Synthesis and Characterization of Biomimetic Co and Fe Complexes with Trispyrazolylborate Ligands

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SYNTHESIS AND CHARACTERIZATION OF BIOMIMETIC CO AND FE COMPLEXES WITH TRISPYRAZOLYLBORATE LIGANDS

by

Praveen Kumar, B.S.

A Dissertation Submitted to the Faculty of the Graduate School,
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ABSTRACT
SYNTHESIS AND CHARACTERIZATION OF BIOMIMETIC CO AND FE COMPLEXES WITH TRISPYRAZOLYLBORATE LIGANDS

Praveen Kumar, B.S.
Marquette University, 2022

Numerous reactions of biological and environmental significance are catalyzed by dioxygenases that incorporate both atoms of \( O_2 \) into the substrate. These enzymes require a transition-metal cofactor for activity, typically a mononuclear nonheme iron center, although dioxygenases with first-row transition metal ions (Mn, Co, Ni) have been discovered. This dissertation focuses on synthetic studies based on mononuclear dioxygenases found in bacterial pathways for the breakdown and assimilation of inert organic compounds, including human-generated pollutants. Such enzymes are essential for bioremediation technologies used to restore contaminated soils and groundwaters. While crystallographic studies have revealed the active-site structures of various types of dioxygenases, the associated catalytic mechanisms are not fully understood, largely due to difficulties in isolating and characterizing transient intermediates. In particular, there is little clarity regarding the structural and electronic factors that govern the reactivity of iron-superoxo and -alkylperoxo intermediates, which play pivotal roles in the putative mechanisms. Here, these challenges are addressed by generating a series of synthetic cobalt and iron containing complexes that replicate key structural, electronic, and chemical features of environmentally important dioxygenases. This “bio-inspired” approach combines coordination chemistry, reaction kinetics, spectroscopic techniques, and computational methods. As the properties of synthetic models can be modified in a straightforward and systematic manner, through their design and synthesis it is possible to illuminate relationships that exist between geometric/electronic structures, spectroscopic parameters, and \( O_2 \) reactivity. Moreover, since the biomimetic approach permits a great deal of control over ligand properties and reaction conditions, it is possible to trap and spectroscopically characterize catalytic intermediates that have been postulated, but never observed, in studies of the metalloenzymes.
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Chapter 1

Introduction: Redox-active Ligands in Synthetic Complexes and Metalloenzymes

I. An Overview of Non-innocent Dioxolene-type Ligands in Metal Complexes

A. The Concept of Redox-active “Non-innocent” Ligands

Coordination complexes have generally been considered to perform redox chemistry through changes in the oxidation state of metal center(s). However, a fascinating class of molecules, known as “non-innocent” ligands can participate in redox processes independent from the metal center. The presence of non-innocent ligands expands the range of oxidation states that are available for coordination complexes and opens the possibility of successive redox events that leave the metal center unchanged. New avenues for reactivity can be accomplished with non-innocent ligands which involve single electron transformations rather than the paired, electron-arrow-pushing catalytic mechanisms which are prevalent in organometallic chemistry. The abundance of ligand-based radicals derived from oxidation of dioxolenes (e.g., catechols) has led to several unique electronic structures which are otherwise not plausible. The study of resulting exchange-coupling interactions, metal-ligand covalency, and unconventional magnetic properties has been advanced by studying the structural and electronic effects from redox-active ligands. Therefore, the utility of non-innocent ligands has been demonstrated in numerous areas of chemistry, most notably, new pathways with radical based-mechanisms and new materials that contain metal species bound to ligand radicals leading to unique magnetic properties. The development of compounds to meet both ends requires robust synthetic methods, stability from metal-ligand complexes that exhibit non-innocence, and a systematic approach towards their design.

Ambiguity in the assignment of ligand oxidation states in metal complexes with non-innocent ligands is a well-known issue. Their ability of such ligands to undergo
single electron transformations without the metal center, often in the presence of air or in moisture, often leads to unconventional electronic configurations. These redox events can markedly alter the different spectroscopic features and magnetic properties of the complexes. In this regard, dithiolenes were the first class of ligands to be recognized as non-innocent in studies by Gray and Eisenberg. Much like other dioxolene-type ligands, they form bis-species under oxidative addition of first row transition metals. An early attempt at generating these species was characterized as square planar [M]^{2+}-dithiolates (Figure 1.00), in which the thiol donors were assumed to be strong-field ligands. Although electronically accurate (based on absorption spectra), the structural description was not commensurate with a low-spin, divalent system. The crystallographic analysis in a later study confirmed that the square planar structure contains ligand-to-metal bond lengths were shorter than expected for divalent metal systems. The π-system of the dithiolene ligand allows for oxidation of electron density beyond the primary sphere of coordination.

![Figure 1.00 General electronic structure of homoleptic thiolate complexes with late transition metal centers.](image)

These dithiolenes belong to a broader class of non-innocent ligands known as dioxolene-type ligands. These are typically ortho- or para-substituted with chalcogen and/or amine donor groups. Common examples include catechols, o-aminophenols, and
When bound to a metal center these compounds can exist across three distinct oxidation states (Scheme 1.A) like in the example of catechols.3,10


Catechols are a class of vicinal diols, that possess multiple oxidation states ranging from mono- or di-anionic catecholates, semiquinonate radicals, and neutral o-benzoquinones. The substitution of one -OH with an amine group yields aminophenolates—another class of dioxolene-type ligands. Due to their easily accessible oxidation pathway and stable coordination to metals, aminophenolate complexes represent a large family of well-researched redox-active metal-ligand complexes.11-13 In their reduced forms, they are π-basic, which is enhanced by substitution of tert-butyl moieties at the ortho position. These sterically bulky groups are widely employed to stabilize ortho-localized semiquinonate radicals, including the first characterized example of an iminosemiquinone ISQ radical species.14 This species can be isolated by conproportionation of fully oxidized benzoquinone with reduced aminophenolate, in good yields (Scheme 1.B). This species is relatively stable under ambient conditions, isolation of this dark blue species shows an intense absorbance in the visible region (600-800 nm), arising from strong intra-ligand charge transfer (often denoted as π → π*). The negative charge in this species is localized on the phenolate moiety with a zwitterionic
charge distribution, yielding an electrostatic interaction between the imine proton and phenolate (Scheme 1.B). This phenomenon was also observed with phenoxy radical, such as the tri-tert-butylphenoxy radical, TTBP•, which has been instrumental in carrying out PCET (proton-concerted electron transfer) chemistry.15,16 Upon complexation to metals, the σ-donating strength of the anion radical allows for a stable electrostatic interaction with usually electrophilic metal centers.3 Phenoxy radicals in the copper-containing enzyme of galactose oxidase (GAO) allowed for elucidation of its enzymatic pathway by synthetic modeling of reactivity.17,18 Examples of such species in biology, with metalloenzyme ligands exhibiting radical character are continually increasing. Bioinorganic studies of these redox-active ligands are of great interest with notable examples found in enzymes like GAO, ribonucleotide reductases (RNR),19,20 isopenicillin N synthase (IPNS),21,22 radical-SAM (S-adenosylmethionine enzymes),23 and mononuclear non-heme iron dioxygenases (MNIDs).24-27

![Scheme 1.B Conproportionation of aminophenol (APH) and (imino)benzoquinone (IBQ) into (imino)semiquinone (ISQ).](image)

The stable coordination chemistry of non-innocent bidentate ligands found in metal-ligand systems with dithiolates,28-30 diimines,3,31,32 and catechols33,34 make them practical compounds for isolation and study. Many reported dioxolene coordination complexes are octahedral in geometry,35,36 however, there is a growing effort to examine
redox-active ligands in four and five coordinate environments which allows for access to trigonal bipyramidal (TBP) and square pyramidal geometries (SPY) – like those found in biological active sites. Electronegativity of dioxolene-type donor atoms (i.e., N, O, S) is usually larger than their metallic counterparts, thus placing their bonding molecular orbitals (MOs) lower in energy. The strength of charge donation to the metal center can be attributed in part, to the in-plane interaction between x- and y-symmetrized π-orbitals and their resulting interaction with metal d orbitals. However, a great deal of electron density in dioxolene-type ligands resides in the π* orbital that is orthogonal to the metal-ligand bonding interaction, making it easier to selectively oxidize them over the metal center. Of course, the resulting oxidized species may have delocalized electron density (usually within a singly occupied MO, or SOMO) which does not always conveniently fit the description of being entirely ligand- or metal-based. Such is the case with dithiolenes, where assignment of formal charge via oxidation state occludes proper assessment of its electronic configuration.

After oxidation by one electron, dioxolene-type ligands exhibit a “two-short/four-long” pattern of double bonds from loss of aromaticity. Often described as “quinoidal,” this distortion in C–C bonds typifies semiquinone (SQ) and benzoquinone (BQ) oxidation states in dioxolenes. The ‘fully’ oxidized, neutral form (BQ) has a diene motif with the donor atoms oxidized as quinones. Visualizing metal d orbitals and frontier MOs of open shell ligands is crucial to understand the nature of each pairing between redox non-innocent ligands and their metal counterparts. This is complicated to a greater extent when electron density of the radical ligand is localized across multiple ligand sites, or if there is mixed-valent behavior across two or more metal centers.
B. Unique Properties of Metal Complexes with Dioxolene-type Ligands

Dioxolene-type ligands in their open-shell forms have been of interest due to the unique magnetic properties they can exhibit in coordination to metals. The magnetic interaction between two paramagnetic centers, such as a ligand radical and metal ion with unpaired electrons, is known as the exchange coupling phenomenon. Metal identity and steric control by auxiliary ligands can influence the overlap of magnetic orbitals, namely metal d and ligand π* orbitals. In this regard, ligand denticity also plays a large role in determining whether open-shell ligands are ferromagnetically or antiferromagnetically coupled to the metal ion.

In the case of nickel(II) semiquinonates, two compounds with similar metal and ligand oxidation states exhibit remarkably different magnetic ground states depending on the denticity of the neutral N-donor ligands. In an example from Gatteschi, the neutral tridentate triazacyclododecane was used as a supporting ligand in coordination to the metal with an open-shell semiquinonate ligand in the five-coordinate complex, $[\text{Ni}^{2+}(\text{Me}_3\text{[12]}\text{N}_3\text{SQ}^{\text{tBu}_2})]\text{ClO}_4$. The resulting antiferromagnetic exchange coupling between this radical and the nickel center yields an $S = 1/2$ spin state. This interaction is due to the overlap between the metal $d_{xz}$ orbital from the distorted trigonal bipyramid and the π*-orbital of the ligand radical. This contrasts from the $[\text{Ni}^{2+}(\text{tren})(\text{N}_{4}\text{-ISQ})]$ complex which is octahedral (with $N_4$-coordinating tren ligand) and contains an orthogonal relationship between the $e_g$ symmetrized metal orbitals and ligand radical occupied π*-orbital. This stark contrast in magnetic behavior was empirically observed by dc (direct current) magnetic susceptibility measurements which allowed for a comprehensive view of the exchange coupling phenomena across a range of temperatures. The behavior of...
antiferromagnetic and ferromagnetic exchange coupling is pronounced in the shape of the magnetization curves. For example, the magnetization of a series of dinuclear copper(II) complexes with exchange coupled radicals has been modeled thoroughly by Kahn. The fitted magnetization curves in Figure 1.01 clearly describe two possible scenarios of exchange coupling; ferromagnetic \( J > 0 \) and antiferromagnetic \( J < 0 \).

![Magnetic susceptibility data](image)

**Figure 1.01** Magnetic susceptibility data recorded from a series of dinuclear Cu\(^{2+}\) compounds with a ligand radical in different exchange coupling schemes reported by Kahn.

Notable developments have been with iron complexes with the \( N \)-aryl-amidophenolate and its oxidized iminosemiquinone ISQ form. In canonical octahedral systems of \([M^{3+}(N_{Ph-ISQ})_3]\) complexes explored by Wieghardt *et al.*, metal identity determines the overall magnetic ground state. These octahedral systems have been prepared with various transition metals to determine how ligand-based radicals behave in coordination to metals with different numbers of unpaired d electrons. The high-spin ferric complex, \([Fe^{3+}(N_{Ph-ISQ})_3]\) has an \( S = 1 \) ground state due to three antiferromagnetically coupled radical ligands and their overlap between three \( \pi \)-symmetric metal d orbitals. In the examination of electronic and magnetic properties of...
iron(III) complexes with three iminosemiquinonate ligands, it was verified that the ligands have radical character based on X-ray crystal data. As shown in Figure 1.02, two ligands with R-groups (R = difluoro- and di-tert-butyl) at the meta positions of the N-aryl moiety were synthesized to probe their magnetic behavior with respect to metal-ligand exchange coupling. Both complexes contain three ligands with a quinoidal distortion consistent with non-innocent behavior. In coordination to the \( S = 5/2 \) paramagnet of high-spin iron(III) tris-(iminosemiquinonate) ligands, this results in an \( S_{\text{tot}} = 1 \) ground state due to antiferromagnetic coupling. With fluoride substituents on the \( N \)-aryl ring, the \( S = 1 \) state is present between 0 and 200 K due to a rather large \( J \)-value of \(-184 \text{ cm}^{-1}\). At higher temperatures, the excited state \( S_{\text{tot}} = 2 \) is populated from thermal excitation, which was observed by a gradual increase in magnetic susceptibility. In contrast, the ferric center in the tert-butyl-substituted complex is low-spin at cryogenic temperatures, affording a diamagnetic ground state \( (S_{\text{tot}} = 0) \). At higher temperatures, the magnetic moment increases gradually to that of an \( S = 1 \) system. This unique behavior is defined as a 2e\(^{-}\) spin-crossover between low- and high-spin ferric spin states.

**Figure 1.02** R-group’s influence on spin-crossover in ferric N-aryl-amidophenolates. R = tBu- and F- groups resulting in high-spin and low-spin configurations at 200 K, respectively.\(^{46}\)
This process is of interest in the development of magnetically responsive materials that can have two independent magnetic states, i.e., ‘bistable’ systems.\textsuperscript{7,9,47-49} Thus, varying the substituents of “π-active” radicals, like in iminosemiquinonate complexes, can have a profound impact on the metal center and overall magnetic properties. The use of multiple spectroscopic techniques such as dc magnetic susceptibility experiments, far-infrared spectroscopy and computational modeling make observing SCO behavior possible.

Our lab has generated a heteroleptic iron aminophenolate complex which exhibits redox non-innocence within the monoanionic, bidentate APH\textsuperscript{tBu2} ligand.\textsuperscript{49} Our initial studies employed hydrotris(3,5-diphenylpyrazolyl)borate (Tp\textsuperscript{Ph2}) which represents the facially-arranged 2-His-1-Carboxylate (2H1C) motif found in the active site of aminophenol dioxygenases. With these ligands, we prepared [Fe\textsuperscript{2+}(Tp\textsuperscript{Ph2})(APH\textsuperscript{tBu2})] which contains a five-coordinate, trigonal bipyramidal geometry (Figure 1.03). The C–C bond distances of the APH\textsuperscript{tBu2} ligand are nearly equidistant at 1.40 Å, indicative of a closed-shell o-aminophenolate donor. Treatment with TTBP\textsuperscript{*} results in H-atom abstraction from the amino group of APH\textsuperscript{tBu2} giving rise to a stable, green-colored species. This ligand-based transformation was confirmed through the characterization of the intraligand bond lengths from the crystal structure of [Fe\textsuperscript{2+}(Tp\textsuperscript{Ph2})(ISQ\textsuperscript{tBu2})]. Like the octahedral iron iminosemiquinonate complexes reported earlier, the high-spin ferrous center (\(S = 2\)) is antiferromagnetically coupled with the ISQ radical yielding an \(S = 3/2\) system. This is the first five-coordinate complex to feature a ferrous center ligated by an ISQ radical, providing a synthetic precedent for the (imino)semiquinone radical believed to exist in nature (\textit{vide infra}).\textsuperscript{50} Chemical oxidation with silver(I) salts resulted in a
cationic species that retains ligand radical character. Surprisingly, the electronic structure of this new oxidized species lies between the limits of [Fe(II)-ISQ/Fe(III)-IBQ] conformations.

Figure 1.03 Top: oxidation of [Fe$^{2+}$(Tp$^{Ph2}$(APH$^{tBu2}$)) by TTBP$^\bullet$ and oxygen reported by our lab. Bottom: thermal ellipsoid plot of the pale green species [Fe$^{2+}$(Tp$^{Ph2}$(ISQ$^{tBu2}$))] (Tp-phenyl groups and protons omitted for clarity).$^{49}$

The study of redox active ligands with transition metals requires an electronic description of the ground state. With dioxolene-type ligands especially, descriptions of metal and ligand oxidation states can be ambiguous. Drawing useful conclusions on electronic and magnetic behavior is made possible through structural correlations from X-ray crystallographic data. Due to the extended $\pi$-network of coordinated dioxolene-type ligands, as the ligand becomes oxidized there can be a large degree of metal-ligand covalency, which may lead to metal-based oxidation. To confidently assign oxidation
states, analysis of ligand bond distances is useful. Like in free ligands, the degree of oxidation can be measured by the C–C bonds, where the degree of quinoidal distortion can identify whether a ligand is in an open- or closed-shell configuration. The growth of high-quality crystals suitable for X-ray crystallographic analysis is often challenging due to instability of open-shell ligands and disorder present within the system. Moreover, systems with few literature precedents limit comparison of bond lengths as a metric with other ligand-oxidized systems. A recently published study collates the metric parameters for crystallographically-characterized metal complexes to provide a systematic tool (coined as MOS or metrical oxidation state) for assessing ligand oxidation state. This gives a standardized treatment for aromatic systems, offering a quantitative measure of the degree of oxidation within a ligand by statistical analysis.

![Diagram of ligand bond layout and population trends](image)

**Figure 1.04** Top: redox-active ligand bond layout proposed by Brown. Bottom: population trends of reported complexes with computed MOS values.
Brown has generously provided a MOS-computing macro (in Excel format) which allows for any crystallographically reported bond lengths (Å) from a dioxolene ligand to yield a MOS value. This acts as a benchmarking tool for the vast array of dioxolene oxidation states which can be analyzed with respect to metal oxidation state, coordination number, and overall charge. The metal complexes which make up this dataset include N-aryl-amidophenolate and catecholate ligands bound to several transition metals. These account for the largest population of reported dioxolene-type ligands with crystallographically-observed oxidation (Figure 1.04). Thus, the report of metrical parameters utilizes bond distances from these studies with various coordination environments. Of the complexes chosen in this study, those with low-valent metals display a predictable relationship between ligand oxidation state and bond distances, regardless of their periodicity. Successive ligand oxidation is accompanied by contraction of C3–C4 and C5–C6 bonds and substantial elongation of the C1–C2 bond. Given the nature of frontier MOs, oxidation of the ligand reduces anti-bonding interactions between O/N-donors and their carbon neighbors (C1, C2). This shortens the heteroatomic bonds as the degree of quinoidal character increases. This quantitative approach for analyzing the oxidation states of dioxolene chelators allows us to compare systems which do not fall discretely under one oxidation state to those that follow ideal quinoidal behavior. Atypical complexes like the iron iminosemiquinone complex prepared by our lab result in predictable MOS values, aiding in their assignment. However, others such as the benzoquinone adduct (which are among the least reported and stable members of the aminophenolate oxidation series), often have non-integer MOS values half-way between ISQ and IBQ limits of [–1] and [0].
Studies based on cobalt tris(α-iminosemiquinonates) [Co\(^{3+}\)(N\(_{Ph-}\text{ISQ})_3\)] and cobalt tris(α-semiquinonates) [Co\(^{3+}\)(SQ\(_{tBu2})_3\)] are keen examples of how two compounds can be isoelectronic but have drastically different magnetic properties due to π-interactions between metal and ligands.\(^{43,52}\) In the both cases, the metal ion is a diamagnetic low-spin cobalt(III), however, the tris-semiquinonate complex is an \(S = 1/2\) system with antiferromagnetic coupling between open-shell ligands (\(\mu_{\text{eff}} = 1.82 \mu_B\) at 5 K). When this complex was substituted with gallium(III) it results in ferromagnetic coupling with an overall \(S = 3/2\) spin state. Wieghardt has reported that the isoelectronic analogue with tris-(2-anilino-iminosemiquinonate) ligands coordinated to low-spin cobalt(III) yields a similar \(S = 3/2\) system. Unlike the semiquinonate complex, the ferromagnetic coupling exhibited by this complex appears dominant at most temperatures (\(\mu_{\text{eff}} = 3.71 \mu_B\) at 15 K). Despite having similar octahedral geometries, the electronic effect of ligand identity and their interaction through the unoccupied MOs of the cobalt ion ultimately creates two different magnetic outcomes. The investigation of cobalt dioxolenes is of interest to us because the large degree of metal-ligand covalency results in a number of unique magnetic properties. In order to control these properties in a systematic way, new metal dioxolene complexes must be synthesized and characterized so that future complexes with desirable properties are more easily and predictably obtained.

\textbf{C. Unique Properties of Cobalt Complexes}

Research into valence tautomerism (VT) has rapidly expanded over the past few decades.\(^{34}\) The presence of non-innocent ligands with metal covalency allows for one-electron transfer to the metal center, affording a species with distinct electronic structural and magnetic properties from the initial species.\(^{53}\) This process occurs in a concerted
manner with spin crossover of the metal center (e.g., low-spin to high-spin). The best studied examples of this one-electron process include cobalt dioxolenes. Illustrated in Figure 1.05 is the canonical valent-tautomeric behavior exhibited by cobalt(III) catecholates which form cobalt(II) semiquinonates at higher temperature. This conversion combines a change in oxidation state and magnetic spin state from diamagnetic cobalt(III) to high-spin cobalt(II) bound to a radical ligand.

\[
\begin{align*}
\text{Co}^{3+} \text{O} & \quad \overset{2^+}{\leftrightarrow} \quad \text{Co}^{2+} \text{O} \\
\end{align*}
\]

**Figure 1.05** Valence tautomerization exhibited between low-spin Co(III)-catecholate and high-spin Co(II)-semiquinonate.

A series of experimental studies of cobalt dioxolenes has been pursued in understanding valence tautomerism in the solid state.\textsuperscript{53-55} Initial studies on the transformation between two degenerate states by thermal excitation was first exemplified by Pierpont and Hendrickson.\textsuperscript{56,57} In these canonical systems, the presence of VT pairs electron transfer between the cobalt(III/II) couple and open- and closed-shell forms of one or more dioxolenes in 6-coordinate complexes. The presence of this transition in \([\text{Co}^{3+}(\text{N}_2)(\text{SQ}^{\text{Bu}_2})(\text{Cat}^{\text{Bu}_2})]\), where N\(_2\) is a series of bidentate N-heterocyclic ligands like bipyridine, phenanthroline, pyrimidine, and pyrazine with various substituents has been reported by both groups with the redox-active [SQ]\(^-\) and [Cat]\(^2-\) ligands containing 3,6-di-\textit{tert}-butyl or 3,5-di-\textit{tert}-butyl groups. These species are neutral, low-spin complexes at lower temperatures and valent tautomerism is exhibited at higher temperatures in the solid state. Depending on the N\(_2\)-donor ligand, the \([\text{Co}^{3+}-\text{Cat}] \rightarrow [\text{Co}^{2+}-\text{SQ}]\) conversion
can occur at relatively low temperatures or prevented entirely. The equilibrium temperature at which the two states coexist is determined by the σ donation strength of the N₂ ligands. In addition, the LUMO of the auxiliary diamine ligands allows for π-backbonding with the metal center. Even without these complex interactions, to fully satisfy the requirement for exhibiting VT, the ligands need closed-shell forms which can be easily converted to an open-shell derivative upon reduction of the metal center. This results in radical character on one or more ligands, which then participates in exchange coupling with the paramagnetic metal center. In summation, this process is entropically favored, resulting in a metal semiquinonate with a higher total spin and greater vibrational degrees of freedom. What separates cobalt, in this regard, from the remainder of first-row transition metals is that the barrier between the two spin-states is rather low. The prevalence of interesting solid-state VT phenomena has provoked many groups to study the bulk properties of cobalt dioxolenes. Depending on the material, several external factors can perform this transformation besides thermal excitation, including photoirradiation, pressure-induced effects, and electric field-induced valence tautomerization. These methods have been explored to generate materials with applications in various molecular devices.

Recently, research groups have studied uniquely bistable cobalt compounds that do not require VT or SCO processes. The design of these bistable magnetic materials is based on their ability to undergo magnetization with a large barrier to relaxation in zero-field. The field of spintronics studies the application of molecular ‘machines’ for quantum computing. Having a material which retains a certain degree of magnetization in the absence of magnetic field is desirable to attain information processing at a higher
density, allowing for smaller devices.\(^8,9\) This subfield represents a growing area of inorganic research dedicated to the rational design of systems that have unconventional magnetic behavior. The use of cobalt(II) complexes has been advanced due to its high non-integer spin value of \(S = 3/2\) which decreases the probability of quantum tunnelling of magnetization.\(^64\) Furthermore, the use of ligand radicals has been explored by T.D. Harris and J.R. Long in their review of single molecule magnets (SMMs), in which they posit that \(J\)-coupling allows for magnetic states with higher spin-relaxation barriers.\(^7\)

The presence of sizable magnetic anisotropy can give rise to magnetic hysteresis. A unique example of this behavior was found in a tetrahedral cobalt(II) ion with homoleptic coordination to the dioxolene ligand 1,2-bis(methanesulfonamido)benzene.\(^65\) This species exists as a “pure spin ion” with an \(S = 3/2\) spin ground state configuration in \(T_d\) symmetry of \(^4\)A\(_2\). This species has enhanced second order spin-orbit coupling effects which induces a large negative zero-field anisotropy \((D)\). The separation of Kramers doublets due to zero field splitting \((2D)\) which exists in the absence of a magnetic field. As a consequence of this behavior, the molecule behaves as a SMM and exhibits slow magnetic relaxation with a barrier of \(U_{\text{eff}}/k_B T = 118 \pm 5 \text{ cm}^{-1}\) which is unprecedented for a mononuclear complex. The high energy barrier is in part due to the strength of ligand field effects.\(^64\) The strong \(\pi\)- and \(\sigma\)- donation from the sulfonamide ligand has been determined by quantum chemical calculations that employed the CASSCF (complete active space self-consistent field) method. Calculations revealed that minor deviations from \(T_d\) symmetry imposed by the ligand field leads to \(D_{2d}\) symmetrized components. This in turn lifts the degeneracies of the \(d_{x^2-y^2}\) and \(d_{z^2}\) metal orbitals and reduces the energy gap between lowest energy excited state and the ground state. Thus, the \(D\) parameter is
greatly increased due to spin-orbit coupling and increases the barrier of relaxation of magnetization. Therefore, the development of novel cobalt dioxolenes with innately high zero-field splitting is desirable and needs further study.

II. Ligand Non-innocence in Metalloenzymes and Relevant Model Compounds

A. Non-innocent Ligands in Ring-cleaving Nonheme Dioxygenases

Microbial degradation is a critical process for the bioremediation of aromatic compounds, which make up a considerable number of pollutants. Ring-cleaving dioxygenases found in bacteria utilize molecular oxygen to oxidatively cleave the C–C bonds of a wide range of aromatic compounds, thus making these compounds available to the carbon nutrient cycle. The resulting products are metabolized by other proteins to allow organisms to use them as sources of carbon and energy. The aerobic degradation of these compounds under ambient conditions is not entirely understood. In addition, the catalytic capacity for activation of oxygen in this manner has not yet become applicable industrially. Extradiol catechol dioxygenases (ECDOs), which break the C–C bonds in a number of aromatics, are among the best-studied class of ring-cleaving dioxygenases. Thus, the degradation of catechols by 2,3-HPCD (homoprotocatechuate 2,3-dioxygenase) a well-known ECDO (Scheme 1.C), is of great interest in the field of bioremediation and represents a challenge for bioinorganic chemists to fully understand. This metalloenzyme was isolated from B. fuscum, a soil dwelling bacterium which derivatizes semialdehydes from dioxolenes such as catechol. This aerobic process couples O₂ activation and challenging ring-cleavage chemistry together allowing facile ring-cleavage under ambient conditions.
The structure of 2,3-HPCD (Figure 1.06) is classified as homo-tetrameric, meaning that each of the four subunits is identical. Like most ring-cleaving dioxygenases, the active site of 2,3-HPCD consists of a ferrous center bound facially to the 2H1C facial triad. This arrangement leaves three coordination sites free for binding the dioxolene substrate and O$_2$. The ensuing ring-cleaving mechanism is shown in Scheme 1.C. After substrate binding, the formation of an Fe/O$_2$ adduct with one-electron transfer from metal-substrate unit to the O$_2$ ligand occurs. The identity of this intermediate remains in contention, without a clear depiction of electronic structure.

![Tetrameric HPCD enzyme and ferrous active site](image)

**Figure 1.06** Tetrameric HPCD enzyme and ferrous active site.

Lipscomb has proposed that O$_2$ binding is accompanied by one-electron oxidation of the catecholate ligand, resulting in a transient Fe$^{2+}$ superoxide with a coordinated semiquinonate form of the substrate. This conclusion has been disputed due to lack of evidence for the oxidation of the native substrate. Instead, the subsequent EPR studies of 2,3-HPCD using a deactivated 4-nitrocatecholate substrate reveals formation of an iron(III)-superoxo species. Computational studies involving DFT (density functional
theory) have suggested that this step instead proceeds via the standard \([M]^{3+}\) superoxide formation.\textsuperscript{72}

In a landmark study, the oxygenation of 2,3-HPCD was studied \textit{in crystallo}, offering a rare glimpse into the \(O_2\) activation pathway.\textsuperscript{73} Within four subunits of the tetrameric enzyme, the crystal data revealed different stages of the ring-cleaving mechanism. In one subunit, the observed \(Fe/O_2\) adduct features a non-planar substrate ligand, suggestive of radical character. The superoxo ligand was bound in a side-on manner forming a hydrogen bond with the neighboring secondary-sphere His residue.

![Scheme 1.C Mechanism of extradiol ring-cleave proposed by Lipscomb.\textsuperscript{72}]

The proximal oxygen atom of the superoxo ligand was found in a position ready for nucleophilic attack on the catechol carbon. In another subunit, the alkylperoxide bridged species was trapped and found to be stabilized by neighboring H-bonding contacts. The formation of this species is supported by its appearance in another subunit.
of the 2,3-HPCD crystal. The reaction continues with homolytic cleavage of the O–O and insertion of the distal O-atom in the ring of the substrate (between C2–C3). The lactone intermediate that arises from this Criegee rearrangement is then hydrolyzed to yield the ring-cleaved product.

Despite remarkable progress, substantial questions regarding the ring-cleavage mechanism of nonheme iron dioxygenases still linger. What is still not understood completely is the manner in which the enzyme controls the regioselectivity of aromatic ring cleavage (e.g., intradiol or extradiol cleavage).\textsuperscript{74} In addition, whether the non-innocence of the catechol substrate is a key factor in the O\textsubscript{2} activation pathway is still not clear. Furthermore, the catalytic mechanism and ability of second sphere residues to serve as proton donors and/or acceptors has not been solved. In a recent paper, Lipscomb and Que examined the effect of metal substitution with other bio-active metals such as Mn and Co in the active site of 2,3-HPCD.\textsuperscript{71} When the metal center was substituted with manganese(II), the enzyme retained its ring-cleavage activity. The native ferrous enzyme is inactive with the presence of H\textsubscript{2}O\textsubscript{2} and other oxidants, whereas the Mn\textsuperscript{2+} variant maintains ring-cleaving activity. Typically, six-coordinate cobalt(III)/O\textsubscript{2} adducts are inert due to their reduced lability and large octahedral splitting energy. The increase in oxidation potential from Fe to Co also suggests that the O\textsubscript{2} binding process is disfavored. However, substitution with Co (Co-HPCD) yielded an enzyme several-fold more active than the native Fe-HPCD or Mn-HPCD (Figure 1.07). Based on kinetic differences between their mechanisms there is a possible explanation from the fast rate of product release. This compensates for the higher oxidation potential, resulting in an efficient conversion. Despite this feat, the lower affinity of Co(II) for dioxygen can be quite
problematic for biological systems. Therefore, it is easy to see why the ferrous cofactor is present *in vivo* where the O$_2$ concentration is not saturated.

![Figure 1.07 Dioxigen activation and resulting ring-cleaved product, muconic semialdehyde, of HPCA/4NC substrates by Fe/Co substituted HPCD enzyme.](image)

In more recent work, the reactivity of Co-HPCD was examined with the alternative 4-nitrocatechol (4-NC) substrate alongside mutation of the second-sphere His-200 residue to asparagine (termed H200N). In comparison with Fe-HPCD, the uptake of 4NC is considerably slower for the mutated variant of Co-HPCD. However, using Co-HPCD, it has been possible to isolate a superoxo intermediate, something that is not feasible with a ferrous active site. In order to trap this intermediate and the resulting species, the sample was freeze-quenched after exposure to O$_2$ at room temperature. The X-band EPR spectrum reveals a decrease in $S = 3/2$ signal intensity from Co$^{2+}$ and formation of a $S = 1/2$ signal that displays an eight-line pattern due to the superoxide radical being in proximity to the Co ($I = 7/2$) nucleus. This provides evidence that a cobalt(III) superoxide intermediate is formed in the first step of catechol ring-cleavage. It was found that using 4-nitrocatechol as a substrate for Co-HPCD did not yield ring-cleaved products because of the deactivated nature of the electron-poor substrate.

Despite these breakthrough discoveries on ECDOs, there are certain limitations that arise when characterizing fast-lived intermediates under physiological conditions. The use of cobalt-substituted enzymes allows for conditions that extend the lifespan of
intermediates due to the the intrinsic inertness of [Co-O₂] adducts. However, activity was traded off in exchange for stability. Still, there are many metalloproteins, some in the MNID family of enzymes,⁶⁶,⁷⁶,⁷⁷ that bind and reduce oxygen in novel ways.

Aminophenol dioxygenases (APDOs) are a closely-related class of enzymes in the same superfamily of dioxygenases that facilitate ring-cleavage of o-aminophenol substrates, resulting in formation of 2-aminomuconic semialdehyde products (Figure 1.08).⁷⁹,⁸⁰ This metabolite then undergoes a series of transformations from other enzymes until finally converting to picolinic acid.⁸¹ APDOs belong to the same family of non-heme dioxygenases as HPCD, sharing the mononuclear ferrous active site within a similar α₂β₂ protein tertiary structure.

![Figure 1.08](image.png)

**Figure 1.08** Extradiol ring-cleavage activity demonstrated by HAD enzyme (HAA = 3-hydroxyanthranilate).⁸¹

Despite their similarities to ECDO’s, aminophenol dioxygenases can perform extradiol oxidative ring-cleavage reaction on numerous ortho-aminophenols, however, they show relatively low activity with catechol (13%), with even lower activity (1%) for 6-methyl aminophenol.⁸²,⁸³ Bacterial APDOs are also important in the degradation of environmentally toxic nitrophenol and p-chloronitrobenzene.⁸⁴,⁸⁵ Their counterpart in humans and other mammals, 3-hydroxyanthranilate 3,4 dioxygenase (HAD), is responsible for catabolism of 3-hydroxyanthranilate, an important amino acid
metabolite. As one of the key components in the kynurenine degradation pathway in humans, HAD is an APDO of great importance to metabolic pathways such as degradation of tryptophan into picolinic and quinolinic acid. While O\textsubscript{2}-activation by this enzyme is poorly understood, it is generally agreed upon that this enzyme follows a similar cleavage mechanism of the catechol dioxygenase 2,3-HPCD.

B. Synthetic Models of Dioxygenases

**Scheme 1.D** Reactions catalyzed by MNIDs.

Insights into enzymatic processes provide a comprehensive knowledge of metal-oxygen binding that enriches our understanding of substrate specificity and regiospecificity of enzyme activity. Thus, studies based on enzymes with structurally conserved active sites primed for O\textsubscript{2}-binding can have synthetic parallels. In this sense, modeling biological activity with synthetic precedents can offer more than structural comparison of metalloprotein active sites alone. Biomimetic compounds can be easily modified, to gain information about enzymatic rates, chemioselectivity, and catalytic mechanisms.

Several groups including ours have prepared biomimetic model complexes in efforts to mimic the structure, activity, and spectroscopic features of ring-cleaving nonheme iron dioxygenases. This research is motivated by efforts to replicate enzymatic behavior, with regards to degrading pollutants such as halogenated aromatic
species and other catalytic processes involving O₂ activation. Studies in the past have employed a variety of different supporting ligands, metal centers, and substrates to evaluate the relationship between structure and O₂ reactivity. Some factors of importance to consider when designing synthetic models of these metalloenzymes include the use of redox-active substrates with access to open-shell oxidized forms, the scrupulous representation of the first coordination sphere of enzyme active sites, and a steric profile amenable to O₂-binding. It has been established that the dioxolene-type substrates of nonheme iron dioxygenases (catechols, aminophenols, and hydroquinones; Scheme 1.D) can behave in a non-innocent manner. Thus, the ability of these ligands to participate in one-electron processes such as proton-coupled electron transfer (PCET) is critical in studies of O₂-binding model complexes. The role of the supporting ligands is to best mimic the first coordination sphere of the enzymatic active sites, in particular, the facial coordination geometry and monoanionic charge of the 2-His-1-carboxylate triad found in dioxygenases like 2,3-HPCD. Biomimetic studies allow for the detection and spectroscopic characterization of short-lived intermediates that cannot be detected in studies of the corresponding enzymes. These intermediates can be stabilized by modifying structural features given that there are coordinatively unsaturated sites for both the substrate ligand and oxygen.

The choice of metal center in model studies has historically been iron, where mixtures of FeCl₂ or FeCl₃ have demonstrated ring-cleavage activity in the presence of catechol, TACN and pyridine. Coordination complexes such as [Fe³⁺Cl(Me₃-TACN)(CatᵗBu₂)] have demonstrated extradiol ring-cleavage of tBu-substituted catechol substrates.
More recently, the Riordan group has reported ring cleavage activity from $[\text{Co}^{2+} (\text{PhTt}^{\text{Bu}2})(\text{SQ}^{\text{Bu}2})]$ which contains an open-shell semiquinonate bound to cobalt(II) in coordination to phenyltris-((tert-butylthio)methyl)borate (Figure 1.09). This complex yields the intradiol product, muconic anhydride, when exposed to oxygen.  

A functional model of aminophenol dioxygenase (APDO) has been synthesized by the Paine group with the formation of picolinic acid from aminophenol (Figure 1.10). This model employs a hexacoordinate coordination environment with a labile pyridyl arm in $[\text{Fe}^{2+}(6-\text{Me}_3\text{-TPA})(\text{APH}^{\text{Bu}2})]$. While it seems counterintuitive to saturate the coordination sphere, the lability of the pyridyl group allows for an Fe/O$_2$ adduct to form in situ. Remarkably, this species goes on to yield ring-cleaved extradiol product, picolinic acid. The formulation of novel coordination environments which replicate the 2H1C motif found in dioxygenases has yielded valuable insights on the structural configuration required to enable this chemistry. While there has been demonstrated success with catechol substrates, many other MNIDs exist for which there no examples of
functional models. Even modest turnovers with current functional models are not possible due to irreversible oxidation of iron.

Efforts by our group to generate biologically relevant intermediates along this O$_2$ activation pathway have aided in understanding the overall mechanism. As mentioned earlier, we isolated and characterized a biologically relevant, ferrous aminophenolate model using the Tp$^{Ph2}$ supporting ligand in [Fe$^{2+}$($T$p^{Ph2}$)(APH$^{tBu2}$)].$^{49}$ This complex undergoes oxidation at the ligand site forming the first example of an iminosemiquinone bound to a five-coordinate ferrous center. In addition to the structural information gained by X-ray crystallography, analysis of related models by Mössbauer spectroscopy, rRaman spectroscopy, and DFT calculations provides evidence for the possibility of semiquinonate adducts in the native enzymatic mechanism.$^{90,91}$

Figure 1.10 Proposed catalytic cycle of functional model of APDO ring-cleavage activity featuring iron(II) aminophenolate complex coordinated with supporting ligand (6-Me$_3$TPA).$^{89}$
While these model studies of APDO offered valuable insights into the ability of the aminophenolate substrate to exhibit non-innocence, they could not replicate ring-cleavage activity.

Remarkably, scorpionate supporting ligands have the ability to replicate the structural confines of MNID active site. This has enabled study of other dioxygenases. To this end, our lab has successfully prepared a series of hydroquinonate dioxygenase (HQDO) model complexes featuring both TIP\textsubscript{Ph2} and [Tp\textsubscript{Ph2}]\textsuperscript{−} supporting ligands.\textsuperscript{92} These systems included both monodentate and bidentate hydroquinone ligands which mirror the native ring-cleavage substrates in HQDOs.\textsuperscript{93,94} Recently, we examined the reactivity of two HQDO models consisting of a ferrous center bound to 2-(1-methylbenzimidazol-2-yl)hydroquinonate. Oxidation of the ferrous center forms a high-spin ferric-hydroquinonate ($S = 5/2$) species. Deprotonation of the -OH group yields a $p$-semiquinonate species retaining the ferrous state of the metal center (Scheme 1.E). These models demonstrate that HQDO models can undergo stepwise (and concerted) proton and electron transfers to afford iron(II) complexes bound to a $p$-semiquinone radical. Reversible protonation of the Fe(II)-SQ complexes triggers an internal electron transfer.

**Scheme 1.E** GDO mechanism paralleled by biomimetic iron complexes.\textsuperscript{92}
(i.e., valence tautomerization), thereby forming a ferric species with a closed-shell hydroquinonate ligand. This study represents one of the few biomimetic investigations on the nature of HQDO and GDO.

Another important MNID our group has targeted with the Tp framework is cysteine dioxygenase (CDO). This metalloenzyme is found in a variety of organisms to carry out the oxidation of thiol substrates derived from L-cysteine. Like most MNIDs, the first step in the proposed catalytic mechanism involves formation of a ferric-superoxide species which has not been characterized \textit{in vivo}. In analogy to the ring-cleaving dioxygenases, it has been suggested that that the thiolate ligand in CDO develops partial radical character to allow for formation of the alkylperoxo bridging species (Fe–O–O–S). This species is believed to undergo homolytic O–O bond cleavage (Scheme 1.F) forming a reactive iron oxo intermediate. Subsequently, insertion of the metal-bound oxygen into the cysteine sulfur is proposed as the last step preceding ligand protonation and release.

Recently, we reported the isolation and characterization of iron-superoxo and cobalt-superoxo species of relevance to CDO. Both complexes feature the hydrotris(3,5-dimethylpyrazolyl)borate (Tp$^{Me2}$) supporting ligand which is ideally suited for the trapping of reactive intermediates. Our model complex with cobalt, [Co$^{2+}$(Tp$^{Me2}$)(CysOEt)], binds O$_2$ reversibly at low temperatures. We were able to trap and study this intermediate through electron paramagnetic resonance (EPR) and resonance Raman spectroscopy.
The Co/O₂ adduct revealed an intense \( S = 1/2 \) signal with modest anisotropy, consistent with a cobalt(III) superoxide. Analysis by resonance Raman spectroscopy revealed a \( \nu(O-O) \) stretching mode at 1152 cm\(^{-1}\) that provides conclusive evidence for the presence of a low-spin cobalt(III) superoxide. In our iron model, we utilized the dioxolene, aminothiophenol in the model compound [Fe\(^{2+}\)(Tp\(^{Me2}\))(ATP)]. At low temperatures the O₂-reaction yields an EPR-silent iron(III) superoxide species which was verified by rRaman spectroscopy (\( \nu(O-O) = 1120 \) cm\(^{-1}\)). This represents the first synthetic example of a mononuclear sulfur-bound iron center coordinated with a superoxide adduct. Analysis by DFT on this superoxide model illuminated the importance of \( S \)-radical character in the thiol dioxygenation mechanism. This study highlights the gathering of important spectroscopic signatures which can aid in studying transient intermediates found in enzymatic studies.

**III. Summary of Research Objectives and Results**

This dissertation presents a series of biomimetic studies in which the non-innocent behavior of dioxolene-type ligands gives rise to cobalt and iron complexes with unique structural, electronic, magnetic, and chemical properties. This approach, with couples the
synthesis of metal complexes with redox-active ligands and O$_2$ reactivity studies, provides valuable insights that complement results obtained from biochemical methods. In this report, it is demonstrated that the study of synthetic cobalt and iron models provides fundamental insights into the O$_2$ activation mechanisms of nonheme dioxygenases. The advantages of using cobalt-based models have been highlighted in previous studies in which intermediates derived from reaction with O$_2$ were isolated and characterized with structural and spectroscopic techniques. Here, iron-based model compounds with the ability to replicate the reactivities of MNIDs are also described. Previous work by the Fiedler group has demonstrated that substituted trispyrazolylborate (Tp$^{R2}$) supporting ligands offer a suitable platform for replicating the protein-derived ligands in the active sites of MNIDs. As described above, the substrates of many MNIDs are dioxolene-type ligands (e.g., catechols, aminophenols, hydroquinones) that display non-innocent behavior in both synthetic and biological contexts. The study of synthetic complexes with redox-active ligands has been instrumental in understanding the electronic structures of metal-radical complexes, and these studies have implications for nonheme dioxygenases enzymes. As shown here, cobalt- and iron complexes with Tp ligands react with O$_2$ give rise to novel species that have been characterized with a variety of structural, spectroscopic, magnetic, and computational techniques. The results have further elucidated the electronic and magnetic landscapes of metal complexes with dioxolene-type ligands and generated O$_2$-derived intermediates that are relevant to dioxygenases.

In **Chapter 2**, we review the origin of magnetic anisotropy in a series of cobalt(II) complexes with dioxolene-type ligands. The high-spin Co(II) centers employed contain the facially-coordinating tris(3,5-diphenylpyrazol-1-yl)borate (Tp$^{Ph2}$) ligand. The use of o-
aminophenolate ligands resulted in predictable bidentate coordination leading to five-coordinate environments. One-electron oxidation of the o-aminophenolate ligand led to the formation of an iminosemiquinone (ISQ) ligand coordinated to cobalt(II). Antiferromagnetic coupling with the high-spin Co(II) center and ISQ radical gives rise to an $S = 1$ ground-state. Further oxidation of the complex generated a Co(II) complex with a neutral $o$-iminobenzoquinone ligand. This series of complexes were investigated through magnetic susceptibility, high-field and -frequency electron paramagnetic resonance (HFEPBR), and far-infrared magnetic spectroscopy (FIRMS), which permitted measurement of zero-field splitting parameters. It was found that the magnetic anisotropy is enhanced by structural constraints imposed by the Tp$_{Ph2}$ ligand. These effects were elucidated through ab initio calculations which provided an accurate assessment of the zero-field splitting energies observed empirically.

Continuing our magnetic investigation of metal complexes with ligand-based radicals, we studied homobimetallic complexes in which Tp-capped metal ions are bridged by $p$-semiquinonate ($p$SQ) ligands. The precursor complexes feature a bridging DMHQ ligand, where DMHQ is dianionic 2,6-dimethoxyhydroquinonate. This architecture resulted in diiron(II) and dimanganese(II) complexes that undergo one-electron ligand oxidation to yield species with a bridging $p$SQ ligand. These complexes are discussed in Chapter 6 where the series of bimetallic complexes was completed through the synthesis of the dicobalt(II) analogs. This study involved the measurement of magnetic properties using direct-current (dc) SQUID susceptibility, which was able to gauge the exchange coupling interactions between the three paramagnetic centers.
In **Chapter 3**, the O\(_2\) reactivities of Co(II)/Tp\(^{Me2}\) complexes with dioxolene-type ligand were examined. The formation of metastable cobalt(III)-superoxo species at low temperature was observed in complexes featuring aminophenolate and aminothiophenolate ligands. This process was irreversible, unlike previously observed Co/O\(_2\) adducts formed by related Co(II) Tp\(^{Me2}\) complexes. After the decay of this species, we observed net loss of a hydrogen atom (1e\(^-\), H\(^+\)) at room temperature which yielded Co(II) complexes featuring iminosemiquinonate (ISQ) or iminothiosemiquinonate (ITSQ) ligands. At low temperatures, the cobalt(II)-radical complexes reversibly bind O\(_2\) binding, forming a novel Co/O\(_2\) adduct containing an unprecedented cyclic alkylperoxide ligand. This species contains new Co–O and O–C bonds formed by the two-electron reduction of dioxygen yielding a bridging spiroendoperoxide intermediate. The O\(_2\)-binding process was studied under different O\(_2\) partial pressures to obtain equilibrium binding constants (K\(_{O2}\)) of this process at various temperatures. To understand how ligand variations alter the stability of the Co/O\(_2\) adducts with superoxo or alkylperoxo ligands, thermodynamic parameters (\(\Delta H\) and \(\Delta S\)) for the O\(_2\) binding reaction were obtained for a series of Tp\(^{Me2}\)-supported Co(II) complexes.

**Chapter 4** presents the O\(_2\) reactivity of an iron(II)-aminophenolate complex based on the Tp\(^{Me2}\) scaffold. This complex undergoes oxidative ring-cleavage upon exposure to O\(_2\), indicating that it is a functional mimic of aminophenol dioxygenases. The enhanced O\(_2\)-reactivity of the Fe/Tp\(^{Me2}\) system allowed us to investigate two intermediates (A and B) along the ring-cleavage pathway that are observed at low-temperatures. Mössbauer spectroscopy, EPR, and resonance Raman spectroscopy were used to characterize these species. Moreover, it is shown that a product of the O\(_2\) reaction is a novel mixed-valent
iron(II)-iron(III) complex with three bridging picolinate ligands, as confirmed by X-ray crystallography.

In Chapter 5, the O₂ reactivities of Tp^{Me2}-based Co(II) and Fe(II) complexes with hydroquinonate ligands are examined. We investigated the formation of a cobalt(III)-superoxide intermediate, along with a cobalt(II) p-semiquinonate species. In addition, the iron(II)-hydroquinonate analogue shows promising reactivity with O₂ at low temperatures with the formation of two intermediates having broad absorptive features reminiscent of pSQ radicals. The room temperature reaction with O₂ leads to formation of ring-cleaved products which further supports the use of Fe(II)/Tp^{Me2} complexes are promising active-site models of hydroquinonate dioxygenase enzymes.
IV. BIBLIOGRAPHY


41. Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, **1993**.


Chapter 2
Magnetic Properties of Cobalt Complexes with Redox-active Dioxolene-type Ligands

Abstract
Coordination complexes that possess large magnetic anisotropy (otherwise known as zero-field splitting, ZFS) have possible applications in the field of magnetic materials, including single molecule magnets (SMMs). Previous studies have explored the role of coordination number and geometry in controlling the magnetic anisotropy and SMM behavior of high-spin Co(II) complexes with redox-active dioxolenes. Building upon these efforts, the present work examines the impact of ligand oxidation state and structural distortions on the spin states and ZFS parameters of pentacoordinate cobalt complexes. We report the synthesis of hydrotris(3,5-diphenylpyrazolyl)borate complexes which contain a series of bidentate aminophenolate and aminothiophenolate ligands. These species have been oxidized by one electron to reveal iminosemiquinone (ISQ) and iminothiosemiquinone (ITSQ) ligand that couple to the cobalt(II) center. Further oxidation unveils the rarely reported iminobenzoquinone (IBQ) and iminothiobenzoquinone (ITBQ) forms of these ligands.

I. Introduction

In our preliminary studies on redox-active ligands, we sought to isolate dioxolene-type ligands in five-coordinate environments. Much like our model studies with iron(II) dioxolenes, the presence of PCET-accessible oxidation is attractive in our efforts to isolate ligand radicals. Using this chemistry, we had success in isolating the first five-coordinate ferrous-iminosemiquinonate (ISQ) complex in which an interaction between magnetic orbitals yields antiferromagnetic (AF) exchange coupling. The $2e^-$ oxidation of $[\text{Fe}^{2+}(\text{Tp}^{\text{Ph}2})(\text{APH}^{\text{tBu}2})]$ resulted in ambiguous ligand and metal oxidation states which fall between the [Fe(III)-ISQ] or [Fe(II)-BQ] limits. As an extension of this work, we sought to study cobalt(II) due to their unique spectroscopic and magnetic properties. Substituting the metal ion would preserve the structural constraints of the Tp ligand which allows trigonal bipyramidal (TBP) or square pyramidal (SPY) geometries. Thus, the interaction between the metal d orbitals and the frontier MOs of redox-active ligands could be analyzed with respect to the unique features of cobalt ions. In subsequently oxidized forms we expect a measurable degree of “quinoidal” distortion and stratified oxidation of the $\pi$-network in redox-active dioxolenes. Indeed, that was the case where we were able to isolate redox series shown in Scheme 2.A, yielding three cobalt(II) complexes with variations of the aminophenolate ligand.

As a starting point, we have isolated two complexes that contain the tris(3,5-diphenylpyrazolyl)borate (Tp$^{\text{Ph}2}$) supporting ligand attached to 4,6-di-tert-butyl substituted aminophenolate and aminothiophenolate ligands (1 and 2, respectively). The complex $[\text{Co}^{2+}(\text{Tp}^{\text{Ph}2})(\text{APH}^{\text{tBu}2})]$ (1) contains vicinal -O and -NH$_2$ donor moieties, whereas $[\text{Co}^{2+}(\text{Tp}^{\text{Ph}2})(\text{ATP}^{\text{tBu}2})]$ (2) contains the aminothiophenolate ligand to provide a
N₄S coordination sphere (Figure 2.00). The oxidation of these complexes under air occurs within hours, transforming the ligands into their respective imino(thio)semiquinonate forms (1₀ˣ and 2₀ˣ). The complex [Co²⁺(Tp²⁺)(ITSQ²⁺)] (2₀ˣ) exists as a diamagnetic species with the low-spin Co(II) center (S = 1/2) bound antiferromagnetically to the open-shell ligand.

![Scheme 2.A](image)

**Scheme 2.A** Bonding environment of cobalt(II) aminophenolate (1) and its oxidized derivatives 1₀ˣ and 4.

As described below, complexes 1₀ˣ and 2₀ˣ were characterized using X-ray crystallography, UV-vis, and NMR spectroscopies. Subsequent treatment of 1₀ˣ and 2₀ˣ with silver(I) hexafluorophosphate revealed that these open-shell semiquinones undergo another oxidation event which is primarily ligand-based. This process was confirmed by spectroscopic and crystallographic characterization of the benzoquinone derivatives, which complete the oxidation series of these dioxolene-type ligands. The chemical oxidation resulted in products [Co²⁺(Tp²⁺)(IBQ²⁺)]PF₆ (4) and [Co²⁺(Tp²⁺)(ITBQ²⁺)]PF₆ (5) which were characterized by X-ray crystallography as cationic cobalt(II) species with benzoquinone and iminobenzothioquinone ligands, respectively. These ligands are neutral and closed-shell.
In addition to structural and electronic characterization, the magnetic properties of the paramagnetic cobalt(II) compounds (with progressively oxidized ligands, APH → ISQ → IBQ) were probed using high-field and -frequency electron paramagnetic resonance (HF-EPR), dc (direct current) magnetic susceptibility, and far-infrared magnetic spectroscopy (FIRMS). All results indicate that 1 is a high-spin $S = 3/2$ complex with a large negative easy-axis anisotropy ($D$). Through analysis of HF-EPR, FIRMS, and magnetic susceptibility data, the large $D$ value for this compound was determined experimentally. The constraints of the Tp scorpionate framework prevent complex from having true TBP symmetry by enforcing 90° angles between the two
equatorial pyrazole donors. This unique scenario allows for greater mixing between the
ground state and low-lying excited states due to spin-orbit coupling, resulting in large
anisotropic values for both 1 and 2.

The oxidized complex \(1^{\text{ox}}\) was also studied using magnetic susceptibility and
FIRMS experiments. This species is an \(S = 1\) complex due to large antiferromagnetic
coupling between its cobalt(II) center \(S_{\text{Co}} = 3/2\) and the coordinated ISQ radical \(S_{\text{ISQ}} = 1/2\). The more oxidized species in this series, 4 contains a novel Co(II)-IBQ derivative.

Analysis with the aforementioned techniques yielded insights into the relationship
between ligand oxidation state and various magnetic parameters (i.e., \(g\)-values, zero field
splitting parameters, and exchange coupling parameter, \(J\)). Much like 1 and 2, the
oxidized species in this series also present large magnetic anisotropy, and magneto-
structural correlations were developed on the basis of multiconfigurational \textit{ab initio}
calculations.

\textbf{II. Results and Analysis}

\textbf{A. Synthesis of Co(II) Complexes}

A synthetic approach for cobalt-Tp complexes was accomplished using the
K[Tp\textsubscript{Ph2}] ligand (IV. Experimental Section). Addition of divalent cobalt precursors like
CoCl\textsubscript{2} and \([\text{Co}^{2+}(\text{OAc})_2\cdot4\text{H}_2\text{O}]\) to the anionic Tp\textsubscript{Ph2} ligand generates complexes with
three pyrazole donors in the canonical ‘scorpionate’ arrangement. To support ligand
substitution with bidentate redox-active ligands, the synthesis of
\([\text{Co}^{2+}(\text{Tp}^{\text{Ph2}})(\text{OAc})(\text{Hpz}^{\text{Ph2}})]\) was adopted by our lab, using the previously reported
method by Harding.\textsuperscript{2} Once recrystallized, this precursor can be reacted with the sodium
salt of bidentate ligands to form the five-coordinate complexes. Complexes 1 and 2 were
generated using the 4,6-di-tert-butyl substituted aminophenol and aminothiophenol pro-
ligands (Scheme 2.B), whereas 3 was synthesized using 3,5-di-tert-butylcatechol
(Scheme 2.C).

Scheme 2.B Two step synthesis of APH\textsuperscript{tBu2} ligand.

Scheme 2.C Synthesis of ATP\textsuperscript{tBu2} ligand.

The syntheses of APH\textsuperscript{tBu2} and ATP\textsuperscript{tBu2} ligands are shown in Schemes 2.B and 2.C, using previously reported methods\textsuperscript{3,4}. The APH\textsuperscript{tBu2} ligand involves the amination and reduction of a 3,5-di-tert-butylbenzoquinone. After purification, this species was deprotonated anaerobically using sodium methoxide (NaOMe) to yield the sodium salt. Aminothiophenolate synthesis began with amination of 3,5-di-tert-butylbenzoic acid by sodium azide in acidic media. The free aniline was isolated and then brominated at the ortho position to undergo attack by potassium thiocyanate. This resulted in a thiazole ring which was treated with excess KOH at 200°C to cleave the C–N bond to form the potassium salt of 3,5-di-tert-butyl-2-mercaptoaniline. Acidic workup allowed for isolation of the ligand as a yellow-green oil, which was then dried under vacuum.
Scheme 2.D Synthesis of cobalt(II) aminophenolate complex, [Co^{2+}(Tp^ Ph^2)(APH^{tBu^2})] (1) and cobalt(II) aminothiophenolate [Co^{2+}(Tp^ Ph^2)(ATP^{tBu^2})] (2). Resulting products of aerobic oxidation [Co^{2+}(Tp^ Ph^2)(ISQ^{tBu^2})] (1^{Ox}), [Co^{2+}(Tp^ Ph^2)(ITSQ^{tBu^2})] (2^{Ox}), and after chemical oxidation with AgPF_6 [Co^{2+}(Tp^ Ph^2)(IBQ^{tBu^2})]PF_6 (4) and [Co^{2+}(Tp^ Ph^2)(ITBQ^{tBu^2})]PF_6 (5).

Under nitrogen atmosphere, addition of the cobalt(II) acetate precursor [Co^{2+}(Tp^ Ph^2)(OAc)(Hp^ Ph^2)] to the sodium salts of APH^{tBu^2} and ATP^{tBu^2} resulted in the formation of the cobalt(II) complexes shown in Scheme 2.D. The crude products were dried by vacuum and then extracted with CH_2Cl_2 for 1 and Et_2O for 2. Filtration of the solutions through Celite allowed for removal of inorganic impurities. Crystals of [Co^{2+}(Tp^ Ph^2)(APH^{tBu^2})] (1) were grown by layering the solution with CH_3CN and
subsequent storage inside a -30°C freezer. The Et₂O extracted portions of [Co²⁺(Tp²⁺)(ATP²⁺)] (2) were dried by vacuum and redissolved in CH₂Cl₂ before layering with CH₃CN. After a few days, both solutions generated red-brown prisms. Analytically-pure material was obtained by decanting the mother liquor of recrystallized product, washing the crystals with hexanes, and drying for several hours.

The oxidation of 1 and 2 was performed in CH₂Cl₂ solvent under ambient conditions (Scheme 2.D). Concentrated solutions of 1 and 2 were sparged with O₂ gas for several minutes and allowed to stir overnight. The resulting green-colored species were isolated by reducing the volume of the solution and layering with CH₃CN solvent. After several days, dark green crystals formed which were then subject to crystallographic analysis. The remaining product was dried for several hours to afford green powders of [Co²⁺(Tp²⁺)(ISQ²⁺)] (1Ox) and [Co²⁺(Tp²⁺)(ITSQ²⁺)] (2Ox) in 95-98% yield. These complexes were then dissolved in 1,2-dichloroethane and treated with one equivalent of AgPF₆ to yield [Co²⁺(Tp²⁺)(IBQ²⁺)]PF₆ (4) and [Co²⁺(Tp²⁺)(ITBQ²⁺)]PF₆ (5). The solutions were then filtered through Celite, and crystals of these species were grown by layering the solutions with CH₃CN and subsequent storage at -30°C. The remaining product was dried to afford red powders of 4 and 5 in good yields.

The complex [Co²⁺(Tp²⁺)(SQ²⁺)] (3), was generated through addition of sodium methoxide and 3,5-di-tert-butylecatecholate to [Co²⁺(Tp²⁺)(OAc)(Hpz²⁺)] in CH₂Cl₂ and methanol (Scheme 2.E). The mixture formed a dark brown color initially, then changed into a dark green color after stirring under aerobic atmosphere. The crude material was dried before extraction with Et₂O. The solution was then filtered through Celite before
storage inside a -30°C freezer. Dark green needles were isolated from the sample, which yielded 74% of product once dried.

Scheme 2.E Synthesis of cobalt(II) semiquinonate complex, \([\text{Co}^{2+}(\text{TpPh}_2)(\text{SQ}_\text{tBu}_2)]\) (3).

B. Characterization of Co(II) Complexes

Figure 2.01 Thermal ellipsoid plot (50% probability) of 1 • CH₃CN/0.5CH₂Cl₂, (3’Ph, tBu- groups, and Tp-phenyl hydrogens omitted for clarity).
The crystal structures of 1-5 were solved from diffraction data measured at 100 K using a Rigaku diffractometer. Crystals of 1 were found to be monoclinic under $P2_1/n$ space group symmetry (Figure 2.01). The crystal system of 2 is trigonal and exhibits $P\text{-}3$ space group symmetry. The counter solvent, acetonitrile, was found equimolar to 1 with half an equivalent of $\text{CH}_2\text{Cl}_2$ in the unit cell (Figure 2.02). The X-ray data reveal that the cobalt centers retain 3N facial coordination by the monoanionic Tp$^{\text{Ph}_2}$ ligand. Equatorial Co–N$_{\text{Tp}}$ bond lengths (Co–N4/N6) in 1 and 2, average between 2.06-2.09 Å which is comparable to those found in previously reported Co-Tp complexes. The complexes are neutral, with two anionic charges each contributed from the amino(thio)phenolate and the Tp$^{\text{Ph}_2}$ ligand. The remaining bonds in the N$_4$O and N$_4$S coordination spheres arise from the bidentate ligands. In the method popularized by Verschoor et al., the amount of distortion from ideal TBP geometry can be approximated using the following equation: $\tau = (\alpha - \beta)/60$. Ideal TBP geometry ($\tau = 1$) and SPY ($\tau = 0$) distortion are determined by the angles, $\alpha$ and $\beta$, which are the largest metal-ligand bond angles. Both 1 and 2 exhibit modestly distorted TBP geometries with $\tau = 0.67$ and 0.71. The phenolate and thiolate
donor atoms have equatorial bonds lengths of Co–O1 = 1.930 Å and Co–S1 = 2.265 Å (Scheme 2.F). The difference in these bond lengths is consistent with the larger atomic radius of sulfur versus oxygen. For the same reason, the aminothiophenolate has a significantly longer C–S bond (Scheme 2.F) than the corresponding C–O bond in the aminophenolate congener (C–S = 1.781 Å, C–O = 1.345 Å). Both complexes have unmistakably closed shell ligands, as reflected in the uniformity of C–C bond distances in the aromatic ring.

Scheme 2.F Bond distances (Å) between cobalt ion in coordination to aminophenolate (1, left) and aminothiophenolate (2, right). Data collected from X-ray diffractions measured at 100 K.

In comparison with the iron(II) aminophenolate complex reported earlier by our group,1 the coordination environment of 1 is closer to an ‘ideal’ TBP geometry while the ferrous analogue is slightly more distorted (τ = 0.61). The N5–Fe–N7 axial unit in the Fe(II) complex exhibits an angle of 173.2° which mirrors the axis of N2–Co–N7 in 1. Remarkably, the Fe–NH2 (2.214 Å), Fe–O (1.931 Å), and Fe–Nₜₚ bond distances are almost identical to the cobalt analogue in 1. These similarities imply that the metal identity does not have a dramatic impact on coordination geometry.

In our attempts to isolate the oxidized species, approximately 200 mg samples of 1 and 2 were dissolved in CH₂Cl₂ and then exposed to O₂ for several minutes. The
resulting solutions were left in an aerobic atmosphere, allowing for conversion to green-colored species. The oxidized complexes ($1^{\text{Ox}}$ and $2^{\text{Ox}}$) were isolated by filtration through Celite and subsequent recrystallization by layering with CH$_3$CN. Crystals of sufficient quality were analyzed via X-ray crystallography, providing the structures shown in Figure 2.03 ($1^{\text{Ox}}$) and Figure 2.04 ($2^{\text{Ox}}$).

The dark green crystals grown from oxidation of 1 are monoclinic with a space group of symmetry $P2_1/c$. The crystallographic data collected at 100 K reveal that $1^{\text{Ox}}$ (Figure 2.03) is a five-coordinate cobalt complex which adopts a distorted trigonal bipyramidal geometry ($\tau = 0.43$). This complex has an axial arrangement of O1–Co–N6 atoms which is significantly different from 1 which contains the aminophenol nitrogen on the axial N2–Co1–N7 motif. In addition to the newfound localization of aromatic bonds, the C–O1 (1.289 Å) and C–N7 (1.355 Å) bond lengths have decreased relative to the bond lengths in 1 (1.345 Å and 1.444 Å respectively).

![Figure 2.03](image)  
**Figure 2.03** Thermal ellipsoid plot (50% probability) of $1^{\text{Ox}}$ (3’Ph, tBu- groups and Tp-phenyl hydrogens omitted for clarity).
The unit cell is absent of charged ions; however, it contains one equivalent of each solvate, CH$_3$CN and CH$_2$Cl$_2$ (not shown). The high-resolution data also show a large degree of crystallographic disorder imparted by solvent molecules onto the aromatic ring of the Tp ligand due to the proximity of the tBu- group.

The immediate change in coordination environments can be seen from the deprotonation of the amino group from 1 (Scheme 2.G). This evidence supports our claims that the reaction with dioxygen involved abstraction of a H-atom. The Co–N$_{Tp}$
bond lengths average at 2.11 Å which is typical of high-spin cobalt(II) complexes like the precursors 1 and 2 (Co–N_{Tp} avg. = 2.107 Å). The ring shows an appreciable degree of ISQ radical character in 1^{Ox}, which is consistent with the predicted one-electron oxidation of the ligand. Brown has catalogued transition-metal ISQ complexes at length to provide a quantitative method of analyzing ligand oxidation states, known as metrical oxidation state (MOS). We have adopted this method which uses the C–N/O and C–C bond distances of aromatic ligands and to minimize the RMSD (root-mean-squared deviation) between them and ‘ideal’ systems with discrete integer oxidation state. From the structural data of 1^{Ox}, the calculated oxidation state of the ligand is −0.95, which is fully consistent with an ISQ monoanionic form. This value has an estimated standard deviation of 0.11 when compared with averages from previously referenced structures. A recent search in the literature reveals very few five-coordinate ISQ complexes beyond the Fe(II)-ISQ complex reported previously by the Fiedler lab. The aromatic bond distances in 1^{Ox} are comparable to those found in the structure of [Fe^{2+}(Tp^{Ph2})(ISQ^{tBu2})]. This complex contains shortened bonds with ligand C–O1 and C–N7 bond distances of 1.285 Å and 1.328 Å, respectively, which is consistent with a quinoidal distortion.

The crystal structure of 2^{Ox} reveals a square pyramidal coordination environment (Figure 2.04). The N_{Tp}–Co bond lengths (avg. = 1.99 Å) are noticeably smaller than the analogous Co(II)-ISQ complex (1^{Ox}). In addition, the ligand displays a pronounced quinoidal distortion, as shown in Scheme 2.6. The contraction of Co–N_{Tp} bonds and one-electron oxidation of the ligand correspond to the formulation [Co^{2+}(Tp^{Ph2})(ITSQ^{tBu2})], where the low-spin cobalt(II) ion is bound to an iminothiosemiquinonate (ITSQ) radical.
Figure 2.05 Thermal ellipsoid plot (50% probability) of 3 • Et₂O (3’Ph, tBu- groups, and Tp-phenyl hydrogens omitted for clarity).

Scheme 2.H Bond distances (Å) from X-ray crystal structure of 3.

In the case of 3, the X-ray crystal revealed a distorted trigonal bipyramid (τ = 0.58) with some square pyramidal character (Figure 2.05). The N6 and O1 atoms are axial with atoms N2, N4, and O2 occupying the equatorial positions. The 5-Ph substituents of Tp are positioned closely in conical arrangement creating a hydrophobic pocket around the borohydride moiety. The chelating ligand features Co–O bonds with lengths (Scheme 2.H) in agreement with previously reported cobalt semiquinonates including [Co²⁺(Tp Cum,Me)(SQtBu²)] and [Co²⁺(Tp Me³)(SQtBu²)]. All three compounds exhibit a pattern of C–C bond lengths known as the four-long/two-short distribution. The average C–O bond length is 1.285 Å, which is a significant contraction from those in
fully reduced catecholates bound to late transition metals. From the extended bond lengths between C1–C2 and the adjacent bonds, we can assume that the SQ radical is *ortho*-stabilized like previously reported examples. The five-membered chelate ring extends outward from the cobalt center in a planar manner with two Et₂O solvates found in the unit cell (not pictured) exhibiting considerable crystallographic disorder around the aromatic carbons of the SQ¹Bu² ligand. The molecule is neutral with no counterions, confirming the expected semiquinonate oxidation state of [−1]. The calculated MOS of this complex is [−0.97] which is consistent with the electronic description derived from formal oxidation state.

**Figure 2.06** X-ray crystallographic data of complex 4 with two crystallographically independent systems, 4A (left) and 4B (right). 3'Ph groups, phenyl protons and tBu-groups have been omitted for clarity.
Figure 2.07 X-ray crystal structure of 5. Some phenyl groups, protons, and tBu-substituents have been omitted for clarity.

Crystals of 4 and 5 were grown by layering concentrated solutions in C₂H₄Cl₂ with acetonitrile (IV. Experimental Section). The oxidized species 4 (Figure 2.06), appears in as two crystallographically-independent complexes (4A and 4B) within the unit cell. The determined Co–Nₜₚ bond distances reveal that the cobalt(II) centers do not experience metal-based oxidation, however, 4 contains longer Co–Nₜₚ bond distances than 5 (avg. = 2.05 Å vs. 1.98 Å), consistent with a high-spin description for the former. Thus, it appears that complexes 4 and 5 retain the respective high- and low-spin cobalt(II) configurations of ¹Ox and ²Ox. In addition, the two structures have distinct geometries where both 4A and 4B fall halfway between the SPY and TBP limits (τ = 0.5), whereas 5 is almost entirely square pyramidal (τ = 0.05; Figure 2.07).

In comparison with ¹Ox and ²Ox, the ligands are further oxidized with a noteworthy contraction of the C–O/S and C–N bond lengths (1.235/1.660 Å and ~1.3 Å, respectively). This occurs in conjunction with further distortion of the C–C bonds (Scheme 2.1), as both ligands have been oxidized to their respective benzoquinone forms. The metric oxidation parameters for 4A and 4B are [+0.07] and [+0.17], respectively,
close to the expected value of zero for a neutral iminobenzoquinone. Complex 5 exhibits a similar distortion with a computed MOS value of near zero. With the neutral charge distribution of the new benzoquinone ligands, the positive charge of the complex is stabilized by a PF$_6$ counteranion. Thus, 4 is a high-spin Co(II) complex with a neutral iminobenzoquinone ligand, while 5 is low-spin complex with a neutral iminothiobenzoquinone ligand.

![Scheme 2.1 Structurally determined bond distances for 4A and 5 measured from X-ray diffraction data (Å).](image)

**Figure 2.08** $^1$H-NMR spectra of 1 (left) and 2 (right) measured at 20°C. The spectral region between 100 to -75 ppm is displayed (400 MHz, CDCl$_3$).

Due to the inherent stability of these complexes, $^1$H-NMR spectra collected at room temperature were used in the characterization of 1-5. Crystals of 1-5 were dried under vacuum and dissolved in CDCl$_3$. With the exception of 2$^{ox}$, these complexes
display a series of peaks beyond the typical spectral region of diamagnetic species (0-14 ppm). This behavior is due to the paramagnetic nature of these complexes.

Figure 2.09 $^1$H-NMR spectrum of 3 recorded in CDCl$_3$ at room temperature.

The Evan’s method was performed at room temperature to measure the magnetic moment of these complexes.$^{10}$ Analytically pure material of 1-3 was dissolved in a CDCl$_3$ (~600 μL of solvent: 1 eq. CDCl$_3$/10 eq. CHCl$_3$) stock solution. From inside of the glovebox, a small glass capillary was filled with the stock solution and submerged inside the NMR sample tube. By referencing the difference in chemical shift (in Hz) to the solvent peak of chloroform found in the analyte solution, we were able to measure magnetic moment of the paramagnetic complexes. These experiments determined spin-only magnetic moments of 4.30 and 4.11 μ$_B$ for 1 and 2, respectively. These values are higher than the ideal spin-only magnetic moment for $S = 3/2$ systems (3.87 μ$_B$). The larger-than-ideal magnetic moment is due to unquenched orbital angular momentum, as discussed in further detail below (Section C).
The reaction of 1 with dioxygen was monitored through $^1$H-NMR spectroscopy, where it was found that the Tp$^{Ph2}$ resonances (51, 23, and -35 ppm) of 1 were not conserved in complex 1$^{Ox}$. However, the observed chemical shifts (Figure 2.10) indicate that the geometry and magnetic environment of these moieties has not changed greatly. The formation of several new singlet peaks between 35 and -40 ppm is consistent with the formation of a new species. The Evans method found a magnetic moment of 2.90 $\mu_B$ ($S = 1$), indicative of antiferromagnetic coupling between the high-spin Co(II) center and the ISQ radical.

Unlike 1$^{Ox}$, $^1$H-NMR spectra indicate that 2$^{Ox}$ is as a diamagnetic complex that only exhibits peaks in the 0-14 ppm region (Figure 2.10). Protons of the tert-butyl groups appear as large singlet peaks in the region between 1-2 ppm, consistent with prior reports in the literature. The protons at the 4-position of the pyrazole rings appear around 6 ppm and the borohydride proton appears at 4 ppm as a broad resonance.

Figure 2.10 $^1$H-NMR data of 1$^{Ox}$ (left) and 2$^{Ox}$ (right) after room temperature (in CD$_2$Cl$_2$) after reaction with O$_2$. 
The $^1$H NMR spectra of 4 and 5 suggest that both complexes are paramagnetic in nature (Figure 2.11). Notably, there are fewer resonances in the negative region of the spectra compared to the previous complexes. Furthermore, the tert-butyl peaks of the benzoquinone ligands are spaced in the diamagnetic region rather than paramagnetically shifted. Values determined by the Evans method confirmed that 4 is a high-spin cobalt(II) complex with $\mu_{\text{eff}} = 4.49 \ \mu_B$ and 5 is a low-spin cobalt(II) complex with $\mu_{\text{eff}} = 1.97 \ \mu_B$ (consistent with a $S = 1/2$ spin state).

Figure 2.12 UV-vis spectra collected at room temperature. Complexes 1 (black line) and 2 (red line) in CH$_2$Cl$_2$ solutions (0.5 and 1.0 mM, respectively).
Samples of 1 and 2 were dissolved in CH$_2$Cl$_2$ to give reddish-brown solutions and electronic absorption spectra were measured at room temperature (Figure 2.12). Both complexes have visible absorption bands arising from d-d transitions. The assignment of electronic transitions is consistent with high-spin d$^7$ systems.\textsuperscript{11} These moderately intense features ($\varepsilon = 500$ M$^{-1}$ cm$^{-1}$) gain some intensity by mixing with LMCT bands which are also broadened due to vibronic coupling.

The reaction between 1 and 2 and dioxygen in CH$_2$Cl$_2$ was monitored over several hours (Figure 2.13 and Figure 2.14). The brown chromophore converts to a dark green species (1$^{Ox}$) which is stable under aerobic conditions. The visible features of this complex show a broad absorption pattern centered at 700 nm with three peaks at 610, 705, and 775 nm, ($\varepsilon = 460$ M$^{-1}$ cm$^{-1}$).

\textbf{Figure 2.13} UV-vis monitored dioxygen reaction of 1 (0.5 mM, black line) yields 1$^{Ox}$ (green line) after 24 hr. at 20°C in CH$_2$Cl$_2$. 

Attempts to observe oxygenated intermediates at low temperatures were not successful for 1 and 2, with no new spectral changes occurring below -20°C. It was possible to generate $2^{Ox}$ in the absence of oxygen by the use of tri-tert-butylphenoxyl radical (TTBP$^\bullet$). This sterically bulky radical acts as an external proton and electron acceptor in a process known as hydrogen atom transfer (HAT). As shown in Figure 2.14, treatment of 2 with (TTBP$^\bullet$) produces a spectrum identical to O$_2$-generated $2^{Ox}$. The TTBP radical loses all of its visible features after HAT as it converts to 2,4,6-tri-tert-butylphenol. This result confirms that both green species formed by aerobic oxidation are products of HAT.

Figure 2.15 compares the absorption spectra of $1^{Ox}$, $2^{Ox}$, 3, 4, and 5. The spectrum of 3 which contains a SQ radical ligand, displays three broad peaks in the visible region (570, 615, and 740 nm, $\varepsilon_{avg} = 500$ M$^{-1}$ cm$^{-1}$) associated with intraligand $\pi \rightarrow \pi^*$ transitions. The previously characterized complex [Co$^{2+}$($\text{Tp}^{\text{Cum,Me}}$)(SQ$^{\text{Bu}_2}$)] exhibits a similar set of peaks at 622 and 722 nm ($\varepsilon = 600$, and 700 M$^{-1}$ cm$^{-1}$).
Figure 2.15 Left: comparison of UV-vis spectra of $1^{\text{Ox}}$ (1.0 mM, black), $2^{\text{Ox}}$ (0.9 mM, green), and $3$ (1.3 mM, blue). Right: UV-vis spectra of $4$ (0.5 mM, black) and $5$ (0.3 mM, red) in CH$_2$Cl$_2$ measured at room temperature.

C. Analysis of Magnetic Properties by EPR, FIRMS, and Computational Methods

Magnetic susceptibility measurements were performed at University of Wisconsin-Madison, by Dr. Daniel SantaLucia from Dr. John Berry’s group, using elementally pure samples of $1$ and $2$. All magnetic susceptibility and magnetization data were modeled using the fitting program PHI v.3.1.5. The data collected in temperature range of 1.8 to 271 K yields the spectra shown in Figures 2.16-2.18. The susceptibility data for $1$, $2$, and $4$ were modeled using the following general form for the spin Hamiltonian:

$$H = \sum_l \beta \vec{S}_l \cdot \vec{g}_l \vec{H} + \sum_l \vec{S}_l \cdot \vec{D}_l \vec{S}_l$$

where $\beta$ is the Bohr magneton, $\vec{H}$ is the applied external magnetic field, and where $\vec{S}_l$, $\vec{g}_l$, and $\vec{D}_l$ are the spin vector, electron $g$-value tensor, and single-ion anisotropy tensor for a given spin center, respectively. The first term of the spin Hamiltonian accounts for magnetic Zeeman interactions of the electron spins with an applied field while the second accounts for single-ion anisotropy (due to ZFS) for each spin center. The $g$-tensors were
modeled with axial components, $g_\parallel = g_\perp = g_z = g_x = g_y$. The ZFS $D$-tensor, was modeled with axial ($D$) and rhombic ($E$) components. Magnetic susceptibility data are often insensitive to the sign of $D$. However, for all data collected, positive values led to physically unreasonable fits, while using negative values for $D$ provided excellent agreement to other spectroscopic measurements; thus, $D$ is reported as negative for each compound. The susceptibility data for 3 were modeled including an extra isotropic exchange term in the spin Hamiltonian to account for antiferromagnetic coupling between the two spin centers in the compound. The Heisenberg-Dirac-Van Vleck exchange Hamiltonian operator was used. It is given by

$$\hat{H}_{\text{ex}} = -2J_{AB}\vec{S}_A \cdot \vec{S}_B$$

where positive and negative values for $J_{AB}$ correspond to ferromagnetic and antiferromagnetic coupling, respectively, between two spin centers $\vec{S}_A$ and $\vec{S}_B$. Fits were accomplished by using PHI software, yielding axial $g$-values; $g_\perp = 1.569$ and $g_\parallel = 2.205$. Interestingly, both complexes feature a sharp decline in magnetic response $\chi_p$ as temperature is decreased between 70 to 1.8 K. This drop in paramagnetism is due to zero-field splitting, which indicates a significant energy gap between the non-integer $m_s$ sublevels.
Figure 2.16 Paramagnetic susceptibility plotted as $\chi_p T$ vs. T (left) and as $\chi_p$ vs. T (right) for 1. The outlier point at T = 10.7 K was excluded for modeling the data, as was the high temperature point at T = 300 K.

Figure 2.17 Paramagnetic susceptibility plotted as $\chi_p T$ vs. T (left) and as $\chi_p$ vs. T (right) for 2. The data was recorded between 1.8 to 300 K.

The fitting of this behavior estimates a large $D$-tensor of 39.4 cm$^{-1}$ which is rather large for a TBP complex.$^{16}$ The rhombic component of ZFS is determined as $E$, which by fitting was determined as 9.8 cm$^{-1}$. These fits could not estimate the sign of $D$, which can only be assumed when using magnetometry measurements.

Magnetic susceptibility data collected for complex 2, shown in Figure 2.17, follow a similar pattern as the isoelectronic analogue in 1. In this case, the value of $\chi_p T$
from 275 K, 3.26 cm$^3$ K mol$^{-1}$, decreases linearly to 2.79 cm$^3$ K mol$^{-1}$ at 75 K before markedly dropping off to 2.17 cm$^3$ K mol$^{-1}$ at 1.8 K. The observed $\chi_P \cdot T$ values at 1.8 K for 1 and 2 agree well with the anticipated spin-only value for high-spin cobalt(II), 1.875 cm$^3$ K mol$^{-1}$, confirming that both are $S = 3/2$ systems. The deviations from the expected spin-only value are typical for mononuclear high-spin cobalt(II) complexes. The data for complex 4, also exhibits the same general trend, albeit with lower-than-expected values for $\chi_P \cdot T$ over the entire temperature range. The magnetic susceptibility data collected for 1, 2, and 4 were modeled using an $S = 3/2$ spin-Hamiltonian and the fits yielded negative axial ZFS ($D$) values of -41.4(1), 77.7(5), and -29.6(3) cm$^{-1}$ for 1, 2, and 4, respectively.

The magnetometry data indicate that 1 and 2 possess very large and negative magnetic anisotropy; this conclusion is further supported by spectroscopic and computational studies (Table 2.A). The large magnitude of the $D$-values is the result of unquenched orbital angular momentum. In such cases, the spin-Hamiltonian model breaks down and the validity of the ZFS parameters is questionable. Nevertheless, the values extracted from our magnetometry experiments provide useful parameters by which to evaluate results obtained from multiple physical techniques, as well as a means to compare our findings to those reported in the literature. The structural basis for the unusually large and negative anisotropy lies in the structural constraints provided by the Tp$^{Ph_2}$ ligand. These complexes, which do not belong to either the tripodal or pincer classes of five-coordinate cobalt(II) species, impose a 90-degree equatorial angle between the $N_{Tp}$ donors from pyrazoles of Tp. This in turn allows for the stabilization of $d_{xy}$ and $d_{yz}$ orbitals through electronic donation.
Figure 2.18 Magnetic susceptibility data for complex $^{1}$Ox (blue circle) and 3 (orange diamonds) plotted as $\chi_p T$ vs. T (K) with fitted data. The TIP (temperature independent paramagnetism) correction for 3 was used as a parameter in the fit, while for $^{1}$Ox a fixed value was used. Fit parameters for $^{1}$Ox: $S = 1$, $g_\perp = 2.049(6)$, $g_\parallel = 3.176(4)$, $D = -168(3)$ cm$^{-1}$, $|E| = 8.68(2)$ cm$^{-1}$, TIP = 0.0017(2) cm$^3$ mol$^{-1}$ (fixed). Fit parameters for 3: $S = 1$, $g_\perp = 2.46(2)$, $g_\parallel = 3.003(6)$, $D = -135(5)$ cm$^{-1}$, $|E| = 11.6(1)$ cm$^{-1}$, $J = -121(4)$ cm$^{-1}$, TIP = 0.00132(5) cm$^3$ mol$^{-1}$.

Due to strong antiferromagnetic coupling between the cobalt(II) center and ISQ radical, complex $^{1}$Ox was modeled as an effective $S = 1$ spin center following the general form of the spin-Hamiltonian above. In contrast, 3 was modeled as two antiferromagnetically coupled spin centers, $S = 3/2$ and $S = 1/2$, where the $g$-tensor of the SQ radical was fixed at $g_{\text{iso}} = 2.00$. After the parameters were obtained from modeling the susceptibility data for complex 3, they were used as fixed parameters in simulations to establish an upper limit for the isotropic exchange coupling constant.

The X-band EPR spectrum of 1 (in frozen CH$_2$Cl$_2$) was collected at 10 K (Figure 2.19). The EPR data contain transitions from the $m_s = \pm 3/2$ manifold, indicative of negative zero-field splitting.$^{18}$ Hyperfine splitting from the $^{59}$Co ($I = 7/2$) nucleus is also evident in the $g = 6.5$ resonance (Scheme 2.J). Similar features were previously observed with the CDO model complex $[\text{Co}^{2+}(\text{Tp}^{\text{Ph2}})(\text{CysOEt})].^{11}$
Figure 2.19 X-band EPR spectrum of 1 measured at 10 K, using in frozen solution (2.6 mM) in CH$_2$Cl$_2$ solvent. Frequency = 9.474 GHz, power = 5.0 mW, modulation amplitude = 10 G. The featured denoted with (*) is from a cupric impurity in the sample cavity.

Scheme 2.J Effective spin Hamiltonian for $S > 1/2$ systems with axial zero-field splitting ($D$) and anisotropic hyperfine splitting coefficient ($A$).

While 2$^{Ox}$ is diamagnetic, the oxidized derivative 5 is best described as an $S = 1/2$ species with no observable zero-field splitting effects. The X-band EPR spectrum of 5 (Figure 2.20), displays the anisotropic signal associated with an axial system with considerable rhombicity. Interestingly, this spectrum contains the transition from the doublet manifold of $m_s = \pm 1/2$ with a temperature dependence of the high-field resonance between 10 and 20 K. In addition, the $S = 1/2$ signal features anisotropic hyperfine splitting $A_{Co} = 68$ G which indicates the bulk of spin density lies on the cobalt(II) center. Additional hyperfine splitting in the resonance at $g = 2.62$ is consistent with the axial nature of this cobalt(II) complex.
Figure 2.20 Left: X-band EPR spectrum of a frozen solution of 5 (2.0 mM) collected in THF at 20 K. Experimental parameters: frequency = 9.386 GHz, power = 0.63 mW, modulation amplitude = 10 G.

Both data from the Evans method and X-band EPR agree with the assignment of $S = 3/2$ ground-states for 1, 2, and 4. However, the deviation from the ideal spin-only magnetic moment, and the origin of the large zero-field anisotropy are not explained entirely by conventional methods. High-field -frequency EPR (HFEPR) is a relatively new technique that can monitor the spin-allowed transitions at multiple frequencies, allowing us to establish a “trajectory” of transitions between Kramers doublets (or between them e.g., inter-Kramers doublets).
Figure 2.21 High-field EPR spectra of 1 (top), 2 (middle), 4 (bottom) collected at 10 K with amorphous powder samples (experimental, black; simulated, red). Complex 1: frequency = 140.1 GHz, \(D = -38.7 \text{ cm}^{-1}\), \(E = -10.0 \text{ cm}^{-1}\) (\(E/D = 0.26\)), \(g_x = 2.20\), \(g_y = 2.08\), \(g_z = 2.51\). Complex 2: frequency = 101.3 GHz, \(D = -77.4 \text{ cm}^{-1}\), \(E = -11.8 \text{ cm}^{-1}\) (\(E/D = 0.15\)), \(g_x = 2.31\), \(g_y = 2.20\), \(g_z = 2.62\). Complex 4: frequency = 101.4 GHz, \(D = -18.8 \text{ cm}^{-1}\), \(E = -6.3 \text{ cm}^{-1}\) (\(E/D = 0.33\)), \(g_x = 2.05\), \(g_y = 2.0\), \(g_z = 2.4\). The three sharp resonances are interpreted as a powder pattern of a low-spin (\(S = 1/2\)) Co(II) impurity and were not simulated.

Using this method, the spin-orbit coupling (SOC) from excited-state coupling to the ground state of Co(II) can be deconvoluted allowing for determination of ZFS parameters (\(D\) and \(E\)). As visualized in Figure 2.21, HF EPR spectra were collected on microcrystalline powders of 1, 2, and 4 using the high-field magnet at MagLab (National High Magnetic Field Laboratory in Tallahassee, Fl). With the expertise of Drs. Jurek Krystek, Andrew Ozarowski, and Mike Ozerov, it was possible to map several more transitions between the \(m_s = \pm 3/2\) manifold. The “effective” \(g\)-values which arise from orientational effects, are eliminated by using multiple high-field measurements of each
transition. For instance, the field-frequency map of complex 1 was completed by measuring spectra between the 90-540 GHz range (Figure 2.22). Once propagated to higher frequencies, the turning point of each EPR-allowed transition is visible at higher field strengths, due to the Zeeman effect. To observe several resonances, this technique employs magnetic fields of up to 16 T. This permits observation of intra-Kramers transitions within $m_s = \pm 3/2$ manifold. All turning points are contained within the $m_s = |\pm 3/2\rangle$ doublet, confirming the negative $D$-value of 1. The high-field frequency maps of 2 and 4 were plotted at various energies (measured between 50-500 GHz) in Figure 2.23, which allowed for the determination of $D$ and $E$, by the use of fitting (see table 2A).

Figure 2.22 2D frequency-field map of magnetic transitions found in powder mulls of 1, transitions from $m_s = \pm 3/2$ manifold (black dots, linear fit = red line).

FIRMS (far-infrared magnetic spectroscopy) experiments were also performed on $n$-eicosane mulls of all the five complexes. The 2D color maps shown in Figure 2.23
depict low-temperature (4.8 K) terahertz normalized transmittance spectra for $S = 3/2$ complexes (1, 2, and 4) at magnetic fields between 0 and 17 T. Resonance absorptions that change position with increasing magnetic field are highlighted in blue, whereas regions lacking field-dependent features are yellow. The vertical stripes are due to spin/phonon coupling modes that are insensitive to magnetic field. In complex 1, we detected a zero-field (zf) resonance of magnetic origin at 84.7 cm$^{-1}$ (Figure 2.23, left). This feature arises from the $m_s = |±3/2⟩ → |±1/2⟩$ transition, which has an energy of $\Delta_{ms} = 2(D^2 + 3E^2)^{1/2}$ for a $S = 3/2$ system. It was not possible to deconvolute $D$ and $E$ from a zero-field experiment on a Kramers system like cobalt(II), thus HFPR experiments were also performed on the same sample in the frequency range of 50-500 GHz. The final spin Hamiltonian parameters for complex 1 were obtained from the combined FIRMS/HFPR 2D field vs. frequency map as shown in Figure 2.23 (left). FIRMS data measured for 2 (Figure 2.23, middle) is partially affected by artifacts originating from strong phonon absorptions, but the inter-Kramers transition of 2 is evident at 161.2 cm$^{-1}$ in zero field. Even though the $E/D$-value of 2 is not known, the large $\Delta$-splitting observed by FIRMS agrees nicely with the sizable increase in magnetic anisotropy from 1 → 2 observed by magnetometry. This effect is predicted due to the higher spin-orbit coupling factor from the substitution of sulfur in this system. The FIRMS spectrum of 4 (Figure 2.23, right) The FIRMS spectra of complex 4 showed a rather weak inter-Kramers resonance at 46 cm$^{-1}$ in zero field. The low-field signal at 1 T at 101 GHz can be clearly identified as the parallel turning point of the intra-Kramers transition within the $m_s = |±3/2⟩$ doublet, analogous to complexes 1 and 2. The group of three sharp resonances at higher field (3-4 T) cannot be reconciled with an $S = 3/2$ system and must represent a different spin
species. We tentatively identify those signals as originating from a low-spin \((S = 1/2)\) Co(II) impurity characterized by a rhombic g-tensor.

Complexes \(1^{\text{Ox}}\) and \(3\) are EPR-silent even at the highest 625 frequencies available, indicative of a very large absolute value of \(D\). A single z\(f\) resonance of magnetic origin was observed by FIRMS at 117.5 and 130.0 cm\(^{-1}\) for \(1^{\text{Ox}}\) and \(3\), respectively (Figure 2.24). Given the negative sign of \(D\), as suggested by magnetometry and calculations, this feature corresponds to the \(|D + E|\) transition, where it is assumed that \(D\) and \(E\) have the same sign. The fact that a second z\(f\) resonance, corresponding to the \(|D \rightarrow E|\) transition, was not observed by FIRMS is consistent with the negative anisotropy of these complexes and indicates a sizable magnitude of \(E\), which makes the next higher-energy spin sublevel \(m_S = |+1\rangle\) unpopulated at low temperature. The \(\Delta m_S = \pm 2\) transition between the \(m_S = |-1\rangle\) and \(+1\rangle\) levels were not observed for either \(1^{\text{Ox}}\) or \(3\), which suggests that the \(E\)-values are smaller than half of the lower boundary of the FIRMS transmittance window (\(\sim 20\) cm\(^{-1}\)). Thus, based on the FIRMS data, we can conclude that the \(D\)-values of \(1^{\text{Ox}}\) and \(3\) fall within the range of -100 to -130 cm\(^{-1}\), in excellent agreement with the magnetometry results.\(^{19,20}\)
Table 2.A Magnetic parameters determined by magnetic susceptibility, HF-EPR/FIRMS, and quantum chemical calculations (QCT).

<table>
<thead>
<tr>
<th>complex (spin)</th>
<th>g-values</th>
<th>ZFS parameters</th>
<th>methods</th>
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<tbody>
<tr>
<td>1 (S = 3/2)</td>
<td></td>
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<tr>
<td>2.08(2)</td>
<td>2.20(3)</td>
<td>2.51(1)</td>
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<td>2.140(2)</td>
<td>2.140(9)</td>
<td>2.6615(4)</td>
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<td>2.012</td>
<td>2.227</td>
<td>2.636</td>
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<tr>
<td>2 (S = 3/2)</td>
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<tr>
<td>2.216(6)</td>
<td>2.326(6)</td>
<td>2.72(1)</td>
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<td>2.096(7)</td>
<td>2.096(7)</td>
<td>2.7898(6)</td>
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<td>1.954</td>
<td>2.186</td>
<td>2.842</td>
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<tr>
<td>1^os (S = 1)</td>
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<tr>
<td>2.040(6)</td>
<td>2.040(6)</td>
<td>2.941(4)</td>
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<tr>
<td>1.903</td>
<td>2.030</td>
<td>3.402</td>
<td></td>
</tr>
<tr>
<td>3 (S = 1)</td>
<td></td>
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<tr>
<td>2.46(2)</td>
<td>2.46(2)</td>
<td>3.003(6)</td>
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<tr>
<td>1.881</td>
<td>2.028</td>
<td>3.436</td>
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<td>4 (S = 3/2)</td>
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<td>2.003(4)</td>
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<tr>
<td>2.143</td>
<td>2.267</td>
<td>2.437</td>
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</table>

a NA = not applicable; ND = not determined. b The sign of $E$ obtained by HF-EPR and magnetic susceptibility is arbitrarily assumed to be the same as that of $D$. c $J$-values were computed using the $H_{ex} = -2J \cdot S_A \cdot S_B$ formalism. d Because FIRMS simulations are largely insensitive to g-values, an isotropic g-tensor ($g_{iso} = 2.00$) was employed. e QCT = parameters derived from quantum chemical calculations employing the CASSCF/NEVPT2 approach (def2-TZVP basis set).
Figure 2.23 Color maps (intensity vs. field and energy/frequency) of far-infrared resonance absorption measured for complexes 1 (left), 2 (middle), and 4 (right) measured at 4.6 K. Regions of magnetic absorption are indicated with blue. The lines are simulations of turning points in the powder spectra that assume the (best-fitted) spin Hamiltonian parameters shown in Table 2.A. The circles at low frequencies (below those accessible by FIRMS) correspond to the observed HFEPR resonances.

Figure 2.24 Color maps (intensity vs. field and energy/frequency) of far-infrared resonance absorption measured for complexes 1°x (left) and 3 (right) at 4.6 K. Regions of magnetic absorption are indicated with blue in the colored FIRMS maps. The lines are simulations of turning points in the powder spectra that assume the spin-Hamiltonian parameters shown in Table 2.A.
Figure 2.25 CASSCF/NEVPT2 computed energies of the five lowest-energy quartet states of complexes 1, 2, and [Co$^{2+}$Cl(tpta)]$^+$. The contribution of each excited state to the molecular $D$- and $E$- parameters is indicated in red and blue, respectively.

Based on insights provided by the CASSCF/NEVPT2 calculations, we are now able to rationalize the much greater negative anisotropy of 1 and 2 compared to five-coordinate cobalt(II) complexes with tripodal ligands, such as TPMA and (Me$_6$)tren.$^{21-22}$ Figure 2.25 compares the LF energies of 1 and 2 to those computed for [Co$^{2+}$Cl(tpta)]$^+$, where tpta is the tetradeinate chelate tris[(1-phenyl-1H,1,2,3-tris(triazol-4-yl)methyl]amine.$^{16}$ The latter complex was the subject of a recent experimental study that found the following spin-Hamiltonian parameters: $g_{1,2,3} = 2.22, 2.32, 2.42; D = -9.02$ cm$^{-1}$; $|E| = 1.64$ cm$^{-1}$. The three equatorial N–Co–N bonds angles of [Co$^{2+}$(X)(tpta)]$^+$ are roughly equivalent at 112°, resulting in $C_{3v}$ symmetry. The $^4A_2$ ground state is accompanied by four low-lying quartet excited states: $^4A_1$, $^4E$, and $^4A_2$ in order of increasing energy. These four excited states are largely derived from the $(e)^3(e)^3(a_1)^1$ configuration. From the experimental absorption spectra,$^{76}$ it was determined that the $^4A_1$
state of \([\text{Co}^{2+}(\text{Cl})(\text{tpta})]^+\) lies 5300 cm\(^{-1}\) above the ground state (somewhat higher than the computed energy of 4800 cm\(^{-1}\)). Like the \(A'(1)\) state in complexes 1 and 2, the contribution of the \(^4A_1\) state to the \(D\)-tensor of \([\text{Co}^{2+}(\text{Cl})(\text{tpta})]^+\) is negative (-24.5 cm\(^{-1}\)). However, this effect is partially offset by the positive contribution of the \(^4E\) state (+17.3 cm\(^{-1}\)), resulting in an overall computed \(D\)-value of -6.7 cm\(^{-1}\).

Although complexes 1, 2, and \([\text{Co}^{2+}(\text{Cl})(\text{tpta})]^+\) share TBP geometries, the structural distortions introduced by the facially coordinating \(\text{Tp}^{\text{Ph}2}\) ligand cause dramatic shifts in ligand-field energies that impact magnetic anisotropy. As noted above, the \(\text{Tp}^{\text{Ph}2}\) ligand of 1 and 2 enforces a \(\sim 95^\circ\) angle between the equatorial pyrazole donors, thereby increasing the equatorial \(\text{N}_{\text{Tp}}-\text{Co}-\text{O/S}\) angles to around 130° (Figure 2.26). The disparity in equatorial bond angles splits the pair of Co 3d\(_{xy}\)- and 3d\(_{x^2-y^2}\)-based molecular orbitals (MOs) of 1 by 3645 cm\(^{-1}\), as illustrated in Figure 2.26. The stabilization of the d\(_{x^2-y^2}\) orbital in 1 and 2 accounts for the low energies of the \(^4A'(1)\) and \(^4A''(2)\) excited states, as these states are generated by one-electron \(d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}\) excitations. Following perturbation theory, the lower relative energy of the \(^4A'(1)\) excited state sharply increases its negative contribution to the magnetic anisotropy. At the same time, the positive contributions of the \(E'\) state in \(C_{3v}\) symmetry are diminished by its splitting into \(A'/A''\) states in \(C_s\) symmetry. Thus, the sizable negative of 1 and 2 is achieved by avoiding the \(C_{3v}\) symmetry of five-coordinate Co(II) complexes with tripodal ligands.
Figure 2.26 Energy level diagram for the cobalt 3d orbitals of $[\text{Co}^{2+}\text{Cl(tpta)}]^+$ and 1. Orbital energies were obtained by application of ligand field theory to the NEVPT2 transition energies, as described by Schweinfurth et al.\textsuperscript{16} The 3d orbitals of 1 are labeled according to their dominant component (the coordinate scheme employed for 1 is indicated in the figure).

To further examine this hypothesis, we generated a computational model in which the tridentate Tp$^{\text{Ph2}}$ ligand of 1 was replaced with three unconstrained, monodentate 1-methyl-3-phenylpyrazole (pz$^{\text{Me,Ph}}$) ligands, i.e., $[\text{Co}^{2+}(\text{APH})(\text{pz}^{\text{Me,Ph}})_3]^+$. The structure of $[\text{Co}^{2+}(\text{APH})(\text{pz}^{\text{Me,Ph}})_3]^+$ obtained by DFT geometry optimization features equatorial N–Co–N/O bonds angles of 115°, 117°, and 123°, which are closer to the ideal value of 120° than those observed in the X-ray structure of 1. Most notably, the change in molecular geometry from 1 $\rightarrow$ $[\text{Co}^{2+}(\text{APH})(\text{pz}^{\text{Me,Ph}})_3]^+$ is accompanied by a dramatic reduction in the magnitude of the computed $D$-value from -49 to -21 cm$^{-1}$. Collectively, these results support our conclusion that unusually large and negative $D$-values of 1 and 2 originate from structural constraints imposed by the Tp$^{\text{Ph2}}$ ligand.
D. Quantum Chemical Calculations of Cobalt-(imino)semiquinonate Complexes

The broken symmetry (BS) approach\textsuperscript{23,24} was applied to DFT calculations of \textit{1}\textsuperscript{Ox} and \textit{3} in order to probe cobalt-ligand exchange interactions. These calculations yielded \( J \)-values of -479 and -176 cm\(^{-1} \) for \textit{1}\textsuperscript{Ox} and \textit{3}, respectively (the \( H_{ex} = -2J \cdot S_A \cdot S_B \) formalism and Yamaguchi method\textsuperscript{25,26} were employed). Thus, DFT correctly predicts that \textit{1}\textsuperscript{Ox} and \textit{3} possess \( S = 1 \) ground states arising from antiferromagnetic (AF) coupling between the high-spin Co(II) center and (imino)semiquinonate radical. Furthermore, in agreement with the magnetic susceptibility data, the DFT calculations found that the AF interaction is much stronger in \textit{1}\textsuperscript{Ox} than \textit{3}, although BS-DFT overestimates the magnitude of \( J \) by \(~50 \) cm\(^{-1} \) in the case of \textit{3}. Exchange coupling parameters were also obtained from CASSCF/NEVPT2 calculations, where the active space consisted of 7 d-electrons in the Co(3d) shell and an unpaired electron in an (imino)semiquinonate-based MO (i.e., CAS(8,6)). This approach yielded a \( J \)-value of -128 cm\(^{-1} \) for \textit{3} – remarkably close to the experimental value of -121(4) cm\(^{-1} \) (Table 2.A). In both complexes, the AF exchange is mediated by overlap between the singly-occupied MO (SOMO) of the radical and the 3d\(_{xy}\)-based MO of cobalt, as illustrated in Figure 2.30. The degree of orbital overlap (\( S \)), as computed by BS-DFT, is greater for \textit{1}\textsuperscript{Ox} (\( S = 0.32 \)) than \textit{3} (\( S = 0.22 \)), which accounts for the observed difference in \( J \)-values.

The CASSCF/NEVPT2 calculations also provide insights into the role of the ligand-based radical in modulating the energies of ligand-field states and, hence, the ZFS parameters. A high-spin Co(II) center possesses 10 quartet LF states, each of which couples to the ISQ or SQ radical to generate a pair of quintet and triplet states. From the relative energies of quintet/triplet pairs arising from the same electronic configuration, it
is possible to derive the LF energies of a hypothetical “uncoupled” complex that lacks AF exchange. The results of this procedure are shown in Figure 2.27 for complex $1^{\text{Ox}}$. In the absence of exchange coupling, the computed energy difference between the ground-state and first excited-state is 793 cm$^{-1}$ (this energy gap is labeled $\Delta E_1^{\text{UC}}$; UC = uncoupled). Comparison of the computed LF energies $1$ and $1^{\text{Ox}}$ suggests that oxidation of APH to ISQ reduces the relative energy of the first excited-state by $\sim 700$ cm$^{-1}$, largely by stabilizing the Co $3d_{x^2-y^2}$ orbital. Thus, changes in ligand oxidation state have a major impact on LF energies, independent of exchange interactions.

In the presence of AF exchange, the lowest-energy excited-state, $3A''(1)$, lies only 650 cm$^{-1}$ above the $3A'(1)$ ground state ($\Delta E_1^{\text{AF}}$ in Figure 2.27). This result suggests that coupling to the ISQ radical shrinks the $\Delta E_1$ gap by $\sim 140$ cm$^{-1}$. In contrast, exchange interactions increase the relative energy of the $3A'(2)$ excited state (i.e., $\Delta E_2^{\text{AF}} > \Delta E_2^{\text{UC}}$), demonstrating that the impact of AF coupling is not uniform across the LF states.
Figure 2.27 Right: CASSCF/NEVPT2 computed energies of the six lowest-energy states of complex 1\textsuperscript{Ox}. Energy splittings between the three triplet states are indicated by $\Delta E_1^{AF}$ and $\Delta E_2^{AF}$ (AF = antiferromagnetic). Left: relative energies of ligand-field states in the absence of exchange coupling between Co(II) and ISQ (i.e., $J = 0$). The energy of each uncoupled (UC) state was calculated by taking the weighted average of the corresponding quintet and triplet energies: $E^{UC} = 3/8 \ E(\text{triplet}) + 5/8 \ E(\text{quintet})$. 

Inclusion of SOC effects in CASSCF/NEVTP2 calculations of 1\textsuperscript{Ox} causes extensive mixing between the $^3A'(1)$ ground state and low-lying $^3A''(1)$ excited state due to their close proximity. As shown in Figure 2.28 for 1\textsuperscript{Ox}, the presence of SOC gives rise to six low-energy states within a 1000 cm\textsuperscript{-1} range. The two lowest-energy states are separated by 17 cm\textsuperscript{-1} ($\delta_1$ in Figure 2.29), while a third lies at 188 cm\textsuperscript{-1} above the ground-state ($\delta_2$). Calculations of complex 3 provided similar $\delta_1$- and $\delta_2$-values of 26 and 226 cm\textsuperscript{-1}, respectively. The computational results provide a helpful framework for interpreting the experimental magnetic and spectroscopic data presented above.

Specifically, we can now assign the zero-field transition observed at 117 and 130 cm\textsuperscript{-1} in FIRMS spectra of 1\textsuperscript{Ox} and 3, respectively, to the $\delta_2$ splitting in Figure 2.29. The CASSCF/NEVPT2 calculations overestimate the size of the zero-field transition by ~50% but correctly predict the modest increase in $\delta_2$ from 1\textsuperscript{Ox} to 3.
As noted previously, the ZFS model must be applied cautiously to complexes like $1^{\text{Ox}}$ and 3 with low-lying LF states. Nevertheless, to a rough approximation, the three lowest-energy states correspond to the $|S, M_S| = |1, \pm 1|$ and $|S, M_S| = |1, 0|$ components of a classical $S = 1$ system with $D < 0$. Following this assumption yields the ZFS parameters reported in Table 2.A. The computed $D$-values are larger in magnitude than those extracted from the magnetic susceptibility data, which suggesting that energy of the lowest excited state is underestimated (i.e., the computed values of $\Delta E_1^{\text{AF}}$ are too low). Despite this, the CASSCF/NEVTP2 results are fully consistent with the large and negative anisotropy observed experimentally for $1^{\text{Ox}}$ and 3.
Figure 2.29 DFT-generated contour plots of the spin-up Co 3d_{xy}-based MO (green and yellow) and spin-down SQ π*-based MO (blue and grey) of complex 3. These two singly-occupied MOs mediate AF exchange interactions between the Co(II) center and SQ radical. The phenyl rings of the pyrazole donors have been removed for the sake of clarity.

E. Quantum Chemical Calculations of Cobalt Iminobenzoquinone Complex

FIRMS and HFEPR studies of complex 4 revealed a strongly rhombic $D$-tensor ($E/D \sim 0.33$) and an inter-Kramers splitting of $\Delta = 46 \text{ cm}^{-1}$, roughly half the magnitude of the $\Delta$-value measured for 1. The X-ray crystal structure of 4•PF$_6$ features two symmetry-independent Co(II) complexes (labeled 4A and 4B) in the unit cell. The geometries of 4A and 4B are similar, and each lies nearly halfway between the SPY and TBP limits. CASSCF/NEVPT2 methods were applied to both structures. The 4B structure yields computed $D$- and $E$-values (-21 and -5.9 cm$^{-1}$, respectively) in excellent agreement with the experimental values of $|D| = 19.9$ and $|E| = 6.64 \text{ cm}^{-1}$ obtained by HFEPR and $D = -29.6 \text{ cm}^{-1}$ obtained by dc magnetic susceptibility. However, the $D$-value of -7.4 cm$^{-1}$ calculated for 4A is considerably more negative. These results suggest that minor changes molecular geometry can have a major impact on ZFS parameters.
The smaller magnetic anisotropy of 4 can be attributed to the arrangement of its three pseudo-equatorial N-donor ligands (N2, N4, and N6). As described above, 1 and 2 exhibit idealized $C_5$ symmetry with equatorial bond angles near 95°, 130°, and 130°. In contrast, the three equatorial angles of 4B display quite different values of 96.6°, 118.9°, and 138.6° (similar angles are observed for 4A). The loss of mirror-plane symmetry causes extensive mixing among the $d_{xz}/d_{yz}$ and $d_{xy}/d_{x^2-y^2}$ orbitals, which increases the rhombicity of the molecular $D$-tensor. Although the energy of the first excited state remains rather low at 2130 cm$^{-1}$ for 4B, the magnitude of its contribution to axial ZFS is sharply reduced. Thus, for this series of Co(II) complexes, it appears that negative magnetic anisotropy is diminished by loss of any molecular symmetry (in this case the mirror plane).

III. Conclusion

The development of inexpensive magnetic materials requires the ability to finely tune the spin-states and magnetic anisotropy of transition-metal complexes through ligand design and modification. In this study, we have examined the geometric structures, magnetic properties, and spectroscopic features of a series of pentacoordinate Co(II) complexes (1-5) prepared with redox-active ligands in multiple oxidation states. X-ray crystallographic analysis found that each complex consists of a high-spin Co(II) center in a distorted TBP coordination geometry formed by the bidentate dioxolene-type ligands and facially coordinating Tp$^{Ph_2}$ ligands. Magnetic susceptibility studies determined that the $S = 3/2$ ground-states of 1 and 2 possess negative (easy-axis) anisotropy. The axial ZFS term ($D$) is sensitive to subtle changes in ligand structure, as evident by the two-fold increase in magnitude when the phenolate O-donor of 1 is replaced with the thiophenolate
S-donor of 2 (Table 2.A). The two complexes with \( o \)-(imino)semiquinonate ligands (\( \text{1}^{\text{Ox}} \) and 3) feature \( S = 1 \) ground states due to antiferromagnetic cobalt-radical exchange interactions. Magnetic susceptibility experiments of 3 indicate that the \( S = 2 \) excited state is partially occupied at elevated temperatures, and data fitting yielded an exchange coupling constant of \( J = -121 \text{ cm}^{-1} \). Although it was not possible to quantify the \( J \)-value of \( \text{1}^{\text{Ox}} \), the inaccessibility of its \( S = 2 \) excited state even at room temperature indicates that cobalt-radical exchange interactions are considerably stronger for \( \text{1}^{\text{Ox}} \) than 3.

By taking advantage of recent advances in far infrared magnetic spectroscopy (FIRMS), we were able to directly measure the zero-field splittings of complexes 1-4. FIRMS data of the three \( S = 3/2 \) complexes (1, 2, and 4) reveal a single magnetic absorption that arises from the inter-Kramers transition, \( m_s = \pm 3/2 \rightarrow \pm 1/2 \). The \( \Delta \)-values of 84.7 and 161.2 cm\(^{-1} \) measured at zero-field for 1 and 2, respectively, are consistent with the large \( D \)-values extracted from the magnetic susceptibility data. Parallel HF-EPR studies of 1 and 4 yielded complete and accurate sets of spin-Hamiltonian parameters, which are listed in Table 2.A. These results demonstrate that two-electron oxidation of the ligand (from \( \text{L}^{\text{O,N}} \) to \( \text{L}^{\text{O,N IBQ}} \)) is accompanied by a decrease in axial anisotropy and an increase in rhombicity (\( E/D \) ratio). In addition, the use of FIRMS proved critical in measuring the ZFS of the two \( S = 1 \) complexes, which are EPR-silent even at high fields. Complexes \( \text{1}^{\text{Ox}} \) and 3 each exhibit a single absorption at 117.5 and 130 cm\(^{-1} \), respectively, that corresponds to the \( |D + E| \) transition of a \( S = 1 \) system. While it was not possible to deconvolute the axial and rhombic ZFS terms, the collective results indicate that the \( D \)-values of \( \text{1}^{\text{Ox}} \) and 3 lie between -100 and -130 cm\(^{-1} \). To the best
of our knowledge, these studies demonstrate the first application of FIRMS to coordination complexes with ligand-based radicals.

The anisotropies of 1 and 2 are considerably larger and more negative than those previously reported for five-coordinate cobalt(II) complexes,\textsuperscript{16,21,22} as well as those reported for related four-coordinate [Co\textsuperscript{2+}(X)] complexes supported by Tp ligands (X = Cl\textsuperscript{−}, NCS\textsuperscript{−}, NCO\textsuperscript{−}, N\textsubscript{3}\textsuperscript{−}).\textsuperscript{27} Based on quantum chemical calculations that employed the multiconfigurational CASSCF/NEVTP2 approach, we ascertained that the sizable $D$-values of 1 and 2 are due to deviations in the equatorial bond angles from the ideal value of 120°. Specifically, the Tp\textsuperscript{Ph2} scaffold constrains the equatorial N\textsubscript{Tp}–Co–N\textsubscript{Tp} bond angle to around 95°, which stabilizes the lowest-energy singly-occupied Co 3d orbital (i.e., the $d_{xy}$ orbital in Figure 2.25). The energy gap between the ground state and lowest-energy excited state is reduced as a consequence, triggering an increase in the inter-Kramers splitting due to spin-orbit coupling. The equatorial distortions are also responsible for the rhombic nature of the spin-Hamiltonian parameters measured for 1. These conclusions are consistent with previous studies by Mallah and coworkers,\textsuperscript{28} which found that the anisotropies of pentacoordinate Co(II) complexes with tripodal ligands become more negative and rhombic as the equatorial bond angles deviate from 120°. While the large and negative anisotropies of 1 and 2 are promising from the standpoint of SMM design, the rhombic nature of their $D$-tensors is likely to diminish performance. Thus, for Co(II) complexes with TBP geometries, there appears to be a trade-off between the magnitude of $D$ and rhombicity. Future efforts on our part will seek to minimize the $E$-values of Tp-based Co(II) complexes while exhibiting highly negative $D$-values.
The sizable ZFS observed for the $S = 1$ complexes ($1^{\text{Ox}}$ and 3) arises from a similar set of electronic and structural factors. However, in these cases, the anisotropy is enhanced by exchange coupling between the Co(II) ion and ISQ radical. As illustrated in Figure 2.27, these interactions perturbing the relative energies of the ligand-field states, diminishing the energy gap the ground and first excited states. The high-degree of SOC-induced mixing between these two triplet states give rise to the large and negative anisotropies of $1^{\text{Ox}}$ and 3. Thus, the use of redox-active ligands offers another means for chemists to modulate the spin-states and ZFS of transition-metal complexes of relevance to magnetic materials.

IV. Experimental Section

General methods

Reagents and solvents were purchased from commercial sources and used without further purification unless stated otherwise. The synthesis and handling of cobalt complexes was carried out under an inert atmosphere using a Vacuum Atmospheres Omni-Lab glovebox equipped with a -30°C freezer. Solvents were deoxygenated prior to use and stored over molecular sieves in the glovebox. The compounds K[Tp$^{\text{Ph2}}$,47 and [Co$^{2+}$(Tp$^{\text{Ph2}}$)(OAc)(Hpz$^{\text{Ph2}}$)] were prepared according to published procedures.2 Elemental analysis performed by Midwest Microlab, LLC in Indianapolis, IN. UV-vis absorption spectra were measured in solution with an Agilent 8453 diode array spectrometer and IR spectra of solid-state samples were obtained with a Thermo Scientific Nicolet iS5 FTIR spectrometer. $^1$H-NMR spectra were measured using a Varian 400 MHz spectrometer. X-band EPR data for 1 was measured using a Bruker EMX instrument equipped with an ER4112 SHQ resonator, collected at liquid He
temperatures (5-10 K) using a ColdEdge/Bruker RDK-408 Stinger recirculating cryocooler. The X-band EPR spectrum of 5 was measured at UW-Madison using a Bruker ELEXSYS E500 spectrometer.

**Synthesis of [Co$^{2+}$(TpPh$_2$)(APH$_{tBu2}$)] (1) Tp$^{Ph2} =$ hydrotris(3,5-diphenylpyrazol-1-yl)borate and APH$^{tBu2}$ = 2-amino-4,6-di-tert-butylphenolate**

Complex 1 was synthesized through a one-pot synthesis in a 10 mL mixture of CH$_3$OH and CH$_2$Cl$_2$ (3:2). Together, equimolar amounts of [Co$^{2+}$(Tp$^{Ph2}$)(OAc)(Hpz$^{Ph2}$)] (224 mg, 0.21 mmol) and APH$_{tBu2}$ (47.4 mg, 0.21 mmol) were added to 1.5 equivalents of NaOMe (17 mg, 0.31 mmol) and stirred for 12 hours. The solution was vacuumed to dryness and dissolved in CH$_2$Cl$_2$. The solution was layered with CH$_3$CN and stored at -30°C inside the glovebox freezer. After 1-2 days, reddish-brown crystals were obtained and dried under vacuum. Yield = 84 mg (42%). Anal. Calcd (%) for C$_{59}$H$_{56}$BCoN$_7$O ($M_W$ = 948.87 g mol$^{-1}$): C, 74.68; H, 5.95; N, 10.33. Found: C, 72.93; H, 5.97; N, 10.07. The minor discrepancy in the carbon value suggests that ~0.3 CH$_2$Cl$_2$ solvate remained after drying.

UV-vis [$\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$) in CH$_2$Cl$_2$]: 395 (1765), 507 (350), 575 (120), 710 (10). FTIR (CH$_2$Cl$_2$): $\nu$ = 3325, 3058, 2613, 2558, 1541, 1441, 1374, 1358, 1375, 1022, 998, 986 cm$^{-1}$. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 70.6 (1H, s, APH$_{tBu2}$), 52.7 (3H, s, 4-$H$-pz), 51.2 (9H, s, -C(CH$_3$)$_3$), 21.7 (6H, s, Tp-Ph-$H$), 14.7 (6H, s, Tp-Ph-$H$), 14.0 (1H, s, APH$_{tBu2}$), 12.4 (3H, s, Tp-Ph-$H$), 4.55 (3H, s, Tp-Ph-$H$), 3.67 (6H, s, Tp-Ph-$H$), 0.98 (9H, s, -C(CH$_3$)$_3$), -28.1 (6H, s, Tp-Ph-$H$) ppm. $\mu_{eff}$ = 4.3 $\mu_B$ (Evans method in CDCl$_3$).

**Synthesis of [Co$^{2+}$(Tp$^{Ph2}$)(ISQ$_{tBu2}$)] (1$^{Ox}$) ISQ = iminosemiquinonate**

Complex 1$^{Ox}$ was synthesized by exposing 1 (102 mg, 0.1 mmol) to oxygen gas at room temperature in CH$_2$Cl$_2$ solvent. The reaction was stirred for 8 hours producing a
dark green solution which was concentrated to 2-3 mL by evacuation of solvent and layered with CH₃CN. After two days, dark green needles were harvested after decanting the remaining solvent and drying under nitrogen. Yield = 97 mg (95%). Anal. Calcd (%) for C₅₉H₅₅BCoN₇O (Mₒ = 947.86 g mol⁻¹): C, 74.63; H, 5.86; N, 10.54. UV-vis [λ_max, nm (ε, M⁻¹ cm⁻¹) in CH₂Cl₂]: 395 (10300), 608 (1130), 710 (980), 790 (730). FTIR (CH₂Cl₂): ν = 3480 (m), 2520 (m), 2375 (m), 2200 (m), 2090 (m), 1620 (w), 790 (m) cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 138.9 (1H, s, ISQ₄Bu₂), 87.1 (1H, s, ISQ₄Bu₂), 30.2 (3H, s, 4-H-pz), 27.0 (6H, s, Tp-Ph-H), 17.2 (6H, s, Tp-Ph-H), 14.6 (3H, s, Tp-Ph-H), 8.28 (3H, s, Tp-Ph-H), 0.42 (6H, s, Tp-Ph-H) -0.44 (9H, s, -C(CH₃)₃), -8.2 (9H, s, -C(CH₃)₃), -38.6 (6H, s, Tp-Ph-H) ppm. μ_eff = 2.9 μ_B (Evans method in CDCl₃).

**Synthesis of [Co²⁺(Tp^Ph₂)(ATP^Bu₂)] (2) ATP^Bu₂ = 2-amino-4,6-di-tert-butyliaminothiophenolate**

Sodium methoxide (33 mg, 0.61 mmol) and 4,6-di-tert-butyl-2-aminothiophenol (120 mg, 0.51 mmol) were dissolved in THF (2 mL) and stirred for 30 minutes. Evaporation of the solvent provided a yellow residue that was combined with a solution of [Co²⁺(Tp^Ph₂)(OAc)(Hpz^Ph₂)] (540 mg, 0.51 mmol) in 4 mL of CH₂Cl₂. The resulting mixture was stirred for two hours, followed by removal of the solvent under vacuum. A red solid was afforded and then extracted with Et₂O (2 × 5 mL). The combined extracts were filtered through Celite and dried under vacuum to give the crude product. Red-brown prisms of 2, suitable for X-ray crystallographic analysis, were obtained by layering a concentrated CH₂Cl₂ solution with CH₃CN. Yield = 302 mg (61%). Anal. Calcd (%) for C₅₉H₅₆BCoN₇S (Mₒ = 964.95 g mol⁻¹): C, 73.44; H, 5.85; N, 10.16. Found: C, 74.41; H, 5.95; N, 10.28. UV-vis [λ_max, nm (ε, M⁻¹ cm⁻¹) in CH₂Cl₂]: 356
Synthesis of $[\text{Co}^{2+}(\text{Tp}^\text{Ph}_2)(\text{ITSQ}^\text{Bu}_2)]$ (2Ox) ITSQ = iminothiosemiquinonate

The precursor complex, $[\text{Co}^{2+}(\text{Tp}^\text{Ph}_2)(\text{tBu}_2\text{ATP-H})]$ (2; 98 mg, 0.102 mmol), was dissolved in CH$_2$Cl$_2$ (5 mL) and stirred in the presence of air. The solution gradually turned to dark purple over the course of two hours. The resulting solution was layered with CH$_3$CN and cooled in a freezer, which provided dark purple crystals suitable for X-ray crystallography. The solvent was decanted, and the crystals were washed with CH$_3$CN and dried in air. Yield = 95 mg (97%). Anal. Calcd (%) for C$_{59}$H$_{55}$BCoN$_7$S ($M_w$ = 963.94 g mol$^{-1}$): C, 73.52; H, 5.75; N, 10.17. Found: C, 74.03; H, 5.71; N, 10.01. UV-vis [$\lambda_{\text{max}}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$) in CH$_2$Cl$_2$]: 495 (1660), 600 (sh), 990 (180). $^1$H-NMR (400 MHz, CDCl$_3$, 20°C): $\delta = 8.30$ (1H, s, N-$\text{H}$), 7.00-6.80 (30H, m, Tp-Ph-$H$), 6.65 (1H, s, ITSQ-$H$), 6.16 (1H, s, ITSQ-$H$), 6.00 (3H, s, 4-$H$-pz), 4.45 (1H, br, BH$_2$), 1.27 (9H, s, -C(CH$_3$)$_3$), 1.05 (9H, s, -C(CH$_3$)$_3$) ppm.

Synthesis of $[\text{Co}^{2+}(\text{TP}^\text{Ph}_2)(\text{SQ}^\text{Bu}_2)]$ (3) SQ$^\text{Bu}_2$ = 3,5-di-$\text{ tert}$-butylsemiquinonate

A vial containing NaOMe (45 mg, 0.83 mmol), 3,5-di-$\text{ tert}$-butylcatechol (91 mg, 0.41 mmol), and $[\text{Co}^{2+}(\text{TP}^\text{Ph}_2)(\text{OAc})(\text{Hpz}^\text{Ph}_2)]$ (437 mg, 0.41 mmol) was added to a 3:1 mixture of CH$_2$Cl$_2$/CH$_3$OH (10 mL total). The brown mixture slowly turned dark green over the course of 16 hours while stirring, signaling generation of the SQ ligand. The solvent was removed in vacuo and the resulting solid was redissolved in Et$_2$O before
filtration through Celite. The filtrate was placed in a -30°C freezer, leading to formation of green X-ray quality crystals. After removal of the mother liquor, the crystalline product was washed once with hexanes and dried to give a green powder. Yield = 295 mg (74%). Anal. Calcd (%) for C_{59}H_{54}BCoN_{6}O_{2} (M_W = 948.86 g mol⁻¹): C, 74.68; H, 5.74; N, 8.86. Found: C, 74.67; H, 5.59; N, 8.77. UV-vis [λ_{max}, nm (ε, M⁻¹ cm⁻¹) in CH₂Cl₂]: 370 (1070), 430 (1040), 575 (310), 615 (330), 740 (390). ¹H-NMR (400 MHz, CDCl₃): δ = 85.4 (1H, s, BH), 53.5 (1H, s, SQ^{Bu²}), 35.6 (3H, s, 4-H-pz), 26.6 (6H, s, Tp-Ph-H), 16.9 (6H, s, Tp-Ph-H), 14.3 (3H, s, Tp-Ph-H), 9.3 (3H, s, Tp-Ph-H), 7.6 (6H, s, Tp-Ph-H), 7.0 (1H, s, SQ^{Bu²}), 0.5 (9H, s, -C(CH₃)₃), -5.6 (9H, s, -C(CH₃)₃), -42.4 (6H, s, Tp-Ph-H) ppm. μ_{eff} = 2.68 μ_B (Evans method in CDCl₃).

**Synthesis of [Co^{2+}(Tp^{Ph²})(IBQ^{Bu²})]PF₆ (4) IBQ = iminobenzoquinone, PF₆ = hexafluorophosphate**

Purified solid material of 1⁰x (257 mg, 0.27 mmol) was dissolved in CH₂Cl₂ (5 mL) to yield a dark green solution. Treatment with AgPF₆ (68 mg, 0.27 mmol) resulted in an immediate color change to reddish-brown. The mixture was stirred for one hour and then filtered through Celite. The volume of the filtrate was reduced by half under vacuum, layered with CH₃CN, and placed in a -30°C freezer. The precipitate that formed after three days was harvested and dried. Yield = 198 mg (61%). Red scales suitable for crystallographic analysis were prepared by vapor diffusion of Et₂O into a concentrated solution in 1,2-dichloroethane. Anal. Calcd (%) for C_{59}H_{55}BCoF₆N₇OP (M_W = 1092.85 g mol⁻¹): C, 64.84; H, 5.07; N, 8.97; F, 10.43. Found: C, 65.75; H, 5.39; N, 8.95; F, 9.50. UV-vis [λ_{max}, nm (ε, M⁻¹ cm⁻¹) in CH₂Cl₂]: 475 (2750), 580 (1800). ¹H-NMR (400 MHz, CDCl₃): δ = 71.6 (1H, s), 66.2 (3H, s, 4-H-pz), 47.2 (1H, s), 10.7 (2 × 6H, s, Tp-Ph-H), 9.2 (6H, s, Tp-Ph-H), 8.5 (3H, s, Tp-Ph-H), 7.6 (3H, s, Tp-Ph-H), 7.1 (9H, s, -C(CH₃)₃),
-3.1 (6H, s, Tp-Ph-H), -9.1 (9H, s, -C(CH₃)₃) ppm. ¹⁹F-NMR (400 MHz, CHCl₃): δ = -61 ppm (d, J = 750 Hz). μₑff = 4.49 μB (Evans method in CDCl₃).

**Synthesis of [Co²⁺(Tp²Ph²)(ITBQ²Bu₂)]PF₆ (5) ITBQ = iminothiobenzoquinone**

Complex 2⁰x (75 mg, 0.078 mmol) was dissolved in 1,2-dichloroethane and treated with one equivalent of AgPF₆ (20 mg, 0.076 mmol). The resulting dark red mixture was stirred for one hour and then filtered through Celite. The volume of the solution was reduced *in vacuo* and layered with CH₃CN (5 mL). After several days, scarlet-colored crystals emerged suitable for X-ray crystallography. The rest of the mother liquor was decanted, and the product was air dried to yield a dark red solid. Yield = 80 mg (93%). Anal. Calcd (%) for C₅₉H₅₅BCoF₆N₇P • 0.5 C₂H₄Cl₂ (Mₚ = 1158.39 g mol⁻¹): C, 62.21; H, 4.96; N, 8.46. Found: C, 61.79; H, 4.80; N, 8.39. UV-vis [λmax, nm (ε, M⁻¹ cm⁻¹) in CH₂Cl₂]: 490 (4900), 540 (4950), 925 (1460). μₑff = 1.97 μB (Evans method in CDCl₃).

**X-ray crystal structure determination**

Single-crystal X-ray diffraction intensities from crystals of complexes 1-5 were measured at 100 K with an Oxford Diffraction (Rigaku Corporation) SuperNova diffractometer. The instrument has dual-wave micro-focus sealed-tube sources (Cu and Mo Kα wavelengths), X-ray mirror optics, an Atlas CCD detector, and an open-flow Cryojet LN₂ cooling device (Oxford Instruments). The data were corrected for usual experimental factors including absorption correction based on the real shape of the crystals followed by a polynomial empirical procedure within the CrysAlis Pro (Rigaku, 2018) program package. Hydrogen atoms were positioned geometrically, and a
riding/rotating model was applied during refinement. A solvent-mask procedure was used
to account for electron density of non-localized solvent molecules in the structure of 2.

**Magnetic susceptibility and reduced magnetization experiments and analysis**

Variable-temperature paramagnetic susceptibility data and reduced magnetization
data for complexes 1-4 were measured with a MPMS 3 Quantum Design SQUID magnetometer at the University of Wisconsin-Madison. The samples were cooled down in the absence of a magnetic field to 1.8 K and subsequently data were collected from 1.8 K to either 300 K or 400 K in an applied 1000 G DC magnetic field. At each temperature, the field was varied from 0 to 7 T while measuring the magnetization of the sample. All magnetic susceptibility and magnetization data were modeled using the fitting program PHI v.3.1.5. Experimental susceptibility and magnetization data were corrected for inherent diamagnetism with the equation: $\chi_D = - \left( \frac{M}{2} \right) \cdot 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. For complexes 1-4, the temperature-independent magnetism (TIM, defined below) was included as a variable in the model of the susceptibility data, while for complex 3, the slope of a linear least squares fit line of the last four high-temperature data points (at T = 199, 220, 244, and 271 K) in the $\chi_T\cdot T$ vs. T plot was used for the TIM correction.

**FIRMS and HFEPR Studies**

HFEPR experiments were performed using a transmission spectrometer modified by the use of Virginia Diodes Inc. (VDI, Charlottesville, VA) sources, generating sub-THz wave radiation in a 50-640 GHz frequency range. The spectrometer is associated with a 15/17-T warm-bore superconducting magnet. FIRMS experiments were performed at the National High Magnetic Field Laboratory using a Bruker Vertex 80v FT-IR spectrometer coupled with a 17 T vertical-bore superconducting magnet in a Voigt
configuration (light propagation perpendicular to the external magnetic field). The experimental setup employs broadband terahertz radiation emitted by an Hg arc lamp. The radiation transmitted through the sample is detected by a composite silicon bolometer (Infrared Laboratories) mounted at the end of the quasi-optical transmission line. Both the sample and bolometer are cooled by low-pressure helium gas to a temperature of 4.6 K. The intensity spectra of each microcrystalline powder sample (7 mg) bonded by \( n \)-eicosane were measured in the spectral region between 14 and 730 cm\(^{-1} \) (0.42-22 THz) with a resolution of 0.3 cm\(^{-1} \) (9 GHz). To discern the magnetic absorptions, the spectra were normalized by dividing with the reference spectrum, which is the average spectrum for all magnetic fields. Such normalized transmittance spectra are only sensitive to intensity changes induced by the magnetic field and therefore are not obscured by nonmagnetic vibrational absorption features. The data analysis was implemented using an in-house written MATLAB code and the EPR simulation software package EasySpin. \(^{30} \)

**Computational Methods**

Calculations were carried out using the ORCA software package (version 4.0) developed by Dr. F. Neese (MPI-CEC). \(^{31,32} \) Computational models of 1-5 were based on the crystallographic structures, although the tert-butyl groups were replaced with methyl groups. The Tp\(^{\text{Ph2}} \) ligand was truncated by replacing the three 5-phenyl substituents with H-atoms to generate a Tp\(^{\text{Ph,H}} \) chelate. Two different Karlsruhe basis sets were employed: (i) valence double-\( \zeta \) basis set with polarization functions (def2-SVP), and (ii) valence triple-\( \zeta \) basis set combined with polarization functions on main-group and transition-metal elements (def2-TZVP). \(^{33} \) Single point calculations of the truncated crystallographic
structures employed Becke’s three-parameter hybrid functional for exchange and the Lee-Yang-Parr correlation functional (B3LYP).\textsuperscript{34,35} The resolution of identity and chain of sphere (RIJCOSX) approximations\textsuperscript{36} were applied in conjunction with the appropriate auxiliary basis sets.\textsuperscript{37} The unrestricted natural orbitals provided by the DFT/B3LYP calculations served as the initial guess for state-averaged CASSCF calculations. The core orbitals were not frozen. For the $S = 3/2$ complexes (1, 2, and 4), the CAS(7,5) active space consisted of seven electrons in the five Co 3d orbitals. All possible states for a d$^7$ configuration (10 quartet and 40 doublet) were calculated. For the $S = 1$ complexes ($1\textsuperscript{ox}$ and 3), the CAS(8,6) active space was comprised of eight electrons distributed across the Co 3d shell and one (imino)semiquinonate-based MO (i.e., the SOMO of the ligand radical). Ten quintet and 35 triplet states were included. Dynamic electron correction was incorporated using $N$-electron valence state second-order perturbation theory (NEVPT2).\textsuperscript{38} Parameters related to spin-orbit coupling ($g$-values and ZFS) were calculated by applying the effective Hamiltonian method to the multi-configurational CASSCF/NEVPT2 wavefunctions.\textsuperscript{39,40} Overall agreement between the experimental and computed parameters was improved by using the NEVPT2 procedure in tandem with the larger def2-TZVP basis set. Thus, all computed values provided in the main text are derived from CASSCF/NEVPT2 calculations that employed the def2-TZVP basis set. Ligand field energies for the Co 3d orbitals were generated from CASSCF/NEVPT2 calculations using a procedure (\textit{ab initio} ligand field theory, AILFT) developed by Atanasov and coworkers.\textsuperscript{41,42} Exchange coupling constants ($J$) were obtained from DFT calculations (B3LYP functional; def2-TZVP basis set) using the broken symmetry approach ($H_{ex} = -2JS_A \cdot S_B$).\textsuperscript{43,44} A geometry-optimized model of the hypothetical
complex, [Co\(^{2+}\)(APH)(pz\(^{Me,Ph}\))\(_3\)]\(^+\), was generated from DFT calculations that employed the Becke-Perdew (BP86)\(^{45,46}\) functional and def2-TZVP basis set.
Table 2.B Summary of X-ray crystallographic data collection and structure refinement.

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*a The CH$_2$Cl$_2$ solvate is disordered over an inversion center and the methylene unit was not located. The CH$_3$CN solvate is partially (20%) replaced by CH$_2$Cl$_2$. b The two solvate positions in the unit cell are disordered and only partially occupied.*
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<td>18543 / [R_{int} = 0.0566]</td>
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<td>0.0639 / 0.1462</td>
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V. BIBLIOGRAPHY


Chapter 3
Probing the O$_2$ Reactivity of Co Complexes with Non-innocent Ligands

Abstract
Cobalt(II) complexes featuring ligand-based radicals are shown to reversibly bind molecular oxygen at reduced temperatures. The complexes replicate the active-site structures of cobalt-substituted dioxygenases such as aminophenol dioxygenase (APDO), catechol dioxygenase (HPCD), and thiol dioxygenases. The synthetic precedent for using dioxolene ligands is based on their ability to undergo one-electron oxidation to yield semiquinonate-type radicals. Exposure of a cobalt(II)-aminophenolate complex to O$_2$ gives rise to two metastable Co/O$_2$ adducts. The first intermediate is a low-spin cobalt(III)-superoxo adduct that was characterized with spectroscopically (UV-vis, EPR). At room temperature, this species converts to a Co(II) complex coordinated to an iminosemiquinone (ISQ) radical. The Co(II)-ISQ complexes is capable of reversible O$_2$ binding. An X-ray crystal structure of the Co/O$_2$ adduct revealed a spirocyclic alkylperoxo ligand that is unique among first-row transition-metal complexes. This structure provides a valuable synthetic precedent of the peroxo-based metallocycles that have been proposed for several dioxygenase mechanisms. Dioxygen binding studies were also conducted with Co(II) complexes featuring semiquinone and iminothiosemiquinone radicals, as well as closed-shell ligands. Equilibrium O$_2$ binding constants ($K_{O2}$) were measured at multiple temperatures, allowing for determination of thermodynamic parameters ($\Delta H$, $\Delta S$) for the O$_2$ binding reaction. The results indicate that metal-ligand cooperativity offers a new approach for the design of molecules and materials for O$_2$ storage and transport.

I. Introduction

Aerobic organisms require molecular oxygen (O\textsubscript{2}) to carry out numerous metabolic processes essential for life, including respiration. The storage, transport, and activation of O\textsubscript{2} in Nature is largely the domain of metalloproteins and metalloenzymes. The best-known examples are O\textsubscript{2} transport proteins such as myoglobin, hemerythrin, and hemocyanin.\textsuperscript{1-3} Other enzymes catalyze the monooxygenation or dioxygenation of amino acids and other metabolites.\textsuperscript{4,5} The function of these biological systems generally involves the formation of O\textsubscript{2}-adducts in which the metal ions are oxidized by one electron, as in the heme and nonheme proteins hemoglobin and hemerythrin, respectively. The affinity of the metal center for oxygen depends on multiple factors, most notably its redox potential and steric accessibility.

The interaction between transition metal ions and dioxygen in biology has inspired the synthesis of coordination complexes capable of binding and activating O\textsubscript{2}. The most famous studies are model compounds, largely prepared in the 1970s and 80s, that contain iron and cobalt “picket-fence” porphyrins. It was found that the O\textsubscript{2} binding affinity of these synthetic models is comparable to that of the native heme.\textsuperscript{6} Since then, numerous studies have shown that Co(II) complexes with tetradentate or pentadentate Schiff-base ligands bind O\textsubscript{2} readily at low temperatures to yield Co/O\textsubscript{2} adducts.\textsuperscript{7-11} Because these adducts are stabilized by the interaction between oxygen and cobalt, their stability can be modulated by changing the donor strength of the supporting ligands.\textsuperscript{12-14}

The bacterial breakdown of organic compounds, including human-generated pollutants, often requires dioxygenase enzymes that oxidatively cleave aromatic carbon-carbon bonds using O\textsubscript{2}.\textsuperscript{15} The active sites of most ring-cleaving dioxygenases feature a
mononuclear nonheme iron center bound facially to one Glu (or Asp) and two His residues. However, recent studies revealed that an extradiol catechol dioxygenase (CatD), homoprotocatechuate-2,3-dioxygenase (HPCD), exhibits equal or greater activity with Mn or Co in the active site. The “promiscuity” of HPCD supports the mechanistic proposal that O\textsubscript{2} activation by ring-cleaving dioxygenases does not necessitate a change in metal oxidation state. Instead, the metal facilitates the transfer of one electron from the coordinated substrate to O\textsubscript{2}, thereby yielding a M(II)-superoxo species with an (imino)semiquinone radical (B in Scheme 3.A). Formation of a substrate-based radical encourages attack by the superoxide ligand to generate a putative alkylperoxo species (C), which undergoes rearrangement to insert an O-atom into the substrate ring (D).

Analogous mechanisms are likely employed by \textit{o}-aminophenol and 1,4-hydroquinone dioxygenases.

Scheme 3.A Proposed catalytic cycle of metal-substituted HPCD activity.

The surprising activity of metal-substituted HPCD has stimulated the synthesis of extradiol CatD models featuring Co and Mn. Recently, the Riordan and Hikichi groups
reported Co and Mn complexes, respectively, that feature a monoanionic catecholate ligand bound in a monodentate manner. Exposure of these complexes to O₂ results in formation of the corresponding M(II)-semiquinonate (SQ) species via loss of an electron and proton (i.e., net H-atom transfer, HAT). Thus, the CatD models fail to replicate the initial O₂ binding step of the enzymatic mechanism. In some cases, further reaction of the Co(II)-SQ complexes with O₂ affords the intradiol ring-cleavage products in low yield.

To avoid the shortcomings of the cobalt-catecholate complexes, we decided to pursue cobalt(II) dioxygenase models that contain an o-aminophenolate or o-aminothiophenolate ligand instead. Aminophenol dioxygenases (APDOs) are closely related to extradiol CatDs both structurally and mechanistically, and although a cobalt-substituted APDO has not been generated to date, it is reasonable to expect such an enzyme to display activity. These studies build upon our previous efforts that demonstrated that a cobalt(II) model complex of cysteine dioxygenase (CDO) binds O₂ reversibly to yield a S = 1/2 cobalt-superoxide species. In this case, the cobalt ion exists in a nonheme environment provided by the hydrotris(3,5-dimethylpyrazolyl-1-yl)borate (TpMe₂) ligand, which mimics the facial coordination of protein ligands in the enzyme active site.

In this chapter we describe the synthesis of three TpMe₂-supported Co(II) complexes that feature an o-aminophenolate or o-aminothiophenolate ligand: [Co²⁺(TpMe₂)(APHtBu₂)] (6), [Co²⁺(TpMe₂)(ATP³Bu₂)] (7), and [Co²⁺(TpMe₂)(ATP)] (8), as shown in Scheme 3.B. As expected, the reaction of these Co(II)/Tp complexes with O₂ yields cobalt(III)-superoxide intermediates (6SO and 8SO) at low temperatures. However, unlike other five-coordinate systems, this process is irreversible and subsequent reactions to form bimetallic μ-peroxo species are absent. Instead, thermal decay releases the bound O₂ to yield intermediates...
that contain ligands in their semiquinone forms (e.g., \( o \)-imino(thio)semiquinone). The electronic structures of these complexes were evaluated on the basis of X-ray crystal data, and spectroscopic analysis.

Remarkably, the cobalt/radical complexes bind \( O_2 \) at low temperatures (-30 to -70°C) to yield species that are distinct from the initial cobalt(III)-superoxo adducts. Warming back to room temperature regenerates the cobalt/radical intermediates, indicating that the process involves reversible \( O_2 \) binding. The low-temperature \( O_2 \) adducts have been characterized with \(^1\)H-NMR spectroscopy, UV-vis spectroscopy and (in one case) X-ray crystallography. The Co/\( O_2 \) adducts possess a unique spirocyclic alkylperoxo ligand that is generated by a concerted two-electron process that involve oxidation of both the cobalt ion and ligand, resulting in formation of Co–O and O–C bonds. This represents that first X-ray structure of a cobalt-alkylperoxo complex with a structure akin to \( C \) in the proposed ring-cleaving mechanism.

The equilibria of the \( O_2 \) binding reactions can be monitored by regulating \( pO_2 \) (oxygen partial pressure) and measuring changes in UV-vis spectral features, which permits determination of binding equilibrium constants (\( K_{O2} \)) through the systematic increase of \( pO_2 \). By collecting data at multiple temperatures, it was possible to obtain thermodynamic parameters (\( \Delta H, \Delta S \)) for the \( O_2 \) binding reaction. These experiments were conducted for Co(II) complexes with both closed-shell and open-shell (radical) ligands. These results found that the two-electron reactions give alkylperoxo ligands more negative \( \Delta H \) and \( \Delta S \) terms relative to the one-electron reaction to yield a superoxo ligand.
II. Results and Analysis

A. Synthesis of Cobalt Complexes

The synthetic protocol of complexes 6-8 and \(9^{\text{Ox}}\) bears resemblance to that of 1-3 but instead employs the acetate precursor \([\text{Co}^{2+}(\text{Tp}^\text{Me}_2)(\text{OAc})]\). The sodium salts of the substrate ligands were prepared in the glovebox, using a solution of 4,6-di-tert-butyl-o-aminophenolate for 6 and 4,6-di-tert-butyl-o-aminothiophenolate for 7. Each were prepared by addition of two equivalents of NaOMe in THF solvent. The synthesis of 8 was reported earlier by Dr. Anne Fischer beginning with deprotonation of the ligand, 2-aminothiophenol (2-ATP, purchased from Alfa Aesar), which was also added to NaOMe in THF. These solutions were stirred for 15-30 minutes and then dried by vacuum. The deprotonated salts were then added to one equivalent of the \([\text{Co}^{2+}(\text{Tp}^\text{Me}_2)(\text{OAc})]\) precursor in CH\(_3\)CN, resulting in formation of the crude products. The purification of these products was accomplished after filtration of the crude material in solution through Celite, and recrystallization of the filtrate in the glovebox freezer at -30°C (the crystal structures of 6 and 7 are reported in Figure 3.00).

Complexes 6-8 change color in the solid state when exposed to air, resulting in a greenish hue within seconds. The oxidized material of these complexes was prepared in solution and recrystallized inside the glovebox as complexes \(6^{\text{Ox}}-8^{\text{Ox}}\) in good yields (~95%). In addition, we prepared the analogous cobalt(II)-semiquinonate complex, \([\text{Co}^{2+}(\text{Tp}^\text{Me}_2)(\text{SQ}^\text{Bu}_2)]\) (9\(^{\text{Ox}}\)). The synthesis of 9\(^{\text{Ox}}\) was performed inside the glovebox under anaerobic conditions. The first step involves the deprotonation of 3,5-di-tert-butylcatechol in CH\(_3\)CN. As depicted in Scheme 3.C, addition of the \([\text{Co}^{2+}(\text{Tp}^\text{Me}_2)(\text{OAc})]\) precursor to the catecholate salt leads to the formation of 9\(^{\text{Ox}}\), which was promptly
filtered through Celite. This solution was concentrated and then stored in an uncapped
scintillation vial open to the atmosphere. Dark green needles formed after slow
evaporation of a CH$_3$CN solution (X-ray structure reported in Figure 3.08). This complex
is air-stable in the solid state and solution under ambient conditions.

Scheme 3.B Synthetic procedure for generation of 6-8 and $6^{Ox}$-$8^{Ox}$.
Scheme 3.C Synthesis of cobalt semiquinonate complex $9^{Ox}$.

B. Characterization of Cobalt Complexes and Reactivity

Figure 3.00 X-ray crystal structures of 6 • 3CH$_3$CN (left) and 7 • 3CH$_3$CN (right) measured at 100 K (solvate molecules and CH$_3$ protons omitted for clarity).

The X-ray structures of 6 and 7 exhibit Co–N$_{Tp}$ (N-pyrazole) bond lengths comparable with other high-spin cobalt(II) complexes with Tp ligands. The largest N$_{Tp}$–Co–O/S bond angles lie between 164-168° for 6 and 7. The amino groups remain datively bound to cobalt in the equatorial plane, as in the Tp$^{Ph2}$ analogs described in the previous chapter. However, the angles between N$_{Tp}$ atoms and the chelate ring of phenolate and thiophenolate average around 90° which puts the N-donor in an apical position. The $\tau$-
values of 6 and 7 (0.05 and 0.13, respectively), are indicative of SPY geometries, in contrast to 1 and 2 which display significant TBP distortions. The C–C bond lengths of the aromatic ligands are consistent with a closed-shell o-amino(thio)phenolate description (Scheme 3.D).

Scheme 3.D Bond lengths derived from solved X-ray structures of 6-8 (reported in Å).

The electronic absorption spectra of 6-8 were collected at room temperature in CH₂Cl₂ (Figure 3.01 and Figure 3.02). The brown-colored solutions reveal low intensity bands centered around 500 nm with low intensities (ε ≈ 100-500 M⁻¹ cm⁻¹) characteristic of d-d bands.

Figure 3.01 UV-vis spectra monitored dioxygen reactivity of 6 in CH₂Cl₂ at room temperature (0.7 mM, red line), initial oxidation results in 6⁰ which forms immediately after exposure to oxygen, and terminal oxidized product after 40 min. (dashed, blue line).
To test the dioxygen reactivity of 6, a sample in CH$_2$Cl$_2$ was exposed to O$_2$ at room temperature (Figure 3.01). Immediately afterwards, the formation of a new species (6$^{\text{Ox}}$) was observed with an intense peak 610 nm ($\varepsilon = 1400$ M$^{-1}$ cm$^{-1}$). A shoulder peak at 780 nm has moderate intensity ($\varepsilon = 370$ M$^{-1}$ cm$^{-1}$). This species begins to decay until a terminal species is formed after 40 min. The resulting reddish-brown species exhibits features similar to those of the cobalt(II)-iminobenzoquinone complex (4). The shoulder peak found at 650 nm ($\varepsilon = 380$ M$^{-1}$ cm$^{-1}$) appears slightly red-shifted relative to the Tp$^{\text{Ph2}}$ derivative (590 nm). Based on the similarity between the absorption spectra of these two species and their respective molar absorptivities, we can assume that the O$_2$ reaction involves sequential formation of a cobalt(II) iminosemiquinone species (6$^{\text{Ox}}$) followed by a cobalt(II) iminobenzoquinone species.

Parallel experiments with 7 and 8 were performed in CH$_2$Cl$_2$ where the room temperature O$_2$-reaction was monitored by UV-vis (Figure 3.02, top). Initially, new species are generated with a dark green color. These species (7$^{\text{Ox}}$ and 8$^{\text{Ox}}$) display intense peaks around 485 and 605 nm. Additionally, there is a broad feature in the near-infrared region centered around 1000 nm. This species is stable for several minutes; however, it eventually decays into a new dark brown species. To ascertain if the O$_2$ reaction proceeds via H-atom abstraction, we treated complexes 6-8 with the hydrogen abstracting agent, TTBP' under anaerobic conditions. Indeed, the reaction generates the same, green-colored species as observed upon aerobic oxidation (Figure 3.02, bottom). Complex 9$^{\text{Ox}}$ displays similar UV-vis features as the Tp$^{\text{Ph2}}$ analogue 3 (Figure 3.03), which confirms that it contains a semiquinonate ligand.
Figure 3.02 Top: room temperature aerobic oxidation of 7 (0.3 mM, solid blue line) and 8 (0.4 mM, solid red line) before and after reaction with oxygen forming $7^{\text{Ox}}$ and $8^{\text{Ox}}$ (dashed blue and red lines) in CH$_2$Cl$_2$ solvent. Bottom: UV-vis spectra of $6^{\text{Ox}}$ and $7^{\text{Ox}}$ from reaction of 6 and 7 with O$_2$ (blue/red solid lines) and TTBP’ (blue/red dashed lines) at room temperature.

Figure 3.03 UV-vis spectra of complexes 3 (1.1 mM, black line) and $9^{\text{Ox}}$ (2.0 mM, red line) recorded at room temperature in CH$_2$Cl$_2$. 
EPR spectroscopy was employed to probe the electronic structures of these cobalt(II) compounds. Samples of 6-8 were prepared in the glovebox with concentrations between 1-2 mM in CH$_2$Cl$_2$ and THF. Spectra of the oxidized species 6$^{\text{Ox}}$-8$^{\text{Ox}}$ were generated by creating UV-vis samples of the precursor complexes and exposing them to O$_2$ until the new absorption features maximized. Shortly afterwards, an aliquot of the reaction mixture was transferred into an EPR tube and frozen under liquid nitrogen. The samples of 6$^{\text{Ox}}$-9$^{\text{Ox}}$ each provided EPR-silent spectra, which suggests they are either integer-spin or diamagnetic.

The spectrum of 6 measured in frozen CH$_2$Cl$_2$ (Figure 3.04) displays an axial pattern with effective $g$-values of 7.6, 1.5, 1.2. The spectrum collected in THF (Figure 3.05) shows higher resolution of the hyperfine splitting pattern arising from the Co ($I = 7/2$) nucleus. This pattern is apparent in the low-field region within the $g = 7.9$ signal, resulting in an $(2I + 1)$ eight-line splitting pattern. The spectrum of 7 collected in frozen THF (77 K, Figure 3.06) is also axial with resonances at $g = 7.54$, 1.74, 1.20. The hyperfine splitting from the cobalt nuclei displays an eight-line pattern at the low-field resonance ($A_{\text{Co}} = 85$ G). A sample of 8 was prepared in frozen CH$_2$Cl$_2$ and an X-band EPR spectrum was measured at 10 K (Figure 3.07). With this sample it was difficult to achieve spectral resolution due to the significant $g$-strain from the complex. However, like the other precursor complexes, the transitions arising from the lowest energy $m_s = \pm 3/2$ doublet were apparent ($g = 7.90$, 1.45, 1.09). In the three sample spectra, there is an artifact due to a $S = 1/2$ signal, which likely arises from a Co/O$_2$ adduct. Regardless, the assignment of 6-8 as $S = 3/2$ systems with negative $D$-values is sustained based on the given EPR data.
Figure 3.04 X-band EPR spectrum of 6 collected in frozen (1.5 mM) CH$_2$Cl$_2$ at 10 K. Experimental parameters: frequency = 9.482 GHz, power = 2.0 mW, modulation amplitude = 10 G. The feature marked with an asterisk belongs to an $S = 1/2$ Co/O$_2$ adduct.

Figure 3.05 X-band EPR spectrum of 6 collected in frozen THF (1.9 mM) at 10 K. Experimental parameters: frequency = 9.475 GHz, power = 2.0 mW, modulation amplitude = 12 G. Inset: low-field region between 400-1300 G with hyperfine splitting $A_{Co} = 90$ G. Feature marked with asterisk (*) corresponds to an $S = 1/2$ impurity.
Figure 3.06 X-band EPR spectrum of 7 collected in frozen CH$_2$Cl$_2$ at 10 K. Experimental parameters: frequency = 9.471 GHz, power = 2.080 mW, modulation amplitude = 10 G. Feature marked with an asterisk (*) indicates a paramagnetic impurity.

Figure 3.07 X-band EPR spectrum of 8 collected in frozen CH$_2$Cl$_2$ at 15 K. Experimental parameters: frequency = 9.471 GHz, power = 2.080 mW, modulation amplitude = 5 G. Feature marked with an asterisk (*) corresponds to an $S = \frac{1}{2}$ oxygen adduct.
C. Oxidation of Redox-active Ligands in Cobalt Complexes

**Figure 3.08** X-ray crystal structures of $6^{\text{Ox}}$ (top left), $7^{\text{Ox}}$ (top right), $8^{\text{Ox}}$ (bottom right) and $9^{\text{Ox}} \cdot \text{CH}_3\text{CN}$ (bottom left) measured at 100 K (solvate molecules and Tp-methyl protons omitted for clarity).

**Figure 3.09** Reported bond distances from crystal structure of $6^{\text{Ox}}$ [$\text{Co}^{2+}(\text{Tp}^{\text{Me}_2})(\text{ISQ}^{\text{Bu}_2})$]. The tBu- groups and Tp ligand have been omitted for clarity. Bond distances determined (Å) at 100 K (left) and 248 K (right).

The dark green crystals grown from concentrated solutions of $6^{\text{Ox}}$ and $7^{\text{Ox}}$ both belong to triclinic systems within the space group of $P1$. Crystals of $8^{\text{Ox}}$ display orthorhombic lattices under $Pbca$ symmetry. The resulting X-ray structures reveal that
The crystal structure of $9^{\text{Ox}}$, which closely resembles the cobalt(II) semiquinonate in 3, does not display contracted Co–NTp bond lengths at 100 K, and by all measures contains a high-spin cobalt(II) center. The Co–NTp distances (2.00-2.10 Å) reveal that the Co(II) center is high-spin with nearly equivalent Co–O bond distances of 2.05 Å. The geometry of $9^{\text{Ox}}$ is similar to 6 and 7 with some degree of SPY character ($\tau = 0.43$). However, the ligand displays a pronounced quinoidal distortion which indicates that the ligand exists in the semiquinonate oxidation state.

The crystallographically determined bond lengths of $6^{\text{Ox}}$, $7^{\text{Ox}}$, and $9^{\text{Ox}}$ are represented in Table 3.A. The C–C bond lengths of the ligands in show appreciable semiquinone character, which is consistent with the predicted one-electron oxidation of

$6^{\text{Ox}}$-$8^{\text{Ox}}$ are five-coordinate cobalt complexes adopting near-ideal square pyramidal geometries (Figure 3.08). The immediate change in coordination environment compared to the 6-8 precursors can be seen from the deprotonation of the amino group. It is evident that the reaction with O$_2$ triggers abstraction of an H-atom, analogous to the conversion of 1 to $1^{\text{Ox}}$ described in Chapter 2. All three species have Co–NTp bonds (avg. = 1.995 Å) consistent with low-spin cobalt ions. While this is expected for the sulfur-containing ligands in $7^{\text{Ox}}$ and $8^{\text{Ox}}$, the low-spin configuration in $6^{\text{Ox}}$ diverges from that of its Tp$^{\text{Ph2}}$ analogue. It is possible that this phenomenon arises from the combination of stronger electronic donation and reduced steric bulk from the Tp$^{\text{Me2}}$ ligand. Surprisingly, when the crystal data was collected at a higher temperature (-25°C; Figure 3.09), Co–NTp bonds become notably longer (avg. = 2.037 Å) and closer to the expected high-spin limit (2.05-2.10 Å). This suggests that the barrier between low-spin and high-spin cobalt(II) is rather low in crystallo.
the aminophenolate and aminothiophenolate ligands. From the extended C1–C2 bond lengths and adjacent bonds we can assume that semiquinone radical is ortho-stabilized, with the bulk of spin density situated on the O–C and S–C units. In addition, the C–O/S and C–N7 bond lengths have decreased significantly relative to each precursor. In 6\textsuperscript{Ox}-9\textsuperscript{Ox}, the metrical oxidation state (MOS) is approximately [−1] in each case, which is consistent with a the open-shell semiquinonate form of each ligand. This suggests that each of these species contains radicals bound to the cobalt(II) centers.

Table 3.A Selected bond distances (reported in Å) from structures of 6\textsuperscript{Ox}, 7\textsuperscript{Ox}, and 9\textsuperscript{Ox} from X-ray data collected at 100 K.

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Figure 3.10 $^1$H-NMR spectra of $6^{\text{Ox}}$ (in CD$_2$Cl$_2$), and $7^{\text{Ox}}$ (in CDCl$_3$) recorded at room temperature.

To examine the spin of the complexes, crystals were dried and dissolved in CDCl$_3$ for characterization by $^1$H-NMR spectroscopy in anaerobically sealed tubes. Using the Evans method, the effective magnetic moments ($\mu_{\text{eff}}$) of 6-8 were found to lie between 4.2-4.5 $\mu_B$, confirming that their ground states are high-spin ($S = 3/2$). Complex $9^{\text{Ox}}$ exhibits a magnetic moment ($\mu_{\text{eff}}$) of 3.2 $\mu_B$ which is consistent for a high-spin cobalt(II) ion bound antiferromagnetically to a semiquinonate radical (i.e., $S = 1$).

After the initial spectra of 6-8 were collected in CDCl$_3$, the NMR tubes were then exposed to the atmosphere and introduced to a dry stream of O$_2$ (by needle). This was followed by agitation through vigorous shaking until the solutions changed color. The resulting spectra of $6^{\text{Ox}}$ and $7^{\text{Ox}}$ are shown in Figure 3.10. The spectrum of $6^{\text{Ox}}$ features paramagnetically-shifted peaks, with resonances spanning a similar region as the starting complex, 6 (80 to -43 ppm). This result suggests that complex $6^{\text{Ox}}$ is paramagnetic. The Evans method was performed alongside this experiment to determine the magnetic moment of 6 and $6^{\text{Ox}}$. The precursor exhibits a magnetic moment of 4.55 $\mu_B$, consistent with the $S = 3/2$ spin state of high-spin cobalt(II). However, the magnetic moment from
the sample of \( \text{6Ox} \) is \( \mu_{\text{eff}} = 3.21 \ \mu_\text{B} \), indicative of an \( S = 1 \) spin system (the spin-only value is 2.83 \( \mu_\text{B} \)). This result is consistent with a description of high-spin cobalt(II) coupled antiferromagnetically to an ISQ radical. The EPR-silent spectrum (in perpendicular mode) and UV-vis signatures’ similarity to \( \text{1Ox} \) implies that \( \text{6Ox} \) has an analogous electronic structure. In contrast to \( \text{6Ox} \), the species \( \text{7Ox} \) and \( \text{8Ox} \) are both diamagnetic, which was also observed for the Tp\( ^\text{Ph2} \) analogue \( \text{2Ox} \). These results suggests that the oxidized derivatives of the sulfur-containing complexes are diamagnetic due to antiferromagnetic coupling between a low-spin cobalt(II) ion and ITSQ radical. Conversely, the ligand could be described as a closed shell \([\text{ATP}]^2^-\) bound to a diamagnetic cobalt(III) ion. However, the X-ray data confirms that there is a significant degree of iminothiosemiquinone character.

Additional exposure of dioxygen to \( \text{6Ox} \) and \( \text{7Ox} \) at room temperature, resulted in the paramagnetic spectra shown in Figure 3.11 and Figure 3.12. This final product of oxidation in \( \text{6Ox} \) has a significantly smaller magnetic moment than its precursor (\( \text{6; S = 3/2, spin-only magnetic moment = 3.87 } \mu_\text{B} \)), which indicates that there may be diamagnetic byproducts formed as a result of its instability. The paramagnetism exhibited by this series (\( \text{6, 6Ox, and the terminal species} \)) parallels the Tp\( ^\text{Ph2} \) series (\( \text{1, 1Ox, and 4} \)) which contains cobalt(II) bound to aminophenolate, iminoquinone, and iminobenzoquinone ligands, respectively. Continued reactivity of \( \text{7Ox} \) with oxygen led to degradation with the formation of \([\text{Co}^{2+}\text{(TpMe2)}_2]\). This species was detected alongside the disulfide product in the room temperature reaction with oxygen (after two hours). In order to isolate the oxidized ligands from the metal compounds the acidic work-up of this reaction was performed for \( \text{6-8} \).
Figure 3.11 Dioxgen-exposed sample (at room temp.) of 6 after 24 hours resulting in new paramagnetic features in $^1$H-NMR (measured in CDCl$_3$).

Figure 3.12 Left: dioxgen-exposed sample (at room temp.) of 7 after 24 hr. resulting in new paramagnetic features in $^1$H-NMR (measured in CDCl$_3$). Right: $^1$H-NMR spectrum of independently generated [Co$^{2+}$(TpMe$_2$)$_2$] in CDCl$_3$.

Samples of 6-8 were dissolved in separate mixtures of CH$_3$CN and CH$_2$Cl$_2$ (1:3) for product analysis. The solutions were treated with O$_2$ and stirred for one hour. The resulting mixture was dried in vacuo and then concentrated HCl was added to hydrolyze the ligands. This process was quenched with water before extraction by diethyl ether and dried to yield ~60% of oxidized ligand. As shown in Figure 3.13, the $^1$H and $^{13}$C-NMR spectra of the product reveal an iminobenzoquinone. These peaks were assigned by
comparison to spectra in Sawyer et al.,\textsuperscript{31} where the 4,6-di-\textit{tert}-butyliminobenzoquinone species features allylic C–H proton resonances at 6.18-6.72 and \textit{tert}-butyl protons at 1.20-1.37. The same procedure was carried out with complexes 7 and 8, and spectra of the resulting disulfide products are shown in Figure 3.14 and Figure 3.15.

![NMR spectra](image)

\textbf{Figure 3.13} \textsuperscript{1}H-NMR spectrum (top) of oxidized product (inset) after reaction work-up of 6, recorded in CDCl\textsubscript{3} with TMS standard (\(\delta = 7.26\)) at 20°C. \textsuperscript{13}C-NMR spectrum (bottom) of product from 6 and dioxygen reaction, recorded in CDCl\textsubscript{3} (\(\delta = 77.2\) ppm) at 20°C.
Figure 3.14 $^1$H-NMR spectrum (top) of degradation product (inset) after work-up of 7, recorded in CDCl$_3$ ($\delta = 7.26$) with TMS standard at 20°C. $^{13}$C-NMR spectrum (bottom) of product from 7 and dioxygen reaction, recorded in CDCl$_3$ ($\delta = 77.2$ ppm) at 20°C.

Figure 3.15 $^1$H-NMR spectrum of O$_2$-degradation product of 8 after acidic work-up, measured in CDCl$_3$ ($\delta = 7.26$) at 20°C. Inset: aromatic region of free disulfide.
D. Low Temperature Intermediates Derived from Dioxygen Reaction

The low temperature reactivity of 6 and 7 was monitored in THF at -70°C. The aminophenolate complex 6 forms a meta-stable intermediate (6SO) at -70°C for several minutes. Treatment with argon gas did not affect the spectral properties which suggests that it contains an irreversibly bound Co/O2 adduct (Figure 3.16, left). Likely, 6SO is a cobalt(III) superoxide species featuring trademark UV-vis features between 400-600 nm. The low temperature oxygen reaction with 7 initially forms features of 7Ox (not shown), indicating that the putative superoxide is not as stable as in the aminophenolate congener. In the unsubstituted aminothiophenolate complex 8, the reaction with oxygen resulted in a new species at -70°C in CH2Cl2 (Figure 3.17). This species (8SO) has features $\lambda_{\text{max}} = 500, 650$ nm that resemble those of other sulfur-bound cobalt superoxide adducts reported previously, such as the putative superoxide generated by low temperature addition of oxygen to [Co2+ (TpMe2)(CysOEt)]. However, unlike the Co/O2 adduct which forms with the cysteinate complex, this process is irreversible much like formation of 6SO. In efforts to study its magnetic properties, X-band EPR spectra of frozen solutions containing 6SO and 8SO were recorded at low temperatures (Figure 3.16 and Figure 3.17). The samples were prepared in THF by isolating 6 and 8 (~2 mM) inside sealed cuvettes and treating them with dioxygen at -80°C. This reaction was monitored by UV-vis spectroscopy until the spectra matched previously recorded data. The resulting O2-treated species were transferred into an EPR tube through a cannula and frozen in liquid nitrogen. In contrast to the spectrum of 6, the EPR spectrum of 6SO in THF (Figure 3.16) displays a lone $S = 1/2$ signal with g-values = 2.084, 2.007, 1.957.
Figure 3.16 Left: UV-vis of low-temperature reactivity featuring $6^{\text{SO}}$ in THF (initial $[6] = 1.25$ mM), measured at $-80^\circ$C. Right: derivative feature centered at $g = 2.007$ from X-band EPR spectrum (red) of $6^{\text{SO}}$ in frozen solution (initial $[6] = 1.9$ mM in THF) collected at $25$ K, frequency = $9.477$ GHz. Simulated spectrum (black) was created using EasySpin with $g = 2.084, 2.007, 1.957$.

The intermediate $8^{\text{SO}}$ also has a single feature centered at $3300$ G, indicative of a $S = 1/2$ system with $g$-values = $2.089, 2.018, 1.986$. Both $6^{\text{SO}}$ and $8^{\text{SO}}$ contain hyperfine splitting ($A_{zz}$) from the $^{59}$Co nucleus ($I = 7/2$). This manifests in the eight-line pattern in the low-field feature found in both spectra. This value shows smaller splitting values ($A_{zz}$ = $28$ G in $6^{\text{SO}}$ and $24$ G in $8^{\text{SO}}$) compared to the precursor complexes. Likely, the signal arises from an unpaired electron localized not on the cobalt center, but rather on the superoxo ligand. Both the UV-vis and EPR spectra for these intermediates are strikingly similar to those reported previously for mononuclear cobalt(III) superoxide species. In particular, the clustering of $g$-values near 2.0 and the small $A_{\text{Co}}$ values are distinctive characteristics of cobalt(III)-superoxo adducts, reflecting localization of the unpaired electron on the superoxo ligand.
Figure 3.17 Left: UV-vis absorption spectrum of \(8^{SO}\) collected at -80°C (initial \([8] = 1.0\) mM in THF). Right: X-band EPR spectrum of \(8^{SO}\) (initial \([8] = 1.4\) mM) centered at \(S = 1/2\) signal, frequency = 9.625 GHz, power = 2.080 mW, modulation amplitude = 8 G. After warming, \(6^{SO}\) and \(8^{SO}\) convert to the oxidized species \(6^{Ox}\) and \(8^{Ox}\) at temperatures greater than -20°C. Contrastingly, the reaction with oxygen at low temperatures (-70°C) for \(7\) initially forms \(7^{Ox}\). However, this species is short-lived, and immediately converts into a dark brown species (Figure 3.18, left). Therefore, \(7\) foregoes superoxide formation and instead rapidly converts into a Co/O\(_2\) adduct after loss of an H-atom (\textit{vide infra}). Similarly, if \(6^{Ox}\) and \(8^{Ox}\) are treated with oxygen at lower temperatures (-70°C) each transform into a new species (\(6^{O2}\) and \(8^{O2}\)). This new species has muted absorption features that are distinct from the partially oxidized derivatives of \(6^{Ox-9^{Ox}}\) and can only be generated when they are treated with O\(_2\) at low temperatures (Figure 3.18 and Figure 3.19). This process was monitored by UV-vis absorption spectroscopy. In the case of \(6^{Ox}\) and \(9^{Ox}\), the new species lacks well-defined absorption features in the visible region (Figure 3.19). For all Co/O\(_2\) adducts, \(6^{O2-9^{O2}}\), the features of the precursor complexes are recovered once the solution is warmed, and this can be repeated numerous times. Thus, the formation of the new species is an entirely reversible process.
Figure 3.18 Left: UV-vis monitored conversion of $\text{7}^{\text{Ox}}:\text{[Co}^{2+}(\text{Tp}^{\text{Me2}})(\text{ITSQ}^{\text{tBu2}})]$ (red solid line) into Co/O$_2$ adduct $\text{7}^{\text{O2}}$ (black dashed line) at -70°C in THF (initial $[\text{7}] = 0.2 \text{ mM}$). Right: UV-vis experiment showing reversible O$_2$ binding between $\text{8}^{\text{Ox}}$ (red dashed and solid lines) and $\text{8}^{\text{O2}}$ (black dashed and solid lines) recorded at -70°C and 20°C in THF (initial $[\text{8}] = 0.6 \text{ mM}$).

Figure 3.19 Left: UV-vis monitored conversion between $\text{6}^{\text{Ox}}$ to $\text{6}^{\text{O2}}$ in O$_2$ saturated solution between room temperature (black) and -50°C (red, $[\text{Co}] = 0.7 \text{ mM}$ in CH$_2$Cl$_2$). Right: UV-vis experiment with 0.8 mM solution of $\text{9}^{\text{Ox}}$ in CH$_2$Cl$_2$ (at 20°C and -10°C, black) in the presence of oxygen, conversion to $\text{9}^{\text{O2}}$ (red) recorded at -70°C.

Crystals of complex $\text{6}^{\text{O2}}$ were grown under aerobic conditions inside a -30°C freezer, from which the structure in Figure 3.20 was determined using X-ray crystallography. The resulting crystal structure revealed a neutral cobalt-alkylperoxo complex in which the O$_2$-derived atoms form a bridge between Co and C1 of the ligand,
thereby generating a five-membered metallocycle. The O2–O3 distance of 1.482(3) Å is typical of alkylperoxo ligands, and the sp\(^3\) hybridization of the C1-atom is evident from its average bond angle of 110° ± 7. The Co–N/O bond distances in \(6^{O2}\) are shorter than those of \(6^{Ox}\) by an average of 0.15 Å, indicating a change from high-spin Co(II) to low-spin Co(III). Comparison of C–C bond distances reveals that the quinoidal distortion of the ligand is significant, and the metric parameters observed for \(6^{O2}\) are characteristic of an iminobenzoquinone. Thus, formation of this Co/O\(_2\) adduct is a two-electron process involving oxidation of both the Co(II) center and ISQ ligand. This “spiroendoperoxide” structure is the first of its kind among first-row transition metal complexes; it represents the only X-ray structure to date of a synthetic dioxygen adduct with direct relevance to ring-cleaving dioxygenases. As for biological precedents, the structure \(6^{O2}\) closely resembles the iron-alkylperoxo intermediate observed by Lipscomb in a crystal structure of HPCD.\(^{22}\) Based on the similarity in UV-vis data for the conversion of \(6^{Ox} \rightarrow 6^{O2}\) and \(9^{Ox} \rightarrow 9^{O2}\) we can assume the same process occurs for the iminothiosemiquinonate derivatives \(7^{Ox}\) and \(8^{Ox}\) which undergo formation of a cyclic alkylperoxide intermediate (Scheme 3.E).

**Figure 3.20** X-ray crystal structure of \(6^{O2}\) measured at 100 K. Bond distances are in red (Å).
Scheme 3.E Top: conversion of \(9^{Ox}\) to \(9^{O2}\) showing reversible \(O_2\) binding process between high-spin cobalt(II) and low-spin cobalt(III) intermediate (-70°C). Bottom: conversion between \(7^{Ox}\) to \(7^{O2}\) showing reversible conversion between low-spin cobalt(II) iminothiosemiquinonate \((S = 0)\) to low-spin cobalt(III) alkylperoxo intermediate.

To supplement our UV-vis absorption data we conducted variable-temperature (VT) \(^1\)H-NMR experiments on the \(O_2\) adducts \(6^{O2}\), \(8^{O2}\), and \(9^{O2}\). In order to prepare comparative spectra, an anaerobic control of each precursor \((6^{Ox}, 7^{Ox}, \text{and} \ 9^{Ox})\) was recorded at low temperatures. Oxidation of this species was performed by introducing a dry stream of \(O_2\) into the NMR tube which allowed for the formation of species \(6^{Ox}\) and \(8^{Ox}\) (Figure 3.10 and Figure 3.23, respectively). Both \(6^{Ox}\) and \(9^{Ox}\) are paramagnetic, however, after formation of \(O_2\)-adducts \((6^{O2} \text{ and } 9^{O2})\), the \(^1\)H-NMR spectra show peaks only in the diamagnetic region (Figure 3.21 and Figure 3.22). The spectrum of \(8^{Ox}\) is diamagnetic (Figure 3.23), which allowed for direct comparison with the Co/O\(_2\) adduct \(8^{O2}\) (Figure 3.24). The common feature among all the oxygenated species \(6^{O2}, 8^{O2}, \text{and} \ 9^{O2}\) are the presence of Tp\(^{Me2}\) peaks in the region between 2-3 ppm. Also, the 4-\(H\)-pyrazole protons appear at a similar position (approximately 5.9-6.1 ppm) with three peaks in close proximity to one another, indicating that the three pyrazole donors are not equivalent in the Co/O\(_2\) adducts.
**Figure 3.21** $^1H$-NMR spectrum of 6$^{O2}$ measured at -70°C in CD$_2$Cl$_2$. The asterisk (*) corresponds to the residual solvent peak (CH$_2$Cl$_2$).

**Figure 3.22** $^1H$-NMR spectrum of 9$^{O2}$ measured at -70°C in CD$_2$Cl$_2$. The asterisk (*) corresponds to the residual solvent peak (CH$_2$Cl$_2$). The dark triangles represent free catechol ligand.
Figure 3.23 \(^1\)H-NMR spectrum of \(8^{0\text{ox}}\) recorded at -30°C in CD\(_2\)Cl\(_2\). The asterisks (*) mark peaks from residual solvents (CH\(_2\)Cl\(_2\), Et\(_2\)O, and pentane).

Figure 3.24 \(^1\)H-NMR spectrum of \(8^{02}\) recorded at -70°C in CD\(_2\)Cl\(_2\). The asterisks (*) mark peaks from residual solvents (CH\(_2\)Cl\(_2\), Et\(_2\)O, and pentane).
E. Thermodynamics of O₂-binding

In order to further study the reversibility of this process, we conducted experiments to measure the equilibrium O₂ binding constant ($K_{O2}$) using the spectrochemical method originally developed by Drago. The absorption features of the oxidized derivatives $6^{ox}$-$9^{ox}$ are easy to measure through variable temperature UV-vis spectroscopy. Therefore, the depletion of the $\pi \rightarrow \pi^*$ absorption bands which occurs upon formation of $6^{O2}$-$9^{O2}$ can be subtracted from the initial intensity in order to solve for the ratio of product to reactant. The change in absorption, which can be measured as the Co/O₂ adduct is formed, allows for the systematic determination of $K_{eq}$ by graphing partial pressure versus the ratio of products formed. The equilibrium binding constant $K$ for the O₂ binding reaction is obtained through the equation:

$$pO_2 = C\left(\frac{pO_2}{A - A_0}\right) - K^{-1}$$

The equation describes the 1:1 equilibrium ($K = O_2$ binding constant) where $A_0$ is the absorbance of the oxidized species (e.g., $6^{ox}$) before addition of oxygen. The measured absorbance after addition of oxygen is $A$ and the O₂ partial pressure is represented by $pO_2$. In our system, $pO_2$ is controlled by altering the ratio of gases (O₂ and Ar) in the headspace of the cuvette. We chose to use argon gas in the mixture due to its inertness and negligible affinity for binding. The experimental setup (as described in IV. Experimental Section) includes argon and oxygen gas cylinders that feed into the sample solution (in CH₂Cl₂) contained within a septum-sealed cuvette. The partial pressures of O₂ and Ar were controlled through pressurized flowmeters, which allowed for the measurement of specific $pO_2$ (atm). Since the concentration of O₂ in solution is
proportional to that in the head space of the cuvette, each increase of $pO_2$ corresponds to a new equilibrium between the precursor and Co/O$_2$ adduct. Therefore, samples of $6^{Ox}$, $7^{Ox}$, and $9^{Ox}$ were prepared in situ, followed by addition of oxygen at different partial pressures ($pO_2 = 0.08, 0.14, 0.26, 0.41,$ and $0.65 \text{ atm}$) at a given temperature in CH$_2$Cl$_2$. An example of each experiment is depicted in Figures 3.25-3.27, with O$_2$ reaction for the $6^{Ox}$ at -22.5°C, $7^{Ox}$ at -40°C, and $9^{Ox}$ at -25°C. For each reaction, the $K_{eq}$ values (summarized in Table 3.B) were determined by using the line of best fit for the plot of $pO_2/A-A_o$ vs. $pO_2$ (inset of figures). From the equation of the line, the inverse of the y-intercept yields $K_{eq}$ for the equilibrium at each temperature. The reaction between $6^{Ox}$ and O$_2$ has the largest of the complexes measured ($K_{eq}$ = 134.0 atm$^{-1}$ at -30°C). This prevented us from gathering multiple data points at lower temperatures due to saturation of $6^{O2}$ after the first addition of oxygen ($pO_2 = 0.08 \text{ atm}$). The O$_2$-reaction of $9^{Ox}$ has the next largest $K_{eq} = 16.8 \text{ atm}^{-1}$ followed by $7^{Ox}$, $K_{eq} = 4.06 \text{ atm}^{-1}$ (both measured at -40°C). This suggests that the affinity for oxygen is greater in both of the high-spin cobalt(II) derivatives with O-atom donors ($6^{Ox}$ and $9^{Ox}$).
Figure 3.25 Reversible O₂ binding by [Co²⁺(TpMe₂)(ISQtBu₂)] (6⃣Ox; conc. = 1.05 mM) in CH₂Cl₂: UV-vis spectral changes at various O₂ partial pressures (pO₂) at -22.5°C. The initial spectrum in the absence of O₂ is shown in black. The features diminish as pO₂ increases to 0.08, 0.14, 0.26, and 0.41 atm (blue line). Inset: a plot of pO₂ versus pO₂/(A–A₀) at 610 nm. The intercept of the line is equal to −1/KO₂.

Figure 3.26 Reversible O₂ binding by [Co²⁺(TpMe₂)(ITSQtBu₂)] (7⃣Ox; conc. = 0.20 mM) in CH₂Cl₂: UV-vis spectral changes at various O₂ partial pressures (pO₂) at -40°C. The initial spectrum in the absence of O₂ is shown in black. The features diminish as pO₂ increases to 0.08, 0.14, 0.26, and 0.41 atm (blue line). Inset: a plot of pO₂ versus pO₂/(A–A₀) at 605 nm. The intercept of the line is equal to −1/KO₂.
Figure 3.27 (a) Reversible O$_2$ binding by [Co$^{2+}$($\text{Tp}^{\text{Me2}}$)(SQ$^{\text{tBu2}}$)] ($9^{\text{Ox}}$; conc. = 1.5 mM) in CH$_2$Cl$_2$: UV-vis spectral changes at various O$_2$ partial pressures ($p_{O_2}$) at -25°C. The initial spectrum in the absence of O$_2$ is shown in black. The features diminish as $p_{O_2}$ increases to 0.12, 0.15, 0.26, 0.33, 0.42, and 0.65 atm (blue line). (b) A plot of $p_{O_2}$ versus $p_{O_2}/(A-A_0)$ at 595 nm. The intercept of the line is equal to $-1/K_{O_2}$. (c) A van’t Hoff plot for the O$_2$ binding reaction measured at $T = -25, -30, -35, -40$, and -45°C.

Table 3.B Measured $K_{eq}$ values for reversible O$_2$-binding reactions performed in CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Reaction: 6$^{\text{Ox}}$ + O$_2$</th>
<th>Temp. (°C)</th>
<th>-30.0</th>
<th>-27.5</th>
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<tr>
<td>$K_{eq}$ (atm$^{-1}$)</td>
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<td>112.86</td>
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<table>
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<th>-40.0</th>
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<td>$K_{eq}$ (atm$^{-1}$)</td>
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<table>
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<tr>
<td>$K_{eq}$ (atm$^{-1}$)</td>
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<td>16.81</td>
<td>7.72</td>
<td>3.31</td>
<td>2.56</td>
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These experiments were all conducted in CH$_2$Cl$_2$ for consistency. However, due to intrinsic differences in O$_2$ affinity across the oxidized species, the O$_2$-binding reactions were conducted over different temperature ranges for each complex. By measuring $K_{eq}$ values (atm$^{-1}$) at different temperatures, the thermodynamic parameters of O$_2$-binding for each process could be determined using the relationship:

$$\ln K_{eq} = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}. $$

Thus, by graphing the log of $K_{eq}$ vs. inverse temperature (K$^{-1}$) it was possible to generate a van’t Hoff plot for oxygen binding by complexes 6$^{Ox}$-9$^{Ox}$ (Figure 3.28). The line of best fit for this plot results in thermodynamic values $\Delta H$ and $\Delta S$ which are the slope and intercept over the ideal gas constant $R$ (summarized in Table 3.C).

**Figure 3.28** Left: van’t Hoff plot of O$_2$-binding events in 6$^{Ox}$ (blue squares), 7$^{Ox}$ (green squares), and 9$^{Ox}$ (red squares) in CH$_2$Cl$_2$. Right: van’t Hoff plots of O$_2$-binding events for [Co$^{2+}$($\text{Tp}^{\text{Me2}}$)(CysOEt)] (pink squares) and [Co$^{2+}$($\text{Tp}^{\text{Me2}}$)(BisPz)] (orange squares).
Table 3.C  Determined thermodynamic parameters ($\Delta H$, $\Delta S$, and $\Delta G$ at $-40^\circ C$) of O$_2$ binding by 6$^{\text{Ox}}$, 7$^{\text{Ox}}$, 9$^{\text{Ox}}$ and O$_2$-reactions with cobalt(II) cysteinate and bispyrazole complexes.

<table>
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<th>Reaction</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G$ (at $-40^\circ C$) (kJ mol$^{-1}$)</th>
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</thead>
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<tr>
<td>6$^{\text{Ox}}$ + O$_2$</td>
<td>$-65 \pm 8$</td>
<td>$-226 \pm 32$</td>
<td>$-12.3$</td>
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<tr>
<td>7$^{\text{Ox}}$ + O$_2$</td>
<td>$-57 \pm 6$</td>
<td>$-231 \pm 26$</td>
<td>$-3.2$</td>
</tr>
<tr>
<td>9$^{\text{Ox}}$ + O$_2$</td>
<td>$-55 \pm 6$</td>
<td>$-215 \pm 27$</td>
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</tr>
<tr>
<td>[Co$^{2+}$(Tp$^{\text{Me2}}$)(CysOEt)] + O$_2$</td>
<td>$-37 \pm 1$</td>
<td>$-174 \pm 6$</td>
<td>$+3.2$</td>
</tr>
<tr>
<td>[Co$^{2+}$(Tp$^{\text{Me2}}$)(BisPz)] + O$_2$</td>
<td>$-30 \pm 3$</td>
<td>$-145 \pm 17$</td>
<td>$+3.6$</td>
</tr>
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</table>

In general, we find that the O$_2$ binding reactions for 6$^{\text{Ox}}$, 7$^{\text{Ox}}$, and 9$^{\text{Ox}}$ have distinctively large and negative enthalpies which favor O$_2$ binding, suggesting that the formation of two new bonds imparts stability to the Co/O$_2$ adducts. However, the large and negative $\Delta S$ values indicate that the O$_2$ binding process is entropically disfavored, due to the decrease in free O$_2$ molecules in solution and the ordered nature of the spiroendoperoxide unit. Therefore, the O$_2$ adduct formation has competing enthalpic and entropic factors, with the former outweighing the decrease in entropy at reduced temperatures. The calculated $\Delta G$ values indicate that all three O$_2$-binding events are spontaneous at low temperatures.

In order to compare the thermodynamic values determined for alkylperoxide formation, we repeated this procedure for Tp$^{\text{Me2}}$-supported Co(II) complexes with redox-inactive ligands, such as [Co$^{2+}$(Tp$^{\text{Me2}}$)(CysOEt)] and [Co$^{2+}$(Tp$^{\text{Me2}}$)(BisPz)]. These complexes were synthesized according to previously published methods and reacted with
oxygen at low temperatures with metered $pO_2$ values to determine $K_{eq}$ and thermodynamic parameters. In these case, reversible $O_2$ binding generates an end-on cobalt(III)-superoxo adduct. As shown in Table 3.C, the $\Delta H$ values for formation of the cobalt(III)-superoxo adducts in the cysteinate and bis-pyrazole complexes is much less negative ($\Delta H = -37.4$ and -30 kJ mol$^{-1}$, respectively) that those for $6^{O_2-9O_2}$. Our results are consistent with previously measured thermodynamic parameters of Co(III)-superoxo binding events.\textsuperscript{8} The 2$e^-$ reduction of oxygen to generate the alkylperoxo complexes $6^{O_2-9O_2}$ is more enthalpically favored due to formation of an additional O–C bond, yet this reaction also has more negative $\Delta S$-values. Thus, the two factors are partially offsetting, although the $\Delta G$-values of $6^{O_2-9O_2}$ at -40°C are more considerably more negative for than those of $[\text{Co}^{2+}(\text{Tp}^{\text{Me}_2})(\text{CysOEt})]$ and $[\text{Co}^{2+}(\text{Tp}^{\text{Me}_2})(\text{BisPz})]$. We posit that this behavior is what makes alkylperoxide bonding favored in presence of dioxolenes with radical character, which sets them apart from other metal-O$_2$ binding reactions.

**III. Conclusion**

As summarized in Scheme 3.F, we have explored the $O_2$ reaction landscape of cobalt aminophenolate, aminothiophenolate, and semiquinonate complexes. These studies led to the isolation and characterization of cobalt(III)-superoxo and -alkylperoxo species that mimic proposed intermediates of ring-cleaving dioxygenases. It is instructive that subtle differences between these synthetic Co/O$_2$ adducts and their enzymatic counterparts account for lack of dioxygenation activity exhibited by our synthetic models. Specifically, the low-spin Co(III) center of intermediates in $6^{O_2-9O_2}$ stabilizes alkylperoxo ligand and prevents subsequent O–O bond cleavage, whereas the high-spin Co(II) ion in the putative enzymatic intermediate facilitates the insertion of distal oxygen
into the ring via Criegee rearrangement.\textsuperscript{22} In our models, the inability for 6\textsuperscript{O2}-9\textsuperscript{O2} to convert to the requisite cobalt(II)-alkylperoxo species is likely due to the lack of unpaired spin density within the [Co\textsuperscript{3+}-APH\textsuperscript{tBu2}] unit, which hinders O–C bond formation. The enzyme avoids this scenario by coupling \textsubscript{O2} binding to a proton transfer from the substrate to a conserved second-sphere His residue. According to DFT studies, this process yields a superoxo-Co(II)-substrate radical that is primed for alkylperoxo formation.\textsuperscript{34,35}

\begin{center}
\textbf{Scheme 3.F} Proposed reaction scheme of cobalt aminophenolate (6) with \textsubscript{O2}.
\end{center}

\section*{IV. Experimental Section}

\subsection*{General Methods}

Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used as received without further purification. Acetonitrile (CH\textsubscript{3}CN), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}), methanol (CH\textsubscript{3}OH), and THF were degassed through several freeze-pump-thaw cycles and stored over molecular sieves. The synthesis and handling of cobalt complexes was carried out under an inert atmosphere using a Vacuum Atmospheres Omni-Lab glovebox equipped with a freezer set to \textdegree{}C. The compounds [Co\textsuperscript{2+}(Tp\textsubscript{Me2})(OAc)], ATP\textsuperscript{tBu2}, and TTBP\textsuperscript{*} were prepared according to
literature procedures.\textsuperscript{30,36,37} The K[Tp\textsuperscript{Me2}] ligand was purchased from TCI America. The ATP\textsubscript{H2} ligand was purchased from Alfa Aesar.

**Physical Characterization**

Elemental analyses were performed at Midwest Microlab, LLC in Indianapolis, IN. UV-vis absorption spectra were collected with an Agilent 8453 diode array spectrometer equipped with a Unisoku Scientific Instruments (Osaka, Japan) cryostat for low temperature measurements. \textsuperscript{1}H-NMR spectra were measured on a Varian 400 MHz spectrometer featuring variable-temperature capabilities. This instrument was also used for magnetic susceptibility measurements carried out using the Evans method. X-band EPR spectra of 6, 8, and trapped superoxide intermediate were measured using a Bruker EMX instrument equipped with an ER4112 SHQ resonator. The X-band EPR spectrum of 7 was measured at UW-Madison using a Bruker ELEXSYS E500 spectrometer. Data was collected at 77 K in a cold finger quartz dewar or liquid He temperatures (5-10 K) using a ColdEdge/Bruker RDK-408 Stinger recirculating cryocooler. Simulations of experimental EPR spectra were conducted with the program EasySpin.\textsuperscript{32}

**Synthesis of [Co\textsuperscript{2+}(Tp\textsuperscript{Me2})(APH\textsuperscript{tBu2})] (6) Tp\textsuperscript{Me2} = hydrotris(3,5-dimethylpyrazol-1-yl)borate**

In a 5:1 mixture of CH\textsubscript{3}CN and CH\textsubscript{3}OH (10 mL), equimolar amounts of [Co\textsuperscript{2+}(Tp\textsuperscript{Me2})(OAc)] (280 mg, 0.7 mmol) and APH\textsuperscript{tBu2} (150 mg, 0.7 mmol) were combined with 2.0 equivalents of NaOMe (71 mg, 1.3 mmol) and stirred for 12 hours. After removal of the solvent, the crude material was dissolved in 4 mL of CH\textsubscript{3}CN and filtered. The resulting solution was stored inside the glovebox freezer (-30°C) and light green crystals formed after 1-2 days. The solvent was decanted, and the crystals were washed with cold CH\textsubscript{3}CN, then dried under vacuum to yield analytically pure compound.
Yield = 136 mg (35%). Anal. Calcd (%) for C_{29}H_{44}BCoN_{7}O (M_W = 576.46 g mol^{-1}): C, 60.42; H, 7.69; N, 17.01. Found: C, 60.92; H, 7.41; N, 16.75. UV-vis [\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1})] in CH_2Cl_2: 307 (2210), 375 (680), 507 (90), 537 (100), 566 (100). FTIR (cm^{-1}, CH_2Cl_2): \nu = 3433, 3428 [\nu(\text{N–H})], 3051, 1374, 1120, 997. ^1H-NMR (400 MHz, CDCl_3): \delta = 72.3 (1H, s, APH^tBu_2), 59.5 (1H, s, BH), 57.5 (9H, s, -C(CH_3)_3), 55.2 (3H, s, 4-H-pz), 29.6 (9H, s, Tp-Me-CH_3), 15.6 (1H, s, APH^tBu_2), 2.68 (9H, s, -C(CH_3)_3), -47.4 (9H, s, Tp-Me-CH_3) ppm. \mu_{\text{eff}} = 4.5 \mu_B (\text{Evans method in CDCl}_3).

**Synthesis of [Co^{2+}(Tp^{Me_2})(ISQ^tBu_2)] (6^{Ox})**

Under nitrogen atmosphere, a solution was prepared with 40 mg (0.07 mmol) of solid [Co^{2+}(Tp^{Me_2})(APH^tBu_2)] dissolved in CH_2CN (5 mL). The sample was exposed into aerobic atmosphere briefly and then placed inside the glovebox freezer (-30°C). After a few days, dark green prisms had crystallized. The crystals were air dried to yield a dark green powder. Yield = 38 mg (95%). UV-vis [\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1})] in CH_2Cl_2: 385, 425 (sh), 465, 610, 775 (sh). ^1H-NMR (400 MHz, CD_2Cl_2, 20°C): \delta = 124.4 (1H, s, ISQ^tBu_2), 76.5 (1H, s, ISQ^tBu_2), 30.7 (9H, s, Tp-Me-CH_3), 23.6 (3H, s, 4-H-pz), 1.43 (9H, s, Tp-Me-CH_3), -3.82 (9H, s, -C(CH_3)_3), -49.1 (9H, s, Tp-Me-CH_3) ppm. \mu_{\text{eff}} = 3.1 \mu_B (\text{Evans method in CDCl}_3).

**Synthesis of [Co^{2+}(Tp^{Me_2})(ATP_{tBu_2})] (7)**

To a solution of ATP_{tBu_2}-H_2 (64 mg, 0.27 mmol) in THF (2 mL). was added 1.2 equivalents of NaOMe (18 mg, 0.33 mmol). The mixture was stirred for one hour and then dried by vacuum. The cobalt precursor, [Co^{2+}(Tp^{Me_2})(OAc)] (122 mg, 0.29 mmol), was added to the residue and the combined solids were re-suspended in CH_2Cl_2. The dark red solution was stirred for two hours before filtration through Celite. The solvent was
removed, and the resulting solid residue was dissolved in CH$_3$CN. Orange needles suitable for X-ray crystallographic analysis were obtained after several days at reduced temperature (-30°C). The crystals were dried to provide a reddish-brown solid. Yield = 104 mg (65%). Anal. Calcd (%) for C$_{29}$H$_{44}$BCoN$_7$S ($M_W = 592.46$ g mol$^{-1}$): C, 58.79; H, 7.49; N, 16.55. Found: C, 59.95; H, 7.17; N, 16.62. UV-vis [$\lambda_{\text{max}}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$) in CH$_2$Cl$_2$]: 470 (780), 570 (590). $^1$H-NMR (400 MHz, CDCl$_3$, 20°C): $\delta = 87.2$ (1H, s, BH$_2$), 85.8 (3H, s, 4-H-pz), 52.7 (6H, s, Tp-Me-CH$_3$), 50.7 (2H, s, -NH$_2$), 44.0 (1H, s, ATP-H)$_2$, 20.1 (3H, s, Tp-Me-CH$_3$), 3.36 (9H, s, -C(C$_3$H$_3$)$_3$), -3.67 (9H, s, -C(C$_3$H$_3$)$_3$), -19.8 (1H, s, ATP-H), -58.3 (3H, s, Tp-Me-CH$_3$), -63.8 (6H, s, Tp-Me-CH$_3$) ppm. $\mu_{\text{eff}} = 4.29$ $\mu_B$ (Evans method in CDCl$_3$).

**Synthesis of [Co$^{2+}$(Tp$^{Me_2}$)(ITSQ$^{tBu_2}$)] (7Ox)**

The precursor complex [Co$^{2+}$(Tp$^{Me_2}$)(tBu$_2$ATP-H)] (30 mg, 0.051 mmol) was dissolved in CH$_3$CN (5 mL) and the solution was purged with O$_2$ for one minute, resulting in a color change to dark green. The vial was placed in the glovebox freezer (-30°C) and green crystals suitable for X-ray crystallography appeared after a few days. The crystals were dried under vacuum and used without further purification. Yield = 28 mg (94%). The complex is unstable at room temperature and was stored in the glovebox freezer. UV-vis [$\lambda_{\text{max}}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$) in CH$_2$Cl$_2$]: 485 (6120), 600 (5600), 1005 (1300).

**Synthesis of [Co$^{2+}$(Tp$^{Me_2}$)(ATP)] (8) ATP = 2-aminothiophenol**

A round-bottomed flask was charged with ATP-H$_2$ (102 mg, 0.81 mmol) and mixed with NaOMe (52 mg, 0.96 mmol) in THF (2 mL) under nitrogen. The resulting yellow solution was stirred for 2 hours followed by removal of solvent under vacuum. In a separate vial, [Co$^{2+}$(Tp$^{Me_2}$)(OAc)] (340 mg, 0.82 mmol) was dissolved in CH$_2$Cl$_2$ (5
144

This solution was added to the flask containing the deprotonated ligand and the mixture was stirred for 3 hours. The brown solution was filtered through Celite and the solvent removed \textit{in vacuo}. The residue was washed with \(\text{Et}_2\text{O}\) and dissolved in \(\text{CH}_2\text{Cl}_2\) (3 mL). Crystals suitable for X-ray crystallography were generated by vapor diffusion of \(\text{Et}_2\text{O}\) into the concentrated \(\text{CH}_2\text{Cl}_2\) solution. The crystals were dried under vacuum to give a brown powder. Yield = 186 mg (48%). Anal. Calcd (%) for \(\text{C}_{21}\text{H}_{28}\text{BCoN}_7\text{S} (M_w = 480.31 \text{ g mol}^{-1})\): C, 52.51; H, 5.88; N, 20.42. Found: C, 53.09; H, 5.90; N, 20.09. UV-vis \([\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1}) \text{ in } \text{CH}_2\text{Cl}_2]: 351 (1800), 385 (sh), 440 (600), 552 (200), 630 (sh).

\(^1\text{H}-\text{NMR} (400 \text{ MHz, CDCl}_3): \delta = 62.0 (1\text{H, } s, \text{ ATP-H}), 61.7 (1\text{H, } br, \text{ BH}), 56.0 (3\text{H, } s, 4-H-pz), 33.6 (9\text{H, } s, \text{ Tp-Me-CH}_3), 31.7 (1\text{H, } s, \text{ ATP-H}), -3.4 (1\text{H, } s, \text{ ATP-H}), -14.9 (1\text{H, s, ATP-H}). -51.9 (9\text{H, } s, \text{ Tp-Me-CH}_3) \text{ ppm. } \mu_{\text{eff}} = 4.27 \mu_\text{B} \text{ (Evans method in CDCl}_3). \]

**Synthesis of \([\text{Co}^{2+}(\text{Tp}^{\text{Me}_2})(\text{ITSQ})] (8^\text{Ox})\)**

The precursor complex, \([\text{Co}^{2+}(\text{Tp}^{\text{Me}_2})(\text{ATP-H})] (65 \text{ mg, 0.14 mmol}), was dissolved in \(\text{CH}_2\text{Cl}_2 \) (2 mL) in a small vial. This vial was then placed within a larger container that contained \(\text{O}_2\)-saturated \(\text{Et}_2\text{O}\). The larger container was sealed and transferred to the glovebox freezer (-30°C). Diffusion of \(\text{Et}_2\text{O}\) and \(\text{O}_2\) into the \(\text{CH}_2\text{Cl}_2\) solution resulted in a color change to blueish-green over the course of several hours. Small needles of 4 formed after several days and these crystals were analyzed by X-ray crystallography. Solvent was decanted from the remaining crystals, which were washed with ether and dried to provide a green powder. Yield = 60 mg (93%). The complex is unstable at room temperature and was stored in the glovebox freezer. UV-vis \([\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1}) \text{ in } \text{CH}_2\text{Cl}_2]: 490 (2500), 615 (1760), 980 (540). \(^1\text{H}-\text{NMR} (400 \text{ MHz, CD}_2\text{Cl}_2, -30^\circ\text{C}): \delta = 9.45 (1\text{H, } s, \text{ NH}), 8.17 (1\text{H, } s, \text{ ITSQ-H}), 7.46 (2\text{H, } s, \text{ ITSQ-H}), 7.29
(1H, s, ITSQ-H), 6.05 (3H, s, 4-H-pz), 3.58 (1H, s, BH), 2.50 (9H, s, Tp-Me-CH₃), 1.79 (9H, s, Tp-Me-CH₃) ppm.

**Synthesis of [Co²⁺(TpMe²)(SQ⁴Bu²)] (9⁰x)**

The 3,5-di-tert-butylcatechol ligand (124 mg, 0.56 mmol) was deprotonated with NaOMe (37.6 mg, 0.70 mmol) in a 3:1 mixture of CH₃CN and CH₃OH. After stirring for 5 min, [Co²⁺(TpMe²)(OAc)] (266 mg, 0.64 mmol) was added and the resulting mixture was stirred for 12 hr. After removal of the solvent by vacuum, the crude product was extracted with diethyl ether, passed through Celite, and further dried to yield a green solid. Yield = 235 mg (64%). Anal. Calcd (%) for C₂₉H₄₂BCoN₆O₂ (M_w = 576.44 g mol⁻¹): C, 60.42; H, 7.34; N, 14.58. Found: C, 60.27; H, 7.33; N, 14.10. UV-vis [λ_max, nm (ε, M⁻¹ cm⁻¹) in CH₂Cl₂]: 377 (2930), 595 (410), 750 (400), 850 (sh). FTIR (cm⁻¹, CH₂Cl₂): ν = 3250, 2520 [ν(B–H)], 2370, 2200, 2085, 1820, 1790, 1715. ¹H-NMR (400 MHz, CDCl₃): δ = 97.0 (1H, s, SQ), 66.6 (1H, s, SQ), 40.4 (9H, s, Tp-Me-CH₃), 37.7 (3H, s, 4-H-pz), 8.39 (9H, s, -C(CH₃)₃), -2.94 (9H, s, -C(CH₃)₃), -64.3 (9H, s, Tp-Me-CH₃) ppm. μ_eff = 3.2 μ_B (Evans method in CDCl₃).

**Determination of Thermodynamic Parameters**

Values for thermodynamic parameters were calculated based on equilibrium binding coefficients (K_o₂) collected between -90 and -20°C. These constants were measured by tracing the change in UV-vis absorption by complexation of O₂. In order to dispense a set partial pressure (pO₂) of oxygen for each data point, a mixture of gases was generated from pressurized cylinders of oxygen and argon (Purchased from AirGas). Our system flows both gases through separate 3/4” red rubber hosing with 1/4” inner diameter through Drierite moisture traps into VWR flowmeters (rated at 5-50 cm³ min⁻¹). To allow
for proper mixing a y-shaped glass adapter was adjoined to both gases which flow through a needle. While continuous absorbance measurements were taken, the $pO_2$ was metered at specific increments into the sample cuvette headspace. Once a change in absorbance was detected by increasing $pO_2$ the needle was quickly sparged through the sample to reach equilibrium. This process was repeated for 4-5 data points (between 0.1-1 atm $O_2$) at each temperature allowing for $K_{O_2}$ determination.
Table 3.D Summary of X-ray crystallographic data collection and structure refinement.

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V. BIBLIOGRAPHY


Abstract

The study of biologically relevant O$_2$-intermediates has proven difficult due to their short lifetimes in situ. The proposed O$_2$ activation mechanism of ring-cleaving MNIDs involve formation of a metal-superoxo adduct, followed by a metal-peroxo species generated via addition of bound superoxide to the coordinated substrate ligand. Current mechanisms include the description of two different O$_2$ intermediates at the preliminary steps of O$_2$-reactivity which remain disputed. The use of synthetic models for activation of oxygen has yielded metal-superoxide complexes with different transition metal centers. Published work by our lab and others has highlighted the intrinsic ability of certain ligands to activate oxygen in a setting close to that found in nature. The recent success of our cobalt model complexes in replicating cysteine and aminophenol O$_2$-adducts through structurally and spectroscopically characterized intermediates is due to the versatility of the Tp$^{Me2}$ framework. Despite our best efforts, we have not been able to replicate the dioxygenation reactivity of cobalt-substituted MNIDs. Iron-based studies with this framework have not received much attention, partially due to the high sensitivity of these complexes to dioxygen and tendency to form unwanted byproducts. Recently, we have investigated the O$_2$ reactivity of Tp$^{Me2}$-supported Fe(II) complexes with an aminophenolate “substrate” ligand. Modelling APDO behavior with [Fe$^{3+}$(Tp$^{Me2}$)(APH$^{Bu3}$)] (11) will be discussed in this chapter. In addition, insights gained into putative O$_2$-intermediates along the ring-cleavage pathway via resonance Raman and Mössbauer spectroscopies will be reported.
I. Introduction

Mononuclear non-heme iron dioxygenases (MNIDs) follow an ordered mechanism in which the substrate binds directly to Fe as a monoanion with concomitant dissociation of the water ligands. The resulting five-coordinate $\text{Fe}^{2+}$ center then activates $\text{O}_2$ in the vacant site adjacent to the bound substrate, yielding a putative iron-superoxo species. For ring-cleaving dioxygenases, the electronic structure of this critical intermediate remains controversial. While $\text{Fe}/\text{O}_2$ adducts are normally described as iron(III)-superoxo species, previous studies suggest that $\text{O}_2$ binding oxidizes the bound aromatic substrate instead, giving rise to a ferrous-superoxide intermediate coordinated to a substrate radical (as shown in Scheme 4.A for aminophenol dioxygenase, APDO). However, formation of a substrate radical during the ring-cleavage mechanism has been questioned by recent computational studies, and it has not been possible to interrogate this intermediate in spectroscopic studies of wild-type MNIDs or related model complexes. It is generally agreed that the nucleophilic superoxide ligand attacks the substrate to yield a bridged alkylperoxo species ($\text{Fe}–\text{O}–\text{O}–\text{C}$), followed by a Criegee rearrangement to insert an oxygen atom into the ring. Subsequent hydrolysis by the Fe-
OH unit yields the ring-opened product. Several studies have demonstrated that dioxygenase catalysis is facilitated by second-sphere residues within the active site. In the extradiol CatDs and APDOs, for instance, a conserved His residue located near the Fe center serves as an acid-base catalyst, accepting a proton from bound substrate upon O₂ binding and donating back the proton after cleavage of the O–O bond (vide infra).

The enhanced reactivity of Tp⁻²⁻supiated metal compounds was highlighted in a study by Hikichi in which the [Fe²⁺(Tp⁻²⁻)(OAc)] complex was first synthesized. In the presence of O₂, this complex immediately dimerizes to form a species bridged by a peroxo ligand. The [Fe(Tp⁻²⁻)(R)] framework can also be modified by addition of a bidentate, bis-imidazolyl-borate ligand which allows for the isolation and characterization of a Fe³⁺-superoxo species that is stable at -60°C in THF. The reaction can be reversed by heating this species to room temperature. Addition of a H-atom transfer (HAT) agent such as 2-hydroxy-2-azaadamante (AZADOL), yields a ferric hydroperoxide intermediate. Scheme 4.B highlights the various routes for formation of O₂-adducts that have been studied structurally and spectroscopically. Characterization of these intermediates with rRaman spectroscopy revealed isotopically-sensitive bands (with 413 nm excitation) due to the ν(O–O) mode of the Fe³⁺-superoxo species. The frequency (~1100 cm⁻¹) and isotopic shift of 80 cm⁻¹ between the ¹⁶O₂ and ¹⁸O₂-treated species is consistent with a superoxo ligand.
Following a similar approach, we attempted to isolate intermediates using the Fe-TpMe₂ framework in combination with substrate ligands that are present in dioxygenase enzymes. To facilitate comparison of previously isolated model complexes with biorelevant intermediates, we studied their spectroscopic characteristics with established methods such as X-band EPR, resonance Raman, and Mössbauer spectroscopy. In 2018, Fischer and Fiedler characterized a metastable nonheme iron-superoxo species derived from a model of cysteine dioxygenase (CDO). The precursor, [Fe²⁺(TpMe₂)(ATP)] (10) shown in Figure 4.00, consists of a high-spin ferrous center bound to TpMe₂, which mimics the facial 3-His triad of the CDO active site. The monoanionic 2-aminothiophenolate (2-ATP) ligand, binds to the iron(II) center in a bidentate manner analogous to the native Cys substrate.

**Scheme 4.B** Spectroscopically characterized complexes reported by Hikichi *et al.*
**Figure 4.00** X-ray crystal structure of [Fe$^{2+}$(Tp$^{Me2}$)(ATP)] (10), Tp-methyl peaks and ATP ligand protons were omitted for clarity.

Exposure of 10 to oxygen at low temperatures (-80°C, in THF) generates a purple chromophore that exhibits three absorption bands with $\lambda_{\text{max}} > 500$ nm (Figure 4.01). This EPR-silent intermediate decays at -80°C, eventually yielding a green EPR-active species. The identity of this Fe/O$_2$ has been established on the basis of rRaman studies (Figure 4.02). Spectra measured in MeTHF and THF-d$_8$ exhibit peaks at 1105 and 1135 cm$^{-1}$, respectively, that are absent in samples prepared with $^{18}$O$_2$. Frequencies between 1100 and 1200 cm$^{-1}$ are typical $\nu$(O–O) modes of $\eta^1$-superoxo ligands in nonheme iron complexes. While the presence of this pair could indicate multiple species, it is more likely that the 1105 and 1135 cm$^{-1}$ peaks correspond to a Fermi doublet centered near 1120 cm$^{-1}$. This conclusion is supported by the fact that the spectrum of the $^{18}$O$_2$-treated analogue in 2-methyltetrahydrofuran (MeTHF) exhibits a single isotope-sensitive peak at 1055 cm$^{-1}$ (this region is obscured by solvent peaks in THF and THF-d$_8$). Isotope-sensitive rRaman features in the low-frequency region also support the proposition that the Fe/O$_2$ adduct is an iron-superoxo species, and this assignment is corroborated by magnetic circular dichroism (MCD) spectroscopy and DFT calculations. This is the first report of a synthetic mononuclear iron-superoxo complex featuring a sulfur-based ligand,
and the first example with direct relevance to a particular MNID active site. Thus, it represents another breakthrough in our efforts to probe unobserved intermediates that participate in the activation of $\text{O}_2$ at nonheme iron centers.

**Figure 4.01** UV-vis spectra of $\text{10}$ (black) and formation of $\text{10}^{\text{SO}}$ (violet) in THF at -80°C.

**Figure 4.02** rRaman spectra of $\text{10}^{\text{SO}}$ in frozen MeTHF or THF-d$_8$. Samples were prepared with $^{16}\text{O}_2$ (black line) and $^{18}\text{O}_2$ (red line) peaks marked (*) are due to solvent.
II. Second-generation APDO Model Studies

Scheme 4.C O$_2$-reactivity profiles of redox-active iron complexes with catechol, aminophenol, and phenylenediamine ligands.$^{15}$

As described earlier by Bittner et al.,$^{15}$ exposure of our first-generation aminophenol dioxygenase models to O$_2$ resulted in formation of the corresponding Fe(III)-ISQ complexes (Scheme 4.C), not oxidative cleavage of the aromatic ring. We surmise that the absence of dioxygenase-type reactivity, as well as the lack of observable Fe/O$_2$ intermediates, might be due to the steric profiles of the 2-TIP$^{\text{Ph}_2}$ and Tp$^{\text{Ph}_2}$ supporting ligands, as Fe- and Co-CDO models with the less-bulky Tp$^{\text{Me}_2}$ ligand form metastable O$_2$ adducts at low temperature. To test this hypothesis, we prepared complex [Fe$^{2+}$(Tp$^{\text{Me}_2}$)(APH$^{\text{tBu}_2}$)] (11), the iron-substituted analogue of 6 which utilizes the sterically accessible Tp$^{\text{Me}_2}$ ligand. The synthesis and X-ray crystal structure of this complex were performed by Dr. Anne Fischer in the Fiedler group. She observed that the reaction of 11 with O$_2$ at room temperature triggers oxidative cleavage of the APH$^{\text{tBu}_2}$ ring, which then quickly cyclizes to yield a 2-picolinic acid product (Figure 4.03). Thus,
unlike its Tp^Ph2-based congener, 11 is a structural and functional aminophenol dioxygenase mimic. In addition, two reactive intermediates are observed by UV-vis spectroscopy after reaction with oxygen at low temperatures (-70°C). Treatment of 11 with O_2 at -70°C initially generates a dark purple species (A) that exhibits a band at 700 nm. This intermediate converts to a green chromophore (B) in minutes, characterized by new features at 500 and 870 nm. Species B is stable indefinitely at -70°C, but decays upon warming to room temperature to give the ring-cleaved product.

**Figure 4.03** Left: ring-cleaved picolinic acid product from dioxygenation of APH^tBu2 Right: UV-vis spectra of 11 (black, solid line), A (blue, dashed line) and B (red, dashed line) in at -70°C (1.2 mM in THF).

Preliminary spectroscopic studies suggest that both species A and B are intermediates in the ring-cleaving mechanism. Raman spectroscopy has been particularly useful in elucidating the geometric structure of the longer-lived B species. As shown in Figure 4.04, four peaks in the spectrum of B shift to lower energy upon 16/18O_2 substitution. The frequencies of these peaks, and the modest isotope shifts (2-8 cm\(^{-1}\)), rule out the presence of an iron-superoxo or -peroxo species. However, it is revealing that
several of the $^{16/18}$O-sensitive peaks also appear downshifted upon $^{15}$N-labeling of the APH$_{tBu^2}$ ligand.

This result is consistent with incorporation of an O$_2$-derived atom into the APH$_{tBu^2}$ ligand, which suggests that B is formed after cleavage of the O–O bond. Based on the proposed APDO mechanism, it is likely that B consists of an Fe center coordinated to a seven-membered lactone ring, as illustrated in Figure 4.05. The peaks at 1092 and 1124 cm$^{-1}$ likely arise from motions of the seven-membered lactone ring, while the lower-frequency (566, 603 cm$^{-1}$) peaks are due to $\nu$(Fe–O/N) vibrations. While functional APDO models have been previously reported by Paine et al.,$^{16}$ species B is the first intermediate in the dioxygenation pathway to be thoroughly characterized.

![Figure 4.04](image-url)  

**Figure 4.04** Raman spectrum of species B in frozen THF, after laser excitation at 407 nm. Samples were prepared with $^{16}$O$_2$ (black), $^{18}$O$_2$ (red), or $^{16}$O$_2$ and $^{15}$N-labeled APH$_{tBu^2}$ ligand (blue). Solvent peaks are marked with an asterisk (*).
The characterization of the initial complex 11 suggests it is a high-spin iron(II) aminophenolate complex. Recently we have been able to generate analytically pure samples of 11 without excess ligand (VI. Experimental Section). We have engaged in further spectroscopic studies to elucidate the geometric and electronic structures of A and B. Unfortunately, efforts to crystallize these intermediates has led to microcrystalline needles not suitable for X-ray crystallography.

III. Mössbauer Studies of O₂ Intermediates

The first step in preparing MB (Mössbauer) samples of this complex involves making the $^{57}\text{FeCl}_2$ precursor. A pure sample of 99.5% enriched $^{57}\text{Fe}$ shipped under argon was purchased from Isoflex USA. The FeCl₂ complex was made by following a procedure reported by Abrecht using iron strips. The isotopically labeled $^{57}\text{FeCl}_2$ precursor was made at 23% and 50% enrichment. The 23% enriched sample of $^{57}\text{FeCl}_2$ was prepared using a Schlenk line by dissolving 83 mg (1.5 mmol) of $^{57}\text{Fe}$ and 282 mg (5 mmol) of Fe (naturally abundant) in a 1.7 M solution of HCl in CH₃OH. The 50% enriched $^{57}\text{Fe}$ was made by the same route, using 114 mg Fe and 116 mg of enriched $^{57}\text{Fe}$.
in a 3.0 M solution of HCl in CH$_3$OH. The two solutions were refluxed for 1-2 days under argon producing light yellow solutions. The solvent was under vacuum for several hours at 40°C. Both enrichments resulted in 80% yield of product as an off-white solid.

Inside the glovebox, one equivalent of APH$^{tBu2}$ and four equivalents of NaOMe were combined in THF (3 mL) and stirred for 15 minutes. The solvent was removed, and the remaining residue was taken up in acetonitrile. This solution was mixed with one equivalent of $^{57}$FeCl$_2$ and K[Tp$^{Me2}$]. The resulting mixture was stirred for over 12 hours, followed by removal of the solvent by vacuum. The solid was taken up in CH$_2$Cl$_2$ and filtered through Celite. Removing the solvent, the product was re-dissolved in CH$_3$CN, filtered, and stored inside a -30°C freezer for several days, yielding dark purple crystals. The resulting $^1$H- NMR spectrum revealed paramagnetically-shifted peaks consistent with the previously characterized complex.

Six samples with $^{57}$Fe concentrations between 1-3 mM in THF were prepared for analysis using Mössbauer spectroscopy in the lab of our collaborator, Dr. Codrina Popescu at the University of St. Thomas in St. Paul, Minnesota. These samples were produced using both the 23% and 50% enriched versions $^{11}$ in THF. For example, a MB sample of the starting complex (enriched by 23%), was made by dissolving 28 mg (0.05 mmol) of complex in 10 mL THF inside the glovebox. This sample was sealed in a vial and brought outside of the glovebox. After freezing the entire vial, the sample container was removed and stored in liquid N$_2$. Species A was generated by freezing the sample container with the starting complex, thawing to -80°C, briefly exposing to the atmosphere, and freezing again after a few minutes. Species B was generated in the same manner, except the exposure to atmosphere is extended for 8 min at -80°C. This
procedure was repeated for the 50% enriched samples and then shipped to our collaborator under cryogenic storage. The samples were probed at 100 K, where THF remains frozen. The MB spectrum of the starting species reported in Figure 4.06 reveals a quadrupole doublet typical of a high-spin ferrous species. The MB spectrum of the sample exposed to O2 for 8 min (species B) is presented in Figure 4.06.

![Mössbauer Spectrum](image)

**Figure 4.06** Top: Mössbauer spectrum of $^{57}$Fe-enriched-11 in THF (collected at 100 K). Bottom: MB spectrum after 8 minutes of treatment with O2. Data collected by Dr. Codrina Popescu at the University of St. Thomas, St. Paul, MN.

The data suggest that the sample that was exposed for 5-8 min to oxygen contains both a doublet and an enveloped species with an isomer shift of 0.3-0.5 mm s$^{-1}$. It is possible that the combination of different spectral features arises from both B and unconverted A. Samples were frozen quickly after exposure to O2 revealing a second integer-spin species that likely corresponds to A. The Mössbauer results are consistent
with a ferrous center bound to a ligand radical, forming a putative iron(II) iminosemiquinonate species. To verify the identity of species A we measured EPR spectra (at 77 K) with the $^{57}$Fe-labeled sample of complex 11. After exposure to $O_2$ at low temperature (-80°C), species A was generated, and the sample was frozen for analysis by X-band EPR. The spectrum of this sample was collected at 77 K (Figure 4.07). This procedure was repeated at -80°C with anaerobic addition of TTBP radical, from which the overlayed spectrum was collected. Based on the similarities between these two spectra it is reasonable to assume that species A is an iron(II) iminosemiquinonate species.

**Figure 4.07** X-band EPR spectrum (measured at 77 K) of $^{57}$Fe-labeled complex (1.3 mM), 11 after O$_2$-reaction (black). Experimental parameters: frequency = 9.615 GHz, power = 2.0 mW, modulation amplitude = 8 G. EPR spectrum (measured at 77 K, red) of $^{57}$Fe-labeled complex 11 after reaction with TTBP radical (1.1 mM, one equivalent). Collected with experimental parameters: frequency = 9.616 GHz, power = 2.0 mW, modulation amplitude = 8 G. The asterisk (*) at $g = 4.3$ marks an iron impurity.
IV. Diiron Picolinate Complex Formed After Dioxygenation Reaction

In attempts to generate the oxidized derivative of \(11\), crystals of an unusual diiron complex formed \((11^{\text{Ox}})\). This species appears paramagnetic by \(^1\text{H}-\text{NMR}\) (Figure 4.09), with the Evans method yielding a magnetic moment \(\mu_{\text{eff}} = 4.49\ \mu_\text{B}\) (close to the value expected of high-spin ferrous iron). The X-ray crystal structure (Figure 4.08) of this species reveals that the iron centers are bridged by the carboxylate motifs of the picolinate ligands. The Fe–N\(_\text{Tp}\) bond distances (Table 4.A) are not symmetrical with Fe1–N\(_\text{avg.}\) = 2.16 Å and Fe2–N\(_\text{avg.}\) = 2.14 Å. Most likely, these carboxylate moieties are delocalized, however the difference in bond distances is clear at 100 K (C=O, 1.24 Å; C–O, 1.27 Å). Thus, as depicted in Table 4.A, the three carboxylate oxygens are bound to Fe2 which contains the shorter Fe–N\(_\text{Tp}\) bond distances and shorter Fe–O bonds, consistent with a ferric center.

**Table 4.A** Bonding scheme and reported bond distances for \(11^{\text{Ox}}\).

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Figure 4.08 X-ray crystal structure (collected at 100 K) of $11^{Ox}$. Hydrogen atoms and Tp-methyl groups were omitted for clarity.

Figure 4.09 $^1$H-NMR spectrum of Fe-dimer, $11^{Ox}$ in CDCl$_3$ collected at room temperature.

The proton NMR spectrum (vide supra) of $11^{Ox}$ resembles the spectrum of $[\text{Fe}^{2+}(\text{TpMe}_2)_2]$ complex produced as a byproduct in the synthesis of the precursor, $[\text{Fe}^{2+}(\text{TpMe}_2)(\text{APH}^{t\text{Bu}_2})]$. Perhaps in the NMR timescale, the relaxation of Fe nuclei or solvent exchange permits the pseudo-symmetric molecule to appear with similar resonances. In any case, there are sizable signals from the picolinate ligand which
account for a large signal in the diamagnetic region, where the Tp resonances collapse to similar resonances to those found in the \([\text{Fe}^{2+}(\text{Tp}^{\text{Me2}})_2]\) complex.

The conversion of 11 to \(11^{\text{Ox}}\) was observed by UV-vis at room temperature (Figure 4.10) over a period of one hour. The initially colorless complex converts into an orange chromophore with an intense feature at 365 nm.

![Figure 4.10 Room temperature UV-vis spectrum of initial ferrous complex 11 (0.4 mM, red solid line). After treatment with oxygen for one hour, the resulting spectrum of 11^{Ox} (black dashed line) in CH\(_2\)Cl\(_2\) is shown.](image)

**V. Conclusion**

Through this study we have illustrated the capabilities of iron with the Tp\(^{\text{Me2}}\) framework. It has been established that 11 is a functional model of the aminophenol dioxygenase activity of ring-cleavage. We derived the picolinic acid product through acidic work-up of oxygenated sample of 11 and also observe the incorporation of picolinates in the diiron complex 11\(^{\text{Ox}}\). Together these provide evidence that ring-cleavage occurs in an extradiol manner, similar to the native type of enzyme APDO. Further studies of the low-temperature intermediates found in this process indicate that there are two species (A and B) derived from reaction with O\(_2\). Based on our current data,
the preliminary MB studies suggest that species A is possibly an iron(II) iminosemiquinone adduct much like related complex generated previously with the Tp\textsubscript{Ph2} ligand. Species B appears subsequently at low temperatures, indicating that it is the next stage of oxygen activation in our system. Our MB data suggests that this species possesses an iron(III) center and a lactone ligand in the coordination sphere. We posit that this species undergoes ligand hydrolysis to form the picolinate rings found in \textit{11}\textsuperscript{Ox}.

VI. Experimental Section

General Methods

Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used as received without further purification. Acetonitrile (CH\textsubscript{3}CN), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}), THF, and MeTHF were degassed through several freeze-pump-thaw cycles and stored over molecular sieves. The synthesis and handling of iron complexes were carried out under an inert atmosphere using a Vacuum Atmospheres Omni-Lab glovebox equipped with a freezer set to -30°C. The APH\textsuperscript{tBu2} ligand was synthesized according to the previously reported method.\textsuperscript{19} The K[Tp\textsuperscript{Mc2}] ligand was purchased from TCI America. Iron-57 was purchased from IsoFlex USA.

Physical Characterization

Elemental analyses were performed at Midwest Microlab, LLC in Indianapolis, IN. UV-vis absorption spectra were collected with an Agilent 8453 diode array spectrometer equipped with a Unisoku Scientific Instruments (Osaka, Japan) cryostat for low temperature measurements. \textsuperscript{1}H-NMR spectra were measured on a Varian 400 MHz spectrometer featuring variable-temperature capabilities. This instrument was also used for magnetic susceptibility measurements carried out using the Evans NMR method. EPR
spectra were measured using a Bruker EMX instrument equipped with an ER4112 SHQ resonator, collected at 77 K in a cold finger quartz dewar.

**Synthesis of [Fe(TpMe2)(APHtBu2)] (11)**

Inside the glovebox, APHtBu2 was added to a vial with THF. Addition of 4-5 equivalents of NaOMe (Sodium methoxide) yields a dark purple solution which was stirred for 30 min. The solvent was removed *in vacuo* and the residue was redissolved in CH3CN (4 mL). Addition of FeCl2 yields a dark red solution to which up to 0.9 equivalents of K[TpMe2] was added in small portions (10-15 mg) over 3-4 hours. The reaction mixture was stirred for 12 hours and dried by vacuum. The crude material was re-dissolved in CH3CN and filtered through Celite before drying by vacuum. The purple solid was then cooled to -30°C and washed with cooled *n*-heptane several times. Anal. Calcd (%) for C29H44BFeN7O (M_W = 573.37 g mol$^{-1}$): C, 60.74; H, 7.73; N, 17.10. Found C, 60.43; H, 7.62; N, 16.77. UV-vis [$\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$) in CH2Cl2]: 285 (4890), 370 (305), 550 (150).

**Synthesis of [Fe2(TpMe2)$_2$(μ-picolinate)$_3$] (11Ox) picolinate = 4,6-di-tert-butylpicolinate)**

In a small vial, 145 mg (0.25 mmol) of 11 was dissolved in approximately 8 mL of dry CH3CN. The solution was bubbled with oxygen until an orange color emerged. After stirring for one hour, the solution was uncapped inside the freezer and set for slow evaporation. Dark orange prisms emerged several days later once 30-40% of solvent evaporated. The solution was removed by decanting excess solvent and further drying. The resulting yellow-orange powder) was sent for elemental analysis. Yield = 122 mg (68%). Anal. Calcd (%) for C72H104B2Fe2N15O6 (M_W = 1409.0 g mol$^{-1}$): C, 61.38; H, 7.44; N, 14.91. Found C, 60.84; H, 4.26; N, 14.90. UV-vis [$\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$) in
CH$_3$CN]: 280 (4800), 365 (2700), 480 (750). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 49.4$ (6H, s, 4-H-pz), 41.1 (18H, s, Tp-Me-CH$_3$), 13.1 (18H, s, Tp-Me-CH$_3$), 8.1 (3H, s, 3-picolinate), 7.6 (3H, s, 5-picolinate), 3.75 (2H, s, BH), 1.8-0.9 (54H, s, -C(CH$_3$)$_3$). $\mu_{\text{eff}} = 4.49$ $\mu_B$ (Evans method).

**Mössbauer Spectroscopy**

Mössbauer spectra were recorded on a closed-cycle refrigerator spectrometer, model CCR4K, equipped with a 0.04 T permanent magnet, cooled between 5 and 300 K. Mössbauer spectra were analyzed using the software WMOSS (Thomas Kent, SEECo.us, Edina, Minnesota). The samples were prepared as solutions inside 1.00 mL Delrin cups, and then frozen in liquid nitrogen.
Table 4.B Summary of X-ray crystallographic data collection and structure refinement.

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VII. BIBLIOGRAPHY


Chapter 5
Iron and Cobalt Model Compounds of Hydroquinonate Dioxygenases

Abstract
The metabolism of aromatic compounds by various bacterial sources is of interest in the field of bioremediation and bioinorganic chemistry. While this process is not fully understood, the active-site structures of metalloenzymes involved in this process exhibit similar structures. The ability of the TpMe2 supporting ligand to successfully replicate the function of enzymes in the dioxygenase superfamily makes it an ideal candidate to explore different substrates with different electron donor and acceptor properties. This report discusses using the TpMe2 framework with both cobalt(II) and iron(II) model compounds featuring p-hydroquinone ligands. By utilizing the cobalt model to help isolate Co/O2 adducts involved in the initial stages of oxygen activation, we can provide a synthetic precedent for the process in vivo. Additionally, the information regarding the products derived from the oxygenation of p-hydroquinonates is obtained from the corresponding iron(II) models.
I. Introduction

Studies in the past have isolated enzymes from soil bacteria that metabolize aromatic compounds.\textsuperscript{1,2} The inherent stability of aromatic rings presents a challenge to bacteria that seek to breakdown these compounds into smaller intermediates that can feed into the Krebs cycle.\textsuperscript{3,4} The catabolism of aromatic compounds allows microbial organisms to use what we consider pollutants as sources of carbon and energy. These enzymes show remarkable activity in the dioxygenation of aromatic species into useful anabolic derivatives. The selectivity of these enzymes extends from single to multi-ring aromatic compounds making them fit for bioremediation technologies adopted from bacteria.\textsuperscript{5} One strategy evolved by Nature employs mononuclear non-heme dioxygenases (MNIDs) that insert O\textsubscript{2} into an aromatic carbon-carbon bond to yield a ring-opened product amenable to more degradation.\textsuperscript{6-8} These ring-cleaving MNIDs have been shown to oxidize a wide variety of substituted aromatics such as catechols, aminophenols, 1,4-hydroquinones, and salicylates (Scheme 5.A).\textsuperscript{8} Thus, the pursuit of understanding bacterial degradation of \(p\)-hydroquinone compounds has become an enduring interest in biochemistry and bioinorganic chemistry. Several biochemical pathways also require MNIDs capable of catalyzing \textit{aliphatic} C–C bond cleavage.\textsuperscript{9,10} A prime example is the biodegradation of bisphenol A (BPA) – a known endocrine disruptor used in the manufacturing of plastics.\textsuperscript{11} The bacterial assimilation of BPA\textsuperscript{12} generates small amounts of dihydroxyacetophenone (DHAP), which is then converted to 4-hydroxybenzoate and formate (Scheme 5.A) by the enzyme DHAP dioxygenase (DAD) found in certain bacterial strains.\textsuperscript{13,14} Structural studies have confirmed that DAD features a mononuclear nonheme iron site.\textsuperscript{15} With these clear structural patterns, and divergent pathways for C–C
bond cleavage, it is imperative to understand the $O_2$ activation process found in these enzymes to help elucidate their mechanisms.

Scheme 5.A Aromatic and aliphatic bond cleavage catalyzed by MNIDs.\textsuperscript{19-25}

With the exception of intradiol catechol dioxygenases, the active sites of most MNIDs consist of a high-spin iron(II) center bound facially to three protein residues, in addition to two or three $H_2O$ molecules in the resting state.\textsuperscript{16-18} Two of the ligands are histidines, while the third is either an Asp/Glu carboxylate or another His imidazole. These structural motifs are referred to as the 2-His-1-Carboxylate (2H1C) and 3-His facial triads, respectively (Scheme 5.B).\textsuperscript{19-21} Extradiol CatDs and most hydroquinone dioxygenases (HQDOs) feature the 2H1C triad,\textsuperscript{22,23} while those belonging to the cupin superfamily – DAD, certain HQDOs, and salicylate dioxygenase (SDO) contain the 3-His triad.\textsuperscript{15,24,25}

The Fiedler group has made significant progress with biomimetic studies of the potential mechanism of action in HQDOs such as GDO (gentisate dioxygenase), HGO (homogentisate dioxygenase) and other related enzymes.\textsuperscript{26,27} In this chapter we will determine the structural and reactive relevance of cobalt and iron Tp complexes with (12-15) with $p$-hydroquinone ligands.
II. Results and Analysis

A. Synthesis of Cobalt Hydroquinonate Complexes

The procedures for synthesis of \([\text{Co}^{2+}(\text{Tp}^{\text{Ph}2})(2,5-\text{DHAP})]\) (12) and \([\text{Co}^{2+}(\text{Tp}^{\text{Me}2})(2,5-\text{DHAP})]\) (13) follow a similar method to the Co/Tp complexes reported earlier. Initially, the deprotonation of 2,5-dihydroxyacetophenone (2,5-DHAP) occurs rapidly in a methanolic solution with NaOMe. Subsequent addition of the \([\text{Co}^{2+}(\text{Tp}^{\text{Ph}2})(\text{OAc})(\text{Hpz}^{\text{Ph}2})]\) and \([\text{Co}^{2+}(\text{Tp}^{\text{Me}2})(\text{OAc})]\) precursors in reddish-orange crude products of 12 and 13 (Scheme 5.C). These mixtures were stirred before filtering through Celite to afford orange-colored solutions. Dark orange crystals of 12 were formed by layering the concentrated solution in CH$_2$Cl$_2$ with pentane. The recrystallization of 13 occurred after slow evaporation of a concentrated solution with toluene and CH$_3$CN. The solved X-ray structures of both complexes are displayed in Figure 5.01 and Figure 5.02.

B. Characterization of Cobalt Hydroquinonate Complexes

Figure 5.00 $^1$H-NMR spectra of 12 (left) and 13 (right) collected at 400 MHz; measured in CDCl$_3$ at 20°C.
Characterization of these species was completed through H$^1$-NMR (Figure 5.00) which shows paramagnetically shifted peaks for the Tp substituents and the coordinated substrate (2,5-DHAP). The Co-Tp$^{ph2}$ variant of the hydroquinonate compound displays a noticeably complex pattern. The phenyl substituents have different chemical shifts for the $o$-phenyl protons (seen at 14 and 5 ppm) compared to the $m$- and $p$-phenyl peaks (26, 17, 5, and -40 ppm). The hydroquinonate aromatic proton resonances are scattered in the downfield region at 56, 46, and 28 ppm. The acetyl -$CH_3$ protons are shifted upfield to -31.9 ppm.

Complex 13 shows many similarities with the spectrum of [Co$^{2+}$(Tp$^{Me2}$)(OAc)]. Here, the pyrazole proton ($4-H$-pz) peaks appear at 57 ppm; slightly shifted from the 61.5 ppm peak found in the precursor. The borohydride peak is conserved at 52.3 ppm (54.8 ppm found in the precursor). The Tp-methyl peaks appear at 38.8 and -59.5 ppm (18 total protons) which is consistent with the peaks at 35 and -40.8 ppm found in the spectrum of the precursor. The three aromatic proton peaks of the monoanionic DHAP ligand appear at 79, 76, and 71 ppm. The aromatic protons appear far downfield compared to 12, whereas the acetyl peak is positioned at -9.1 ppm. The Evans method was performed on both complexes 12 and 13 resulting in magnetic moments of 4.24 and 4.35 μ$B$, respectively. This value is larger than the expected value for $S = 3/2$ spin ($\mu_{eff} = 3.87 \mu_B$), which has been the trend in the high-spin cobalt(II) complexes reported so far.
Crystals of \textbf{12} and \textbf{13} were examined with Mo (K\(\alpha\)) source with reflections collected at 100 K. The crystals of \textbf{12} (Figure 5.01) were determined to be orthorhombic in the \(P2_12_12_1\) space group whereas \textbf{13} (Figure 5.02) are monoclinic within the \(P2_1/c\) space group. The structural characterization of both complexes shows that a bidentate ligand is coordinated to each cobalt center through the acetyl- and the hydroquinonate
oxygen. The three N$_{TP}$ donor atoms of both complexes are coordinated facially to the cobalt center.

In the structure of 12, the cobalt center is bound to the acetyl group with a bond distance of 2.039 Å. The angle between the cobalt center and acetyl carbon is (C7–O1–Co1) is 130.25°. Adjacent to the Co-acetyl bond is the Co-phenolate moiety with an angle (C2–O2–Co1) of 126.18°. The Co–O2 bond distance of 1.936 Å is shorter than the Co–O1 bond by 0.10 Å. This structure presents a TBP coordination geometry with a small degree of square pyramidal distortion ($\tau = 0.63$) with the axial unit comprised of O1–Co1–N4. The average Co–N$_{TP}$ bond distances in 12 is 2.094 Å, which is consistent with a high-spin Co$^{2+}$ center. The C–C bond lengths within the hydroquinonate ligand show that the aromaticity of the ring is maintained. However, the C3–C4 and C5–C6 bond distances are somewhat contracted (1.372 and 1.377 Å) from the others.

The crystal structure of 13 shows an additional coordination by acetonitrile molecule forming a six-coordinate species. As seen in crystallo, the octahedral geometry of 13 contains a O1–Co–N6 unit which is nearly linear (179.5°C). The average Co–N$_{TP}$ bond distance (2.112 Å) and the cobalt-acetyl and -phenolate bond distances (2.084 and 2.003 Å) are almost identical to those observed in 12. The C–C bond distances of the acetophenone ligand appear be aromatic, with very similar measurements as 12. The crystal packing of this species shows intermolecular hydrogen bonding between the asymmetric units nearby unit cells (Figure 5.03). This occurs between the 5-hydroxy proton and the phenolate oxygen (O2) of the adjacent molecules. The presence of hydrogen bonding is a strong indicator of this model’s resemblance to the native enzyme.

In the proposed catalytic cycle of GDO, a nearby His residue (H292) is believed to form a
hydrogen bond with the para-hydroxy substituent of the substrate. This salient interaction is important in the intradiol cleavage cycle proposed by Titus.\textsuperscript{28}

The structural characterization of \textbf{12} and \textbf{13} are high-spin Co\textsuperscript{2+} complexes with facial arrangement of pyrazole donors from the Tp ligand. Each complex contains an acetophenone bound in a nearly identical configuration with bidentate coordination of acetyl and hydroquinone oxygen atoms. Repeated exposure to oxygen to the solid material of \textbf{12} indicates that it is air-stable, unlike \textbf{13} which turns green in aerobic atmosphere.

\textbf{Figure 5.03} Crystal packing of \textbf{13} found in adjacent asymmetric units shows hydrogen bonding contacts between O2 and O3.
C. Spectroscopic Studies and O₂ Reactivity of Cobalt Hydroquinonates

The UV-vis absorption spectra of both complexes 12 and 13 were collected at room temperature (shown in Figure 5.04), reveal almost identical absorption features in CH₂Cl₂. Characteristic of complexes with a Tp scaffold, intraligand transitions make up most of the near-UV region. The visible area of both compounds exhibits broad low-intensity features between 500-700 nm (ε_{avg} = 400 M⁻¹ cm⁻¹).

![Figure 5.04 UV-vis spectra of 12 (0.9 mM, red dashed line) and 13 (0.7 mM, gold solid line) measured at 20°C in CH₂Cl₂.](image)

The features in the visible region are most likely consequence of d-d transitions with some degree of MLCT by excitation of d electrons into the antibonding orbital of acetyl carbonyl. This was determined by in a study by Baum et al., through TD-DFT of previously characterized [Fe²⁺(Tp^{Ph2})(BIHQ)] complex.²⁶ within a similar coordination environment. In complexes 12 and 13, a high-intensity band at ~400 nm arises from substrate π → π⁺ transitions. As observed in the previous chapters, O₂ reactivity is significantly different between complexes with Tp^{Ph2} and Tp^{Me2} supporting ligands. To examine this more closely, the UV-vis spectra of 12 and 13 (in CH₂Cl₂) were monitored in the presence of dioxygen. Surprisingly the Tp^{Ph2} congener in complex 12, does not
show any reactivity with O\textsubscript{2} in solutions of THF or CH\textsubscript{2}Cl\textsubscript{2}. This may be due to the sterically imposing \textit{Tp}\textsuperscript{Ph\textsubscript{2}} ligand.

To study O\textsubscript{2}-reactivity of \textbf{13} several UV-vis experiments were conducted by exposure of oxygen into the sample cuvette. At -70°C, a solution of \textbf{13} in CH\textsubscript{2}Cl\textsubscript{2} was exposed to O\textsubscript{2} sparging gas through the sample cuvette (Figure 5.05).

![Figure 5.05](image)

**Figure 5.05** Dioxgen reaction with \textbf{13} (gold line) at -70°C in (1.5 mM) CH\textsubscript{2}Cl\textsubscript{2} forms \textbf{13SO} (black line).

The UV-vis spectrum shows the rapid formation of a brown colored species \textbf{13SO} within seconds. The new species has signatures at 580 and 660 nm from ligand-to-metal charge transfer (LMCT) bands. This intermediate also shows new shoulder peaks at 440 nm and 490 nm. Like other superoxide intermediates derived from oxygenation of cobalt dioxolenes (Chapter 3), this species is stable for many hours at -70°C.

Furthermore, sparging Ar through the sample does not produce any changes to the spectrum, indicating that this process is irreversible. When the sample is warmed to -30°C, a new species (\textbf{13Ox}) forms slowly over the course of three hours (Figure 5.06, left). This species is unique in that the visible region contains peaks at 580 and 660 nm containing relatively high intensity compared to the previous intermediate and the starting
complex. Based on previous studies with redox-active ligands, it is feasible to assume that this species corresponds to a ligand radical.

![UV-vis spectrum](image)

**Figure 5.06** Left: UV-vis spectrum of 13 at -30°C in (1.5 mM) CH$_2$Cl$_2$ before (gold line) and after addition of oxygen forming 13$^{Ox}$ (solid blue line). Right: further oxidation at room temperature (solid black line).

When the reaction is attempted at low temperatures (-70°C) with THF or CH$_3$CN solvent, there are no observable changes in the spectrum. The inhibition of the low temperature is due to coordination of the complex by the solvent. This is evidenced by the low temperature crystal structure (100 K), in which CH$_3$CN molecules occupy the axial position – indicating a thermodynamic preference for coordination.

The room temperature reaction of 13 with dioxygen in non-coordinating solvents reproduces the spectrum of 13$^{Ox}$. This short-lived species contains absorption features centered at 635 nm. The peaks associated with this species begin to decay after several hours resulting in the chromophore shown in Figure 5.06. This species contains low-intensity peaks at 565 and 635 nm. In comparison with 13, the O$_2$-treated species shares some resemblance. However, the intense ligand-centric absorption band at 415 nm is not found in this species.
The conversion of $^{13}\text{SO}$ to $^{13}\text{Ox}$ at -70°C occurs slowly over the course of 2-3 hours. In the room temperature reaction, the initial formation of $^{13}\text{Ox}$ occurs much faster (10-15 minutes for complete conversion). At low temperatures (-70°C), $^{13}\text{Ox}$ can also form when treated with one equivalent of TTBP radical in CH$_2$Cl$_2$ (Figure 5.07). This reaction also occurs slowly at lower temperatures with the resulting spectrum observed after three hours.

![Figure 5.07](image)

**Figure 5.07** Conversion of $^{13}$ (gold) to $^{13}\text{Ox}$. Comparison of $^{13}\text{Ox}$ (solid blue line) generated by O$_2$ addition at -30°C (initial [13] = 0.7 mM in CH$_2$Cl$_2$). Formation of $^{13}\text{Ox}$ (dashed blue line) by addition of TTBP’ (one equivalent) in CH$_2$Cl$_2$ (at -70°C).

In this case, $^{13}\text{Ox}$ is formed at a lower temperature, however, unlike previously reported oxidized intermediates (Chapter 3), the introduction of oxygen to this sample does not produce any changes at low temperatures. In the starting complex, the only proton that can be abstracted by TTBP’ is the para-hydroxy proton. This would suggest that the ligand has been oxidized by one electron and one proton. To evaluate this possibility and study the O$_2$-adduct, X-band EPR spectroscopy was used to examine the starting complex (Figure 5.08) and all the low-temperature intermediates (Figure 5.09 and 5.10).
Complex 13 was dissolved in CH$_2$Cl$_2$ and an aliquot was frozen inside an EPR tube anaerobically. The resulting X-band spectrum was taken at 10 K (Figure 5.08). This initial spectrum displays a $S = 3/2$ system with $g$-values = 8.21, 1.97, 1.42. These values are consistent with the previously observed high-spin cobalt(II) complexes (Chapters 2 & 3). Another sample was prepared after exposure of O$_2$ into a solution of 13 at low temperature (-70ºC) until a brown chromophore emerged (13$^{\text{SO}}$). This sample was quickly frozen in liquid nitrogen and an X-band EPR spectrum (Figure 5.09) of the resulting sample was taken at 10 K. The spectrum shows an intense derivative peak at $g = 2.083, 2.023, 1.980$. This signal shows modest anisotropy with an asymmetrical derivative feature. The presence of this signal supports the formation of a $S = 1/2$ species. It is likely that 13$^{\text{SO}}$ is a cobalt(III) superoxide, which contains a low-spin cobalt ion bound to a superoxide radical anion. Unfortunately, a higher resolution of the hyperfine splitting pattern was not obtainable.
Figure 5.09 Low-field region (3000–3800 G) of X-band EPR spectrum of $^{13}\text{SO}$ measured at 10 K in frozen CH$_2$Cl$_2$ (initial [$^{13}\text{S}$] = 1.1 mM). Experiment conducted with parameters: frequency = 9.477 GHz, power = 2.08 mW, modulation amplitude = 10 G.

The remaining sample of $^{13}\text{SO}$ was then heated to -30°C until the UV-vis features were replaced by those of $^{13}\text{Ox}$. A sample of this light-green solution was frozen and the resulting X-band EPR spectrum was measured at 10 K (Figure 5.10). The frozen solution of $^{13}\text{Ox}$ reveals the same derivative feature of $^{13}\text{SO}$ centered at $g = 2.02$. This signal is likely from residual cobalt(III) superoxide which has dramatically decreased in intensity (by tenfold), suggesting that $^{13}\text{Ox}$ is EPR-silent. Based on the current data, it can be concluded from the absence of a new signal that $^{13}\text{Ox}$ is likely a high-spin Co$^{2+}$ center bound to a $p$-semiquinonate radical. This species features antiferromagnetic coupling between the ligand-based radical and an unpaired electron from the metal center. The stability of $^{13}\text{Ox}$ at low temperatures shows that it is stable for several hours. Unfortunately, attempts at crystallizing this species have not been successful thus far.
Figure 5.10 X-band EPR spectrum of $^{13}{\text{Ox}}$ (blue) collected at 10 K in frozen CH$_2$Cl$_2$ (initial $[^{13}\text{I}] = 1.1$ mM). Experimental parameters: frequency = 9.475 GHz, power = 2.0 mW, modulation amplitude = 10 G. This spectrum is overlayed with the spectrum of $^{13}\text{SO}$ to show that residual superoxide is present without other signatures.

Product analysis of aerobic oxidation of 13 was performed at room temperature. A sample of 13 was dissolved in THF and also in CH$_2$Cl$_2$. Each was treated with O$_2$ by bubbling through the solution with a needle. The following solutions were stirred for 1-2 hours, and the resulting product was worked up in acidic media. After purification, a $^1$H-NMR spectrum of each product was recorded in CDCl$_3$ (Figure 5.11). Product analysis of the O$_2$ reaction with 13 in THF reveals primarily 2-hydroxyacetophenone ligand. The product from the dioxygen reaction in CH$_2$Cl$_2$ reveals some free ligand peaks and also another species with peaks at 7.91, 7.52-7.39, 7.33, and 2.53 ppm. The integration of these new product features with those of the starting ligand yield a ratio of 3:1.
It is unclear exactly what the new species is, but it does not correspond to expected proton NMR resonances for 1,4-acetylbenzoquinone. It is apparent that the new features are not the starting ligand (2,5-DHAP) and the new peak at 2.53 ppm suggests that the acetyl moiety is conserved in this product. In addition, the downfield shifted aromatic peaks suggest that there are conjugated bonds with protons experiencing electron-withdrawing effects by nearby carbonyl moieties. With these factors in mind, the possible intradiol ring-cleavage may yield one of the products shown in Scheme 5.D.
Scheme 5.D Cyclization of intradiol ring-cleaved product forming seven-membered lactone derivative.

Figure 5.12 $^1$H-NMR spectrum (collected in CDCl$_3$ at room temperature) of product after reaction low temperature reaction of 13 with O$_2$ in CH$_2$Cl$_2$ (stirred at -80°C). Asterisk (*) marks the solvent peak from residual CH$_2$Cl$_2$.

The presence of mostly starting ligand after product work-up (in both conditions) opens the possibility of successive oxygenation in the presence of acidic conditions. Biomimetic studies by led by Gebbink$^{29}$ and Brunold$^{30}$ have shown potential for multiple types of ring-cleavage by a single model complex. Therefore, it is imperative to find out which conditions lead to the dissociation of initial ligand, and which potentially lead to ring-cleavage of hydroquinonate.
According to the spectroscopic insight gained from the intermediates of the O\textsubscript{2} reactivity of 13 proceeds as shown in Scheme 5.E. After the formation of the Co(III) superoxo intermediate, conversion to 13\textsuperscript{Ox} occurs at temperatures greater than -50°C. This mirrors the decomposition of 6\textsuperscript{SO} and 8\textsuperscript{SO} into oxidized derivatives 6\textsuperscript{Ox} and 8\textsuperscript{Ox} (Chapter 3). The generation of 13\textsuperscript{Ox} by treatment of the precursor with TTBP’ suggests H-atom abstraction is occurring on the hydroquinonate moiety. Most likely, this species contains cobalt(II) bound to a \(p\)-semiquinonate species, which results from the net loss of a proton and electron from the ligand. At room temperature and this species proceeds to undergo oxidation, converting into the terminal oxidized product.

\[
\begin{array}{c}
[\text{Co}^{2+}(\text{Tp}^{\text{Me}_{2}})\text{DHAP}] \xrightarrow{\text{O}_2} 13\text{SO} \xrightarrow{-70^\circ\text{C}} 13\text{Ox} \xrightarrow{-30^\circ\text{C}} \text{terminal oxidized product} \xrightarrow{20^\circ\text{C}}
\end{array}
\]

**Scheme 5.E** Dioxygen reactivity of cobalt hydroquinonate complex, 13.

**III. Model Studies with Iron Hydroquinonate Complexes**

Currently, our understanding of the HQDO mechanism using cobalt hydroquinonate model complexes is missing details with regards to activation of O\textsubscript{2}. It is decidedly known binding of Co/O\textsubscript{2} adducts is supported with the Tp\textsuperscript{Me}_{2} framework as evidenced by formation of 13\textsuperscript{SO}. However, the subsequent steps in the activation of the substrate 2,5-dihydroxyacetophenone, remain undefined. The use of the iron-Tp\textsuperscript{Me}_{2} framework and with the same hydroquinonate ligands was then pursued to elucidate how the ring cleavage of DAD (dihydroxyacetophenone), GDO, other related HQDO enzymes proceed. In previous attempts from our group, we have successfully synthesized and characterized through X-ray crystallography, an iron(II) complex with Tp\textsuperscript{Me} scaffolding
ligand and 2-HAP ([Fe$^{2+}$(TpMe$_2$)(2-HAP)], 14). The substrate in this complex is 2-hydroxy substituted variant of the acetophenone ligand in 13. This complex displayed reactivity with dioxygen despite not having a labile protonated moiety. In more recent efforts, we have managed to synthesize an analogue of complex 13 with a ferrous center ([Fe$^{2+}$(TpMe$_2$)(2,5-DHAP)], 15) containing both the 2,5-dihydroxyacetophenone substrate and TpMe$_2$ supporting ligand.

A. Synthesis of Iron Hydroquinonate Complexes

Scheme 5.F depicts the ideal synthetic route for complexes 14 and 15. In addition to this method, FeCl$_2$ can also be used as a precursor, but this approach suffers from byproducts such as the octahedral species [Fe$^{2+}$(TpMe$_2$)$_2$]. The use of ferrous precursor [Fe$^{2+}$(TpMe$_2$)(OAc)], avoids the formation of unwanted byproducts. The acetate precursor is air sensitive, and the corresponding synthesis reported by Hikichi uses a Schlenk line. In this procedure, the reaction flask was charged with a mixture of [Fe$^{2+}$(TpMe$_2$)(OAc)] precursor in CH$_3$OH and cooled to -80°C. This was followed by dropwise addition of K[TpMe$_2$] in THF. The resulting product was filtered through Celite and re-dissolved in CH$_3$CN before recrystallizing at -10°C. The purification of both complexes was completed after vacuuming the solvent mixture and re-dissolving in Et$_2$O, the resulting solution was then filtered through a syringe filter with Celite and evaporated. The resulting amorphous powder was re-dissolved in CH$_3$CN before storage inside the glovebox freezer (-30°C) for several days. Orange crystals of 15 suitable for X-ray diffraction of were obtained after several days (Figure 5.13). The $^1$H-NMR spectrum of 15 was measured in CDCl$_3$ from the recrystallized product (Figure 5.14). The Evans
method was performed with a sample of 15 revealing a high-spin ferrous system with a magnetic moment \( \mu_{\text{eff}} = 5.27 \ \mu_B \).

Scheme 5.F Synthetic route for iron complexes 14 and 15.

**B. Characterization and \( \text{O}_2 \) Reactivity of Iron Hydroquinonate Complexes**

**Figure 5.13** Thermal ellipsoid plot (50% probability) of 15 (Tp-methyl hydrogens omitted for clarity, O3 has been assigned as the acetyl oxygen).
UV-vis spectroscopy was used to study intermediates of the O$_2$-reaction with 15 under various conditions. In particular, the O$_2$ reactivity of 15 at low temperatures (-70°C) was examined to see if it can facilitate the one-electron oxidation of iron and form the corresponding ferric-superoxo species. In CH$_2$Cl$_2$, 15 shows spectral changes (Figure 5.15) when introduced to dioxygen at low temperatures. The resulting species has a broad, high-intensity feature at 725 nm, in contrast with the starting spectrum where low intensity d-d transitions are observed at 500-700 nm.

Figure 5.15 UV-vis monitored dioxygen reaction of complex 15 (gold line) at -70°C in (0.6 mM) CH$_2$Cl$_2$ to form oxidized species 15$^{0x}$ (green).
In this reaction, a new intermediate form after five minutes. This species is indefinitely stable, however, when the reaction is warmed to -30°C it begins to decay slowly. A new species forms in its wake, with a large absorption profile centered around 740 nm. Warming a sample of this species to room temperature over the course of several hours leads to 15'^Ox'.

**Figure 5.16** Left: UV-vis monitored dioxygen reaction of 15'^Ox' (green line) at -70°C in (initial [15] = 0.6 mM) CH2Cl2. Formation of intermediate 15'^B' (blue dashed line) after twelve hours at -30°C. Bottom: decay of product at room temperature (black dashed line).

The product analysis was conducted through acidic work-up (via addition of concentrated HCl) to a concentrated solution of 15 after treatment with O2 at low temperatures (-80°C) for 8 hours. The product was then neutralized with sodium bicarbonate before extraction with diethyl ether. The resulting 1^H-NMR spectra reveal a mix of products with virtually no starting ligand (Figure 5.17).
IV. Conclusion

Overall, we have assessed the utility of TpMe₂ framework with the use of p-hydroquinonates featuring iron and cobalt centers. Through their O₂-reactivity, complexes 13 and 15 exhibit possibly replicate key enzymatic features. This framework may serve as a model for HQDOs, from which we can derive useful information that has yet to be observed in vivo. The cobalt complex 12 is kinetically inert towards oxygen activation, however the less sterically-hindered 13 undergoes formation of a cobalt(III) superoxide at low temperatures. This species converts to the H-atom abstracted intermediate in 13Ox, with ligand-radical character. The iron analogue in 15 undergoes oxidation with spectroscopically accessible UV-vis features of two intermediates observed at low temperatures. Through the stability of these intermediates at cryogenic temperatures, we can establish conversion between one species to another by monitoring
spectroscopic signatures such as $\nu$(O–O) stretching frequencies from Raman spectroscopy, or chemical and isomer shifts from Mössbauer spectra. Both 13 and 15 show promising reactivities when oxygenation is carried out at low temperatures, however, further studies are necessary to determine the products of the O$_2$ reaction and the intermediates derived from these mechanisms. Furthermore, ligand modifications on the p-hydroquinone ligand could unveil important structural correlations to reactivity.

V. Experimental Section

General Methods

Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used as received without further purification. Acetonitrile, dichloromethane, hexanes, and THF were degassed through several freeze-pump-thaw cycles and stored over molecular sieves. The synthesis and handling of the iron and cobalt complexes was carried out under an inert atmosphere using a Vacuum Atmospheres Omni-Lab glovebox equipped with a freezer set to -30°C. The 2,5-DHAP and 2-HAP ligand were purchased from Alfa Aesar. The K[Tp$^{Me2}$] ligand was purchased from TCI America and the K[Tp$^{Ph2}$] ligand was synthesized according to a previously published method. 32

Physical Characterization

Elemental analyses were performed at Midwest Microlab, LLC in Indianapolis, IN. UV-vis absorption spectra were collected with an Agilent 8453 diode array spectrometer equipped with a Unisoku Scientific Instruments (Osaka, Japan) cryostat for low temperature measurements. $^1$H-NMR spectra were measured on a Varian 400 MHz spectrometer featuring variable-temperature capabilities. This instrument was also used
for magnetic susceptibility measurements carried out using the Evans NMR method. EPR data was measured using a Bruker EMX instrument equipped with an ER4112 SHQ resonator, collected at liquid He temperatures (5-10 K) using a ColdEdge/Bruker RDK-408 Stinger recirculating cryocooler.

**Synthesis of** $[\text{Co}^{2+}(\text{Tp}^{\text{Ph2}})(2,5-\text{DHAP})]$ (12) **DHAP = dihydroxyacetophenone**

Starting with DHAP ligand (23.8 mg, 0.16 mmol), the first step was carried out in 5 mL CH$_3$CN with one equivalent of NaOMe (8.45 mg, 0.16 mmol). The mixture was dried under vacuum after stirring for 15 minutes. Solid powder (166 mg, 0.16 mmol) of $[\text{Co}^{2+}(\text{Tp}^{\text{Ph2}})(\text{OAc})(\text{Hpz}^{\text{Ph2}})]$ was dissolved in 5 mL CH$_2$Cl$_2$ and added to the previous mixture. This reddish-orange solution was stirred over 24 hours and filtered through syringe filter. The solution was then vacuumed to dryness and the resulting solid was dissolved in CH$_2$Cl$_2$ before layering with pentane. Red-orange crystals appeared after a few days and were analyzed by X-ray crystallography before air-drying. Yield = 85 mg (60%). UV-vis $[\lambda_{\text{max}}, \text{nm} \ (\epsilon, \text{M}^{-1} \text{cm}^{-1})$ in CH$_2$Cl$_2$]: 400 (2700), 525 (310), 565 (195), 650 (30). $^1$H-NMR (400 MHz, CDCl$_3$): δ = 80.0 (1H, s, 3-DHAP), 74.1 (1H, s, BH), 56.3 (1H, s, 4-DHAP), 54.6 (3H, s, 4-H-pz), 46.3 (1H, s), 28.5 (1H, s), 26.2 (6H, s, Tp-Ph-H), 17.1 (6H, s, Tp-Ph-H), 14.1 (3H, s, Tp-Ph-H), 4.9 (6H, s, Tp-Ph-H), -31.9 (3H, s, -CH$_3$), -40.9 (6H, s, Tp-Ph-H) ppm.

**Synthesis of** $[\text{Co}^{2+}(\text{Tp}^{\text{Me2}})(2,5-\text{DHAP})]$ (13)

A mixture of 2,5-DHAP (45 mg, 0.3 mmol), $[\text{Co}^{2+}(\text{Tp}^{\text{Me2}})(\text{OAc})]$ (122 mg, 0.3 mmol), and NaOMe (16 mg, 0.3 mmol) was dissolved in (3:1) CH$_3$CN and CH$_3$OH solution. The resulting mixture was stirred for 12 hours and afterwards the solvent was removed by vacuum. The resulting product was washed with hexanes to remove
unreacted ligand. After drying, the residue was then dissolved in Et₂O and filtered through syringe filter. The dark red solution was dried in vacuo. Toluene was added to dissolve a small portion of the solid, with dropwise addition of CH₃CN to completely dissolve the remaining solid. After slow evaporation of this solution, orange crystals suitable for X-ray crystallography formed. This product was further dried by vacuum to yield an orange powder. Yield = 53 mg (36%). UV-vis $[\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1})$ in CH₂Cl₂]: 415 (6960), 500 (650), 565 (360), 650 (200). $^1$H-NMR (400 MHz, CDCl₃): $\delta =$ 79.0 (1H, s, BH), 76.2 (1H, s, 6-DHAP), 71.2 (1H, s, 3-DHAP), 57.6 (3H, s, 4-H-pz), 52.4 (1H, s, BH), 38.8 (9H, s, Tp-Me-CH₃), -9.1 (3H, s, CH₃), -59.5 (9H, s, Tp-Me-CH₃) ppm.

**Synthesis of [Fe²⁺(TpMe₂)(2,5-DHAP)] (15)**

The 2,5-DHAP ligand (15.6 mg, 0.1 mmol) was dissolved in a 1:1 mixture of CH₃OH and CH₃CN and stirred with NaOMe (6.7 mg, 0.12 mmol) for one hour. The mixture was dried by vacuum and then added to [Fe²⁺(TpMe₂)(OAc)] (41.4 mg, 0.1 mmol) with 2 mL of additional CH₃OH/CH₃CN. The solution was stirred for 12 hours and then dried by vacuum to produce an orange residue. The solid was dissolved in CH₂Cl₂ before filtration through Celite. The dark orange solution was then dried by vacuum and re-dissolved in CH₃CN. Storage of this solution at -30°C yielded red-orange crystals after several days, fit for X-ray crystallography. Yield = 28 mg (54%). UV-vis $[\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1})$ in CH₂Cl₂]: 405 (4670), 500 (800), 560 (880). (400 MHz, CDCl₃): $\delta =$ 60.43 (1H, s, BH), 59.2 (3H, s, 4-H-pz), 32.9 (1H, s, 6-DHAP), 27.1 (9H, s, Tp-Me-CH₃), 13.1 (1H, s, 3-DHAP), -27.6 (9H, s, Tp-Me-CH₃), -47.2 (3H, s, -CH₃) ppm.
Table 5.A Summary of X-ray crystallographic data collection and structure refinement.

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<td>1.063</td>
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VI. BIBLIOGRAPHY


Abstract

The existence of magnetic properties such as hysteresis and single-molecule magnetism in transition metal complexes depends upon a thermal barrier to magnetic relaxation. The magnitude of this barrier depends on two factors: the overall spin ($S$) and the magnetic anisotropy (represented by the zero-field splitting parameter, $D$). One strategy for generating complexes with large overall spin-states requires the ferromagnetic coupling of paramagnetic centers. Continuing previous work from the Fiedler lab, the present chapter details the synthesis and structural characterization of a series of dinuclear M(II) complexes ($M = \text{Mn, Fe, Co}$) that feature bridging $p$-hydroquinonate ligands. The M(II) ions are capped by the hydrotris(3,5-diphenylpyrazolyl)borate ($\text{Tp}^\text{Ph}_2$) supporting ligand. One-electron oxidation of these complexes is ligand-based, results in formation of bridging $p$-semiquinonate group between the divalent metal ions. The unique properties of these complexes have been investigated with spectroscopic methods and magnetometry. These results found that the M(II) ions are uncoupled in the $\mu$-hydroquinonate complexes. However, in the $\mu$-semiquinonate complexes, the spins of the metal ions are aligned due to the mediation of the bridging radical ligand, resulting in large overall spins of $S = 9/2$ (Mn), 7/2 (Fe), and 5/2 (Co). These results suggest that the use of bridging dioxolene-type ligands gives rise to multi-metallic complexes with unique magnetic properties.
I. Introduction

Numerous studies of synthetic complexes and metalloenzyme active sites have highlighted the ability of certain ligands to behave in a “non-innocent” (i.e., redox-active) manner, thereby resulting in ligand radical formation. When attached to a paramagnetic transition metal center, the presence of ligand-based radicals has a dramatic impact on the magnetic properties of the molecules or materials. A well-known example is the valence tautomerism exhibited by cobalt complexes bound to dioxolene-based ligands. These complexes display a reversible and temperature-dependent conversion between low-spin Co(III)-catecholate and high-spin Co(II)-semiquinonate configurations. The “switchable” nature of these complexes has potential application in the areas of molecular electronics and spintronics. Recent years have also seen a dramatic increase in reports of single-molecule magnets (SMMs) that feature one or more radical ligands. This strategy often employs radicals as bridging ligands between paramagnetic centers to create multi-metallic complexes with large $S$-values. Strong exchange coupling ($J$) between the metal and ligand radical has been shown to facilitate slow magnetic relaxation by discouraging quantum tunneling and increasing the energy gap between the ground and excited states.

Multi-metallic complexes have been recognized as ideal candidates for use as SMMs. The exchange coupling mechanism has been instrumental in the development of SMMs with slow magnetic relaxation. For instance, the ferromagnetic interaction between two metal centers allows for a greater barrier of magnetic relaxation ($U = S^2|D|$) due their combined spin, $S$. Typical dinuclear systems employ bridging ligands with simple motifs like $\mu$-oxo or $\mu$-cyano units, which provide short interatomic distances, and therefore strong coupling regimes between the metal centers.
Recent advances have shown that strong ferromagnetic exchange can be induced in the bridged quinoidal complex, \([\text{Fe}_2(\text{Me}_3\text{TPyA})_2(\text{L})](\text{BAr}_4^\text{F})_2\) where \(\text{L} = 2,5-\text{di}(2,6-\text{dimethylanilino})-3,6-\text{dibromo}-1,4-\text{benzoquinone}\).\(^{11}\) This complex (Figure 6.00) exhibits ferromagnetic coupling via the superexchange mechanism resulting in an \(S = 4\) spin state. Interestingly, this species can be oxidized by one electron to generate a mixed-valent Fe(II)-Fe(III) system with sizable exchange coupling \((J = 8.9 \text{ cm}^{-1})\) via the double-exchange pathway. This leads to a higher total spin, with a high blocking temperature for SMM behavior. Its extended \(\pi\)-network permits the diamagnetic quinoidal ligand to exhibit ferromagnetic exchange by an electron-hopping mechanism at a large distance of 8.029 Å between the two iron centers.\(^{11}\)

![Figure 6.00 Magnetic susceptibility plots featuring exchange-coupling from \([\text{Fe}_2(\text{Me}_3\text{PyA})_2(\text{L})](\text{BAr}_4^\text{F})_2\) and oxidized derivative.\(^{11}\)](image)

Using the same tripodal framework, Harris and coworkers have explored the use of redox-active tetraoxolenes such as benzoquinoids as bridging ligands.\(^{12}\) Bridging quinoidal ligands have been shown to mediate exchange coupling between two metal centers.\(^{13-15}\) This is especially true in the oxidized semiquinonate form which exhibits antiferromagnetic exchange with the combined spin of both metal centers. The use of a
radical bridging ligands allows for direct overlap between magnetic orbitals of dinuclear metals and the $S = 1/2$ ligand. The strength of this interaction is noticeably larger than that found in superexchange coupling pathways and allows for the generation of large overall spin states. Therefore, the pursuit of radical bridged systems or redox-active dinuclear complexes is a key endeavor in the pursuit of single molecular magnets with unique magnetic properties.

II. Summary of Previous Work

Our previous efforts in generating iron hydroquinonate models lead to the formation of a dinuclear iron complex $[(\text{Fe}^{2+})_2(\text{Tp}^{\text{Ph}2})_2(\mu-\text{DMHQ})]$ (16) which is bridged by the 2,5-dimethoxy-1,4-hydroquinonate ligand (DMHQ). This complex contains two iron(II) centers facially capped by $\text{Tp}^{\text{Ph}2}$ ligands with a dianionic $\mu$-hydroquinonate bridge. This bimetallic species is largely centrosymmetric, and the high-spin iron(II) centers ($S = 2$) are uncoupled. The ability for this complex to undergo oxidation of the hydroquinonate moiety was investigated earlier by our group. The reaction with silver(I) salt, AgPF$_6$, resulted in one-electron oxidation to give a new species, which was characterized by X-ray crystallography. The structure revealed that the DMHQ ligand was oxidized instead of the iron center(s) thereby forming a semiquinonate (DMSQ) as the bridging ligand. This generates a half-integer spin state with a much larger ground-state spin due to exchange coupling between the ligand and Fe(II) sites. The oxidized species 16$^{\text{Ox}}$ exhibits antiferromagnetic exchange with the bridging ligand, resulting in an overall $S = 7/2$ state (Scheme 6.A).
Scheme 6.A Left: magnetic coupling diagram in $[{(Fe^{2+})_2(Tp^{Ph2}_2)_{2}(\mu-DMSQ})]PF_6 (16^{Ox})$. Right: visualization of SOMO orbital from oxidized DMSQ ligand.\textsuperscript{16}

III. Results and Analysis

A. Synthesis of Manganese and Cobalt Bridged Species

In order to expand on the series of bimetallic complexes, we chose other first-row transition metals such as Mn$^{2+}$ and Co$^{2+}$ to construct isoelectronic analogues. The inclusion of these complexes in the series is motivated by our interest in tuning the magnetic interactions between the metal centers. In order to gain information about the degree of exchange coupling and other magnetic properties we aim to use magnetic susceptibility and far-infrared magnetic spectroscopy (FIRMS). In order to accomplish this goal, these species must be prepared with analytical purity, which has proven challenging. The synthesis and characterization of the dimanganese analogue, $[{(Mn^{2+})_2(Tp^{Ph2}_2)_{2}(\mu-DMHQ})] (17)$, was reported earlier by Dr. Amanda Baum.\textsuperscript{17} The oxidation of this species generated the one-electron oxidized DMSQ ligand, although slight overoxidation of the ligand to the benzoquinone form was detected by X-ray crystallography. Each unit cell contained an excess of PF$_6$ counteranion (1.27 equivalents instead of 1.0). In our efforts to isolate this species, we utilized AgPF$_6$ in a 1:1 ratio to successfully generate the corresponding oxidized species $[{(Mn^{2+})_2(Tp^{Ph2}_2)_{2}(\mu-DMSQ})]PF_6 (17^{Ox})$. Crystals of this species were grown using a concentrated solution in 1,2-dichloroethane and hexanes. The crystal structure of this complex is reported in Figure
6.01, which shows two [Mn$^{2+}$(Tp$^{\text{Ph}_2}$)] moieties bridged by the semiquinonate ligand, DMSQ. The cobalt derivative of [(Co$^{2+})_2$(Tp$^{\text{Ph}_2}$)$_2$(µ-DMHQ)] (18) was generated using a cobalt acetate precursor, [Co$^{2+}$(Tp$^{\text{Ph}_2}$)(OAc)(Hpz$^{\text{Ph}_2}$)] with NaOMe and triethylamine as bases (Scheme 6.B). This species was isolated as a brown powder with analytical purity; however, stable crystals were not isolable. We proceeded with the oxidation of 18 with AgPF$_6$. When stirred together with the silver(I) salt in CH$_2$Cl$_2$, a dark green solution of [(Co$^{2+})_2$(Tp$^{\text{Ph}_2}$)$_2$(µ-DMSQ)]PF$_6$ (18$^{\text{Ox}}$) emerged. Crystals of this species were grown using CH$_2$Cl$_2$ and pentane in a solvent-layering experiment (Figure 6.02). Unfortunately, it was difficult to obtain analytically pure material of this oxidized species, as evident by low percentages for F. This result suggests that some of the dicobalt(II) precursor remained.


Scheme 6.D Synthesis of $16^{\text{Ox}}$-$18^{\text{Ox}}$. 
B. Characterization of Cobalt and Manganese Bridged Dimers

Figure 6.01 X-ray crystal structure of $17^{0\times} \cdot PF_6$ collected at 100 K. $3'$Ph groups, Tp-phenyl protons, and solvent molecules have been omitted for clarity.

Figure 6.02 X-ray crystal structure of $18^{0\times} \cdot PF_6$ collected at 100 K. Solvent molecules, $3'$ and $5'$Ph groups, Tp-phenyl protons, and PF$_6$ counterion have been omitted for clarity.
Table 6.A Selected bond lengths (Å) from $16^{\text{Ox}}$-$18^{\text{Ox}}$.

![Diagram of the bridging ligand]

<table>
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<th>$17^{\text{Ox}}$ • PF$_6$</th>
<th>$18^{\text{Ox}}$ • PF$_6$</th>
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X-ray structural parameters were collected for complexes $16^{\text{Ox}}$-$18^{\text{Ox}}$, which each contain a PF$_6$ counteranion in their respective unit cells (Table 6.A). Each complex crystallizes as a triclinic system in the $P$-1 space group. With the exception of $16^{\text{Ox}}$ ($\tau = 0.34$), these complexes have metal centers which lie around the midpoint of TBP and SPY geometries ($17^{\text{Ox}}$ and $18^{\text{Ox}}$; $\tau = 0.55$ and 0.50). The C–C bond distances in the bridging ligand display a quinoidal distribution with C1–C2 bond lengths elongated to 1.44 Å and C2–C3 bond lengths shortened to 1.36 Å. This confirms that the hydroquinonate ligand is now oxidized to its semiquinonate form.
\(^{1}\)H-NMR spectroscopy was employed to study the proton peaks of 16-17 and their oxidized derivatives, however, few peaks were observed for both complexes due to extremely fast relaxation of protons. Fortunately, this method allowed us to characterize 18 and its oxidized derivative 18\(^{\text{Ox}}\) which both exhibit sharply defined peaks. The spectral data (Figure 6.03) shows that both species are paramagnetic with discernable peaks between 130 and -40 ppm. Upon oxidation, there are significant changes to the peaks of the Tp\(^{\text{Ph}2}\) and bridging ligands.

**Figure 6.03** \(^{1}\)H-NMR spectra of 18 (left) and 18\(^{\text{Ox}}\) (right) in CDCl\(_3\). The asterisk (*) marks residual CHCl\(_3\).

**Figure 6.04** UV-vis spectra of 17 (0.6 mM, black line) and 17\(^{\text{Ox}}\) (0.6 mM, red line) measured at room temperature in CH\(_2\)Cl\(_2\) solvent.
Electronic absorption spectra of 16 and $16^{\text{Ox}}$ were reported earlier by Baum et al. in CH$_2$Cl$_2$ solution. The reduced dinuclear species 16 contains weak bands between 400-600 nm. However, upon oxidation by AgPF$_6$, there appear two intense absorption features at 365 and 440 nm ($\varepsilon = 13.0$ and $8.0$ mM$^{-1}$ cm$^{-1}$). A similar change occurs with the dimanganese and dicobalt derivatives, 17 and 18 upon conversion to $17^{\text{Ox}}$ and $18^{\text{Ox}}$ (Figure 6.04 and Figure 6.05). In the spectrum of $17^{\text{Ox}}$ two new features at 410 and 480 nm ($\varepsilon = 1.3$ and $1.6$ mM$^{-1}$ cm$^{-1}$) evolve after oxidation by AgPF$_6$. The spectrum of reduced precursor 18, contains a small band at 580 ($\varepsilon = 0.5$ mM$^{-1}$ cm$^{-1}$) which may correspond to d-d bands with some MLCT character from the bridging ligand. When this dark brown species is treated with AgPF$_6$ two features emerge at 395 and 435 nm ($\varepsilon = 12.0$ and $10.9$ mM$^{-1}$ cm$^{-1}$).
C. Magnetometry Results and Analysis

Figure 6.06 Magnetic susceptibility data collected for complex 16 (left) and \( \text{16}^{\text{Ox}} \) (right). Data was collected by Dr. Daniel J. Santa-Lucia from the University of Wisconsin in Madison, WI.

Magnetic susceptibility data were collected between 2-300 K for complexes 16-18 and their oxidized derivatives. The presence of zero-field splitting in the bridged diiron complex (16) is evident in the sharp decline in \( \chi \cdot T \) at temperatures below 50 K (Figure 6.06, left). At higher temperatures, the \( \chi \cdot T \) value levels off at 6.3 cm\(^3\) K mol\(^{-1}\), which is the expected value for two uncoupled \( S = 2 \) centers (\( J \approx 0 \)). Upon oxidation to the semiquinonate form, the paramagnetic susceptibility (Figure 6.06, right) dramatically increases to 8.9 cm\(^3\) K mol\(^{-1}\) at its maximum near 50 K, which is consistent with a \( S = 7/2 \) system. The steady decline in paramagnetic susceptibility at temperatures above 50 K is due to depopulation of the \( S = 7/2 \) ground state in favor of the \( S = 5/2 \) excited state.

Based on the fitting of magnetic susceptibility curve (using PHI software),\(^{18}\) the exchange coupling constant (\( J \)) between the Fe(II) center and DMSQ radical has a value of -151 cm\(^{-1}\) (\( J = -2J \text{S}_A \cdot \text{S}_B \) formalism), which is indicative of strong antiferromagnetic coupling. The average \( g \)-values for the Fe centers and SQ radical were 2.10 and 2.00, respectively.
The magnetic susceptibility data (Figure 6.07, left) for the dimanganese derivative 17 shows $\chi T$ values expected for two isolated Mn(II) centers ($\chi T = 7 \text{ cm}^3 \text{ K mol}^{-1}$) at 50 K. Upon decrease in temperature there is a moderate decline in $\chi T$ until 2 K. This suggests that there is zero-field splitting (indicative of a high-spin Mn$^{3+}$ impurity). The gradual increase in magnetic susceptibility above 50 K is due to temperature independent paramagnetism (TIP). Based on the fitting of the curve, the spin Hamiltonian parameters derived from this data indicate that there is a significant deviation from isotopic $g$-values expected at low temperature. The lower-than-expected $g$-values and modest zero-field splitting both indicate the presence of Mn(III) in the sample. Oxidation of this species into 17$^{Ox}$ results in the spectrum on the right (Figure 6.07).

![Graphs showing magnetic susceptibility data](Image)

**Figure 6.07** Magnetic susceptibility data collected for complex 17 (left) and 17$^{Ox}$ (right).

The $\chi T$ vs. $T$ plot reveals that the two Mn(II) centers are each coupled antiferromagnetically to the bridging semiquinone radical. This results in a $\chi T$ value of 9.5 cm$^3$ K mol$^{-1}$ (at 50 K) which is consistent with an $S = 9/2$ system. Again, the spin Hamiltonian parameters suggest that the $g$-values are lower than expected for Mn(II) ions ($g_{\text{avg}} = 1.79$), perhaps due to the presence of an impurity. Fitting of the data allowed us to
extract an antiferromagnetic coupling constant of $J = -140 \text{ cm}^{-1}$, which is comparable to the value obtained for the diiron analogue.

Complex 18 was studied by magnetic susceptibility and the resulting data is reported in Figure 6.08. This complex behaves as an uncoupled Co(II) complex with zero field splitting responsible for the decrease in $\chi T$ at temperatures below 50 K. The drop-off in paramagnetic susceptibility was modeled to yield an axial zero-field parameter $D = -48.2 \text{ cm}^{-1}$. This is larger than the previously reported complexes, but within the expected range for Co(II) complexes with the Tp$^{\text{Ph}}$ ligand (Chapter 2). Attempts at measuring magnetic susceptibility of the oxidized species, 18$^{\text{Ox}}$, yielded data which is consistent with the precursor complex – indicating that the majority of the sample is 18.

![Figure 6.08](image.png)

**Figure 6.08** Magnetic susceptibility data collected for complex 18.

**IV. Conclusion**

The well-defined bimetallic complexes presented here provide a unique opportunity to probe the effect of ligand-based radicals in this benzoquinoidal bridged series of complexes 16-18. These complexes behave as typical dinuclear metal complexes with negligible exchange coupling between the metal centers. Through their oxidation
(complexes 16^Ox-18^Ox) we have established the formation of a series of oxidized complexes which contain the μ-semiquinone ligand bridging the homobimetallic sites. In this unique scenario, the overall spin-state is actually greater than the precursors, leading to half-integer spin states which are a result of antiferromagnetic coupling between the ligand radical and the metal centers. Thus, we have generated dicobalt(II), dimanganese(II), and diron(II) congeners bridged by semiquinonates, leading to \( S = 5/2, 9/2, \) and 7/2 spin states, respectively.

The estimation of magnetic properties including zero-field splitting, \( g \)-values, and exchange coupling constants will allow us to explore the effects of metal substitution and the unusual magnetic landscape of these complexes. To extract these parameters, we will employ high field and frequency electron paramagnetic resonance (EPR) and far infrared magnetic spectroscopy (FIRMS). The design of non-innocent bridging ligands with uniquely accessible oxidation states will hopefully inspire development of SMMs and interesting magnetic properties.

V. Experimental Section

General Methods

Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used as received without further purification. Acetonitrile (CH\(_3\)CN), dichloromethane (CH\(_2\)Cl\(_2\)), 1,2-dichloroethane, hexanes, and THF were degassed through several freeze-pump-thaw cycles and stored over molecular sieves. The synthesis and handling of the metal complexes was carried out under an inert atmosphere using a Vacuum Atmospheres Omni-Lab glovebox equipped with a freezer set to -30°C.
The K[Tp\textsubscript{Ph2}] and 2,5-DMHQ ligands were synthesized according to previously reported methods\textsuperscript{19,20}.

**Physical Characterization**

Elemental analyses were performed at Midwest Microlab, LLC in Indianapolis, IN. UV-vis absorption spectra were collected with an Agilent 8453 diode array spectrometer equipped with a Unisoku Scientific Instruments (Osaka, Japan) cryostat for low temperature measurements.

**Synthesis of [(Fe\textsuperscript{2+})\textsubscript{2}(Tp\textsuperscript{Ph2})\textsubscript{2}(\mu-DMHQ)]\textsuperscript{16} (DMHQ = 2,5-dimethoxyhydroquinone)**

The synthesis of this complex was carried out using the previously published procedure from our lab\textsuperscript{16}. In 2 mL of THF, 84 mg (0.49 mmol) of 2,5-DMHQ ligand was mixed with 80 mg (1.48 mmol, 3 equiv.) of NaOMe. After stirring for one hour, the solvent was evaporated by vacuum. In a separate vial, anhydrous FeCl\textsubscript{2} (125 mg, 0.99 mmol) and K[Tp\textsuperscript{Ph2}] (699 mg, 1.0 mmol) were stirred in 3 mL of CH\textsubscript{3}CN. This mixture was slowly added to the dried sodium salt and stirred for 12 hours. After the crude product precipitated, the solvent was extracted and the remaining solid was dried. Extraction by CH\textsubscript{2}Cl\textsubscript{2} (4 mL), followed by filtration through Celite yielded a dark yellow solution which was layered with pentane. After two days at -30°C, the product crystallized as a yellow solid which was recovered and dried before analysis. Yield = 389 mg (49\%). Anal. Calcd (%) for C\textsubscript{98}H\textsubscript{76}B\textsubscript{2}Fe\textsubscript{2}N\textsubscript{12}O\textsubscript{4} (M\textsubscript{w} = 1619.07 g mol\textsuperscript{-1}): C, 72.70; H, 4.73; N, 10.38. Found: C, 70.29; H, 4.94; N, 10.39.

**Synthesis of [(Fe\textsuperscript{2+})\textsubscript{2}(Tp\textsuperscript{Ph2})\textsubscript{2}(\mu-DMSQ)]\textsuperscript{16\textsuperscript{Ox}}**

Purified material of 16 (172 mg, 0.1 mmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} and added to AgPF\textsubscript{6} (26 mg, 0.1 mmol), the dark brown solution was stirred for one hour before
filtration through Celite and layering with pentane. Red crystals were harvested after several days inside a -30°C freezer. The resulting product was washed with Et₂O and dried by vacuum. Yield = 146 mg (78%). Anal. Calcd (%) for C₉₈H₇₆B₂F₆Fe₂N₁₂O₄P (Mₘ = 1764.05 g mol⁻¹): C, 66.73; H, 4.34; N, 9.53; F, 6.46. Found: C, 66.46; H, 4.48; N, 9.74; F, 6.24.

**Synthesis of [(Mn²⁺)₂(TpPh₂)₂(µ-DMHQ)] (17)**

Inside a small vial, 2,5-DMHQ (58 mg, 0.34 mmol) was charged with NaOMe (37 mg, 0.69 mmol) and dissolved in 2 mL THF. This mixture was stirred for an hour before the solvent was removed by vacuum. Solid MnCl₂•4H₂O (137 mg, 0.69 mmol) was crushed to a fine powder and added to 4 mL of CH₃CN. This mixture was added to the ligand residue and K[TpPh₂] (488 mg, 0.69 mmol) before stirring overnight. Afterwards, the free solvent was decanted and the remaining solid was washed with Et₂O before drying by vacuum. The product was dissolved in CH₂Cl₂ before filtration through Celite and subsequent desiccation to yield a yellow powder. Yield = 257 mg (46%). Anal. Calcd (%) for C₉₈H₇₆B₂Mn₂N₁₂O₄ (Mₘ = 1617.26 g mol⁻¹): C, 72.78; H, 4.74; N, 10.39. Found: C, 72.54; H, 4.78; N, 10.24.

**Synthesis of [(Mn²⁺)₂(TpPh₂)₂(µ-DMSQ)]PF₆ (17Ox)**

Purified solid powder of 17 (238 mg, 0.15 mmol) was dissolved in 1,2-dichloroethane and treated with one equivalent of AgPF₆ (37 mg, 0.15 mmol). The dark red solution was stirred for one hour before filtration through Celite. Crystallization was performed by layering this solution with hexanes and storing inside a -30°C freezer. Reddish-brown needles which formed after several days of storage were dried by vacuum. Yield = 204 mg (79%). Anal. Calcd (%) for C₉₈H₇₆B₂F₆Mn₂N₁₂O₄P (Mₘ =
1762.23 g mol\(^{-1}\)): C, 66.79; H, 4.35; N, 9.54; F, 6.47. Found: C, 67.82; H, 4.73; N, 9.69; F, 6.26.

**Synthesis of [(Co\(^{2+}\)\(_2\)(Tp\(^{Ph2}\))\(_2\)(\(\mu\)-DMHQ)] (18)**

The DMHQ ligand (43 mg, 0.25 mmol) was dissolved in THF and treated with 0.5 equivalents of NaOMe (7 mg, 0.13 mmol). After stirring for one hour, the solution was then dried by vacuum. Addition of two equivalents of [Co\(^{2+}\)(Tp\(^{Ph2}\))(OAc)(Hpz\(^{Ph2}\))] (534 mg, 0.5 mmol) in 5 mL of CH\(_3\)CN was accompanied by stirring. The purple mixture was then stirred for 15-20 minutes before addition of excess triethylamine. A dark brown color emerged from the mixture, which was then stirred over several hours. The crude material was dried *in vacuo* before washing with ether. Then after air drying, the solid was taken up in 5 mL of CH\(_2\)Cl\(_2\) and filtered through Celite. After several hours of drying, the resulting brown material was sent for elemental analysis. Yield = 268 mg (66%). Anal. Calcd (%) for C\(_{98}\)H\(_{76}\)B\(_2\)Co\(_2\)N\(_{12}\)O\(_4\) (\(M_W = 1625.25\) g mol\(^{-1}\)): C, 72.42; H, 4.71; N, 10.34. Found: C, 70.15; H, 4.84; N, 10.20.

**Synthesis of [(Co\(^{2+}\)\(_2\)(Tp\(^{Ph2}\))\(_2\)(\(\mu\)-DMSQ)]PF\(_6\) (18\(\text{Ox}\))**

Purified solid of 18 (197 mg, 0.12 mmol) was dissolved in 5 mL of CH\(_2\)Cl\(_2\) and treated with one equivalent of AgPF\(_6\) (31 mg, 0.12 mmol). The resulting green solution was stirred for one hour before filtration through Celite. The solution was then concentrated by vacuum before layering with hexanes. Green prisms which precipitated out of solution were harvested and dried for analysis. Yield = 152 mg (71%). Anal. Calcd (%) for C\(_{98}\)H\(_{76}\)B\(_2\)Co\(_2\)F\(_6\)N\(_{12}\)O\(_4\)P (\(M_W = 1770.22\) g mol\(^{-1}\)): C, 66.50; H, 4.33; N, 9.50. Found: C, 66.95; H, 4.23; N, 9.66.
Magnetic Susceptibility and Reduced Magnetization Experiments and Analysis

Variable-temperature paramagnetic susceptibility data and reduced magnetization data for complexes 16-18\textsuperscript{ox} were measured with a MPMS 3 Quantum Design SQUID magnetometer at the University of Wisconsin-Madison. The samples were cooled down in the absence of a magnetic field to 1.8 K and subsequently data were collected from 1.8 K to either 300 K or 400 K in an applied 1000 G dc magnetic field.
Table 6.B Summary of X-ray crystallographic data collection and structure refinement.

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VI. BIBLIOGRAPHY


