately, this behavior is not clear and thus far only the observation of the apparent relationship between the basic character of the solvent and the oxygenation rates can be noted.

In contrast to the $[\text{Cu}(I)(\text{imidH})_2\text{DAP}]^+$ species, the reduction product of $[\text{Cu}(II)(\text{py})_2\text{DAP}]^{+2}$ does not react with $O_2$. The cyclic voltammograms are identical in all solvents saturated with $N_2$ or $O_2$. There is no reaction with $O_2$ even after holding the potential at $-0.61\ \text{V}$ for 30 s in $\text{CH}_3\text{CN}$. This is probably the best method for verifying that the electrochemically prepared Cu(I) species does not react with $O_2$. However, for $[\text{Cu}(I)(\text{py})_2\text{DAP}]^+$, a well defined reversible wave appears under $N_2$, but no wave is observed in $O_2$ saturated solutions. A broad, ill-defined wave can be regenerated only after bubbling $N_2$ through the solution for five minutes. Considering the slow, continuous, irreversible uptake of $O_2$ by solutions of this complex, it appears likely that a ligand centered oxidation process is occurring which may be catalyzed by the presence of Cu(I). Such catalytic properties of Cu(I) species are known to be a problem in direct chemical synthesis of Cu(I) compounds, probably due to unstable intermediates.$^{32}$ Nevertheless, this behavior is somewhat surprising because of the apparent stabilization of Cu(I) by the $(\text{py})_2\text{DAP}$ ligand as compared to the $(\text{imidH})_2\text{DAP}$
ligand.

**ESR Studies.** Consistent with the stoichiometry of $O_2$ uptake, the final product of the oxygenation reaction for $[\text{Cu(I)(imidH)}_2\text{DAP}]^+$ is formulated as a binuclear adduct, $[\text{LCu(II)} - O_2^- - \text{Cu(II)L}]$. It is likely (but not certain) that the adduct would be diamagnetic via antiferromagnetic exchange between the formally Cu(II) ($S=1/2$) centers in the binuclear complex (Figure 16). This situation is invoked to explain the diamagnetism and silent esr behavior of the oxyhemo-cyanins. In Figure 17, the esr spectra of $[\text{Cu(II)(imidH)}_2\text{DAP}]^{+2}$ and $[\text{Cu(I)(imidH)}_2\text{DAP}]^+$ are shown as $\text{Me}_2\text{SO}$ glasses at ca. 100 K. Both spectra have the characteristic signature of a magnetically dilute Cu(II) centers with normal (but different) $g_{||}$ and $g_{\perp}$ values as listed in Table XI. The Cu(II) complex yields the signal shown in (a), and (b) - (f) are the spectra for oxy/deoxy cycles of the Cu(I) complex. A freshly prepared solution of Cu(I) complex yields spectrum (b), obviously containing a significant amount of Cu(II) species, surely due to Cu(II) impurities from starting material. Integration of the signal indicates about 20% of the available copper is accounted for [i.e., is present as Cu(II)]. If this original red solution is oxygenated, spectrum (c) results, with no perceptible increase in the Cu(II) signal strength. Thus, it can be inferred that the $O_2$ adduct is essentially diamagnetic and that the detected Cu(II) species are due to by-products of the oxygenation reaction such as those shown in Figure 16. If the oxygenated solution is deoxygenated, spectrum (d) results, of about the same intensity as (b) and (c), but with a slight upfield shift of $g_{||}$ and a slight increase in the signal at $g = 2.1$. 
FIGURE 17

ESR Spectra for the Complexes Recorded at X-band
Frequencies in Me₂SO at ca. 100 K. [Cu] = 10⁻³ M.

a) [Cu(II)(imidH)₂DAP](ClO₄)₂

b) [Cu(I)(imidH)₂DAP](ClO₄)

c) Solution (B) exposed to O₂
(i.e., oxy of first cycle)

d) Solution (C) deoxygenated
(i.e., deoxy of first cycle)

e) Solution (D) exposed to O₂
(i.e., oxy of second cycle)

f) Solution (E) deoxygenated
(i.e., deoxy of second cycle)
TABLE XI

ESR Data for the Complexes as Me₂SO Glasses at ca. 100 K, Recorded at X-band Frequencies. [Cu] = 10⁻³ M.

<table>
<thead>
<tr>
<th>Complex</th>
<th>gₘ</th>
<th>A x 10³, cm⁻¹ (A in Gauss)</th>
<th>g₁</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="ClO%E2%82%84">Cu(II)(imidH)₂DAP</a>₂</td>
<td>2.27</td>
<td>18.0 (170)</td>
<td>2.06</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Cu(I)(imidH)₂DAP</a>*</td>
<td>2.22</td>
<td>15.0 (145)</td>
<td>2.10</td>
</tr>
<tr>
<td>b)</td>
<td>2.23</td>
<td>14.6 (140)</td>
<td>2.10</td>
</tr>
<tr>
<td>c)</td>
<td>2.22</td>
<td>15.5 (150)</td>
<td>2.09</td>
</tr>
<tr>
<td>d)</td>
<td>2.22</td>
<td>15.5 (150)</td>
<td>2.09</td>
</tr>
<tr>
<td>e)</td>
<td>2.22</td>
<td>15.0 (145)</td>
<td>2.09</td>
</tr>
<tr>
<td>f)</td>
<td>2.21</td>
<td>15.5 (150)</td>
<td>2.05</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Cu(II)(py)₂DAP</a>₂</td>
<td>2.21</td>
<td>15.5 (150)</td>
<td>2.05</td>
</tr>
</tbody>
</table>

* Refer to Figure 17.
Spectra (e) and (f) are for the second cycle oxy and deoxy solution, respectively, and again no significant increase in Cu(II) concentration is observed for these recycles. It is curious, however, that overall Cu(II) concentration does not seem to increase upon successive oxy/deoxy cycles, although initially decomposition products were considered to be irreversibly oxidized species. It appears, therefore, that at least some of the oxygenation by-products may also be diamagnetic, which means that the ligand may be affected by oxidation. The esr spectrum of $[\text{Cu(II)}(\text{py})_2\text{DAP}]^{+2}$ has the same features as $[\text{Cu(II)}(\text{imidH})_2\text{DAP}]^{+2}$ but with slightly shifted $g$ values. The $[\text{Cu(I)}(\text{py})_2\text{DAP}]^{+}$ cation yielded no signal which is consistent with its relative $\text{O}_2$ insensitivity in solution.

Unfortunately, the esr spectra provide inconclusive information about the molecular structure of the complex, but they are similar to spectra for other well known pentacoordinate Cu(II) species. For example, $[\text{Cu(II)}(\text{NH}_3)_2(\text{SCN})_3]\text{Ag}$ (with a trigonal bipyramid structure), and the pentacoordinate Cu(II) complex of glycylglycinate and 2,9-dimethyl-1,10-phenanthroline, $[\text{Cu(II)}(\text{glygly})(\text{phen})]$, both have a very similar esr spectrum to that shown in Figure 17(a). Finally, it is very interesting to note that the esr signal from oxidized hemocyanin [the Cu(II) form] also exhibits an esr spectrum remarkably similar to that of $[\text{Cu(II)}(\text{imidH})_2\text{DAP}]^{+2}$ in Figure 17(a).

Conclusion. Accumulated spectral, manometric, and electrochemical data have unquestionably proven that the $[\text{Cu(I)}(\text{imidH})_2\text{DAP}]^{+}$ cation is a reversible Cu(I) $\text{O}_2$ carrier in solution. This discovery is particularly exciting because Cu(I) is notoriously sensitive to irreversible
oxidation by O$_2$ in solution, yet this small molecule has none of the safeguards against irreversible oxidation such as those afforded by a protein environment. The [Cu(I)(imidH)$_2$DAP]$^+$ cation represents an excellent model for the hemocyanin active site interaction with O$_2$ because the compound undergoes multiple reversible oxygenation cycles at room temperature. Furthermore, the Cu:O$_2$ stoichiometry is identical to that observed in hemocyanin, and the Cu(I) center is ligated by two imidazole moieties, as is apparently the case in the protein.

The donor set unquestionably plays a dual role which aids in the facile oxidation/reduction required for the formation of the O$_2$ adduct. The presence of imidazole helps stabilize both oxidation states, allowing for the formation and dissociation of the O$_2$ adduct. The flexible multidentate ligand provides coordination geometries stabilizing both states. This behavior is quite different if the imidazole moieties are replaced by pyridine groups, as in [Cu(I)(py)$_2$DAP]$^+$, in which O$_2$ adduct formation is inhibited. The superior π-accepting (py)$_2$DAP system apparently helps stabilize the Cu(I) oxidation state by providing a mechanism for better electron delocalization.

These and other related Cu(I) model systems should reveal much about the heretofore unknown reversible binding of O$_2$ by Cu(I) complexes. The model reported here is a good first step toward understanding such compounds, which, unlike their biologically relevant Co(II) and Fe(II) counterparts, have escaped detection for 30 years.
REFERENCES AND NOTES


10. This list of reviews on hemocyanin covers most of the information in the text:


(h) N. Shaklai, A. Gafni, and E. Daniel, Biochem., 17, 4438 (1978).


29. Imidazole is thought to be present as a ligand in hemerythrin, see Reference 9. It has been postulated to be the mechanism of antiferromagnetic coupling for cytochrome c oxidase, see: G. Palmer, G. T. Babcock, and L. E. Vickery, Proc. Natl. Acad. Sci. USA, 73, 2206 (1976).


54. Professor I. Bernal, University of Houston, private communication. The [Zn(II)(imidH)2DAP](ClO4)2 and [Cu(II)(imidH)2DAP](ClO4)2 structures are presently undergoing further refinement, and a structure is planned for the Cu(I) species.


58. Probably the best method that will allow O₂ detection is a gas chromatographic experiment where the gas evolved is collected and then analyzed by gc. Use of an oxygen electrode to monitor O₂ evolution was not successful.


64. Substitution at the amine hydrogen by a methyl group would more clearly define the role of the imidazole proton; efforts are continuing; L. J. Wilson, private communication.


66. Ligand oxidation is known to occur in a variety of Fe(II) and Ru(II) complexes by oxidative dehydrogenation; see for example: V. L. Goedken, Chem. Comm., 207 (1972); V. L. Goedken and D. H. Busch, J. Am. Chem. Soc., 94, 7355 (1972); and F. R. Keene, D. J. Salmon, and T. J. Meyer, J. Am. Chem. Soc., 98, 1884 (1976). In situ generation of the Cu(I) species by interfacing esr and electrochemical techniques would be the best way to investigate these processes.

APPENDIX I

A NOTE ON THE USE OF THE WARBURG MANOMETER

A complete description of the use of the Warburg apparatus appears in Umbreit, Burris, and Stauffer's "Manometric Techniques,"¹ so only a brief summary appears here. The apparatus originally was used for measurements of oxygen uptake and is also called a Warburg respirometer. Warburg manometers have commonly been used to monitor oxygen and carbon monoxide uptake by various Co(II) complexes.²-⁴ Once the volume in the apparatus is known, the pressure difference in the manometer is measured by the difference in the manometer fluid levels wherein the volume of gas is kept constant but the pressure varies, allowing the determination of moles of gas evolved or absorbed.

Figure 1a illustrates a standard Warburg apparatus and Figure 1b shows the pressure change in an uptake experiment. The "dead space" volume is measured by filling it with mercury and weighing the amount of mercury required to fill the manometer to a premarked level. The calibration with mercury should be performed three or four times. This method of calibration is discussed fully in Chapter 4 of Reference 1 and in Reference 5 and is shown in Figure 2. As it is unlikely that one can fill the manometer to the same M₂ level (see Figure 2) on each calibration run, a mercury weight vs. M₂ plot yields a straight line from which mercury weight, and thus volume, can be determined at various points along the manometer scale. Each manometer, with its own marked flask, should be calibrated in this manner.

Once the gas volume is known, the manometers are filled by syringing a fluid into the reservoir (see Figure 1). This requires a
FIGURE 1

a) The Warburg constant volume manometer.
   
   F = flask
   S = sidearm
   G = sidearm stopper with side vent
   R = fluid reservoir
   T = three-way stopcock

b) Illustration of gas uptake.

See Reference 1, page 1.
Method for Calibration of Warburg Flasks and Manometers (see Reference 5).
fluid that is sensitive enough to relatively small pressure changes. Mercury is too dense to be used in this way. Ideally, a colored solution with a density between 1 and 5 g/mL should be used, and since most organic solvents are too volatile or too reactive, various H₂O solutions are used. For experiments in this work, the manometer fluid was prepared by adding 10 mL of bromthymol blue and 5 drops of liquid Alconox (as surfactant) to 500 mL H₂O. The density of this solution varied slightly with each preparation, but usually gave a value of approximately .99 g/mL. Any water soluble indicator or dye which will darkly color the solution is adequate for use in the fluid.

To calculate the volume of gas uptake, one must consider the initial gas and solution volumes and pressure difference after uptake. To accomplish this most simply, values are considered in terms of standard conditions, thus

\[
\frac{P_o V_o}{T_o} \text{ (at STP)} = \frac{P V_g}{T}
\]

where \( V_g \) is the "dead space" volume of the gas, \( T \) is the temperature of a run, and \( P \) is the pressure inside the manometer. \( P \) has components due to the pressure of the pure, dry gas and the vapor pressure of the solvent, so the total pressure is \( P - R \). Therefore, initially,

\[
V_o = \frac{V_g (273/T)(P-R)}{P_o}
\]

At the end of an uptake measurement period, the gas pressure changes by an amount \( h \), but \( V_g \) and \( T \) have remained constant, so
\[ V_f = V_g \frac{(273/T)(P-R-h)}{P_0} \]

Thus, \( V_{\text{uptake}} = V_f - V_0 = -h \frac{V_g (273/T)}{P_0} \)

which can be simplified to \( V_{\text{uptake}} = h \times k \), where \( k \) is the flask constant, which is calculated knowing the total volume of the apparatus, the temperature, and the standard pressure, \( P_0 \).

For example, in a typical measurement the total volume of the manometer when the fluid level was set at the 20 cm mark was 23.84 mL, or 23,840 \( \mu \text{L} \). When 3 mL of solvent is used, this results in a \( V_g \) of 20,840 \( \mu \text{L} \). Mercury has a density of 13.5462 g/mL at 20°C (293 K), and the manometer fluid had a density of .99775 g/mL. Thus,

\[ P_0 = 760 \times \frac{13.5462}{.99775} = 10318. \]

This yields a \( k \) of \( \frac{23840}{10318} \times \frac{273}{293} = 1.8818 \). The difference between manometer fluid levels is \( h \), so a typical volume would be equal to \( h \) (\( = 60 \text{ mm} \)) \( \times k \) (\( = 1.8818 \)) = 112.9 \( \mu \text{L} \). Thus, 112.9 divided by molar volume at STP (22.6 \( \times 10^6 \) \( \mu \text{L} \)) equals 5.04 \( \times 10^{-6} \) moles \( O_2 \).

For every solvent in these uptake experiments, several solvent blanks were run to determine the amount of gas absorbed by the solvent alone. The solvent was deoxygenated by purging with \( N_2 \) for 15 minutes and syringed into the flask. Then the manometer was flushed with \( N_2 \) for a few minutes to allow the solvent to reach constant temperature in the water bath, and then the manometer was flushed with \( O_2 \) for exactly one minute. Then, as rapidly as possible, and in this order,
1) the O₂ line was removed, 2) the sidearm stopper was positioned, and 3) the top stopcock was closed. The system was allowed to equilibrate in the water bath for one minute, the pressure was adjusted to be equalized with the atmospheric pressure, and the entire apparatus was then tilted to effectively mix gas and solvent. When an uptake measurement on a sample was performed, the solid was weighed into the side port, and the solvent was added to the flask and then the contents were treated as described above for the blank. It is essential that the blank and the sample runs be treated identically, as there is undoubtedly some oxygen absorption as soon as flushing with O₂ begins. The h for the blank was subtracted from the h for the run and the uptake volume calculated. Data for several runs of [Cu(I)(imidH)₂DAP]-(ClO₄) in Me₂SO are summarized in Table I.

The Thermobarometer. The initial pressure is assumed to remain constant; however, over the time of a run (typically, 20 minutes), slight ambient temperature or pressure changes will affect h. To compensate for any changes, a second Warburg manometer, containing approximately the same amount of solvent as the first, is used. At the beginning of a run the pressure in this manometer is adjusted to atmospheric, and the stopcock closed. It is not necessary to flush this manometer with any gas. Figure 3 illustrates the use of the second manometer, or thermobarometer, to account for temperature or pressure differences of the surroundings. The h from the thermobarometer is subtracted from h of the manometer for each run. Table II shows typical readings for several blank runs of 2.6 mL Me₂SO samples.
TABLE I

Manometric Measurements and Results

for \([Cu(\text{imidH})_2\text{DAP}](\text{CIO}_4)\) in \(\text{Me}_2\text{SO}\).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Moles of Sample ((x 10^6))</th>
<th>((h_{m-h_{TB}})-h_{\text{blank}})</th>
<th>(k)</th>
<th>Moles (O_2) ((x 10^6))</th>
<th>(O_2/Cu)</th>
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FIGURE 3

Illustration of the Use of the Thermobarometer.

(Taken from Reference 1, Page 6)
**TABLE II**

Blank Runs on 2.6 mL Samples of Me₂SO.

<table>
<thead>
<tr>
<th>$h_m$(mm)</th>
<th>$h_{TB}$(mm)</th>
<th>$h_{blank}$(mm)</th>
<th>T(°C)</th>
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<tr>
<td>-22</td>
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REFERENCES


FIGURE I

Nujol Mull Infrared Spectrum of

A) Histamine, free base.

B) \{Bis-2,6[1-(2-imidazol-4-ylethylimino)ethyl]pyridine\}-copper(I) Perchlorate.
FIGURE 2

Nujol Mull Infrared Spectrum of

A) \{\text{Bis-2,6[1-(2-imidazol-4-ylethylimino)ethyl]pyridine}\}-copper(II) Perchlorate.

B) \{\text{Bis-2,6[1-(2-imidazol-4-ylethylimino)ethyl]pyridine}\}-zinc(II) Perchlorate.
FIGURE 3

Nujol Mull Infrared Spectrum of

A) 2-(2-Aminoethyl)pyridine.

B) {Bis-2,6[1-(2-pyrid-2-ythylelimino)ethyl]pyridine}-copper(I) Perchlorate.
FIGURE 4

A) \([\text{Bis}-2,6[1-(2\text{-pyrid-2-ylethylamino})\text{ethyl}]\text{pyridine}]\text{-copper(II) Perchlorate.}\)

B) \([\text{Bis}-2,6[1-(2\text{-pyrid-2-ylethylamino})\text{ethyl}]\text{pyridine}]\text{-zinc(II) Perchlorate.}\)
VITA

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