THE EFFECT OF ELECTRONIC SPIN ON THE REACTIVITY OF SPIN-COUPLED TRANSITION METAL COMPLEXES

By

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ABSTRACT

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Variable temperature X-ray crystal structures for the spin coupled $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+$ complex were acquired and studied computationally, where it was found there was observable structural effects attributed to increasing the thermal occupation of higher spin states. These effects were manifest as structural changes in the exchange coupled dimer that were not present in a structural analogue. It was determined through computational studies that these structural changes act to reduce the exchange coupling between the Fe^{III} centers which previous studies have shown could affect the potential reactivity of this system. Detailed mechanistic studies on the spin coupling have shown this change in coupling is mediated primarily by a change in the (μ -OH) bond distance, which may or may not be due to the thermal occupation of higher spin states or could be due to other external effects.

A covalently linked intramolecular donor-acceptor assembly consisting of a ruthenium polypyridyl bound to a $Mn^{II}Zn^{II}$ bearing macrocycle was characterized and the variable temperature time resolved emission of this compound was investigated where the presence of a thermally activated quenching process was discovered. This quenching of the emissive excited state of the Ru donor by the macrocyclic acceptor was determined to have a thermal barrier of 80 ± 20 cm⁻¹ and was found to be proceeding via a Dexter energy transfer mechanism. The origin of this barrier was determined to be due to a reorganization process that raised the energy of the acceptor due to the rigid medium in which these compounds were studied. This assignment was confirmed through supporting density functional theory calculations.

Related to the $Mn^{II}Zn^{II}$ donor-acceptor system, computational studies on the exchange coupled Mn^{II}_2 Schiff-base macrocycle that was previously studied as the acceptor in a donor-acceptor assembly were performed to provide insight as to the observed increased quenching rate in an analogous Mn^{II}_2 donor-acceptor system compared to $Mn^{II}Zn^{II}$ system. The spin coupled states were investigated via the broken symmetry formalism, and the electronic structure of ligand field excited spin coupled states was also studied. The orbital mechanisms of the exchange interaction were studied and it was determined that the linking ligand in the donor-acceptor assembly has minimal impact on the spin coupling of this system, so excited states of the energy donor would have little impact on the thermal occupation spin state in this system. Interestingly, it was also found through the broken symmetry electronic structure investigations that there were substantial thermodynamic differences in the ligand field based excited states of the two systems such that the observed thermal barrier to quenching in the $Mn^{II}Zn^{II}$ system is deduced to be non-existent based on the computational results. In this way there is potential that the spin coupling interaction has affected the dynamics of this system.

Copyright by JOHN ANDREW KOUZELOS 2015 This dissertation is dedicated to my parents and the rest of the Kouzelos family

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KEY TO ABBREVIATIONS

NMR	Nuclear Magnetic Resonance
DFT	Density Functional Theory
НОМО	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
SCF	Self Consistent Field
UKS	Unrestricted Kohn Sham
GGA	Generalized Gradient Approximation
B3LYP	Becke 3-parameter hybrid functional with Becke 88 exchange and LYP correlation.
UB3LYP	Unrestricted B3LYP
BPW91	Density functional with Becke 88 exchange and PW91 correlation.
UBPW91	Unrestricted BPW91
STO	Slater Type Orbital
BS	Broken Symmetry
SP	Single Point Energy
O ₂ CCH ₃	Acetate
HBpz ₃ ⁻	Trispyrazolylborate
CCD	Charge Coupled Device
NPA	Natural Population Analysis
VT	Variable Temperature
EPR	Electron Paramagnetic Resonance
LS	Low Spin electronic state
HS	High Spin electronic state
NMO	Natural Magnetic Orbital
ESI-MS	Electro-Spray Injection Mass Spectrometry
DMSO	Di-Methyl Sulfoxide

UV/Vis	Ultraviolet/Visible Absorption Spectroscopy
CV	Cyclic Voltammetry
THF	Tetrahydrofuran
2-Me-THF	2-Methyl-Tetrahydrofuran
CH ₂ Cl ₂	Dichloromethane
DPV	Differential Pulse Voltammetry
LT	Low Temperature
RT	Room Temperature
ОРО	Optical Parametric Oscillator
CW	Continuous Wave Experiment
LC	Liquid Chromatography
OAc	Acetate
mcb	4-methyl-4'-carboxy-2,2'-bipyridine
(CF ₃) ₂ -bpy	4,4'-bis(trifluoromethyl)-2,2'-bipyridine
bpy	Bipyridine
(L)	Symmetric Macrocycle (see Chapter 3 for details)
(L')	Asymmetric Macrocycle (see Chapter 3 for details)
MLCT	Metal-to-Ligand Charge Transfer State
PF ₆	Hexafluorophosphate
ClO ₄	Perchlorate

Chapter 1: Overview of the Concepts and Modeling of Spin Exchange Coupling and its Effects on Photoinduced Electron/Energy Transfer Dynamics.

1.1 Introduction

As chemists, we are introduced early on to the concept of the valence electrons of atoms and their participation in chemical bonding, the most studied form of interaction between atoms. In much the same way that bonding interactions can be rationalized through the electronic structure of the interacting atoms or molecules, the inverse relationship is also true and the electronic structure must be used to understand chemical properties and reactivity; this constitutes the general discipline of chemistry.

An important property of electrons is their quantum mechanical spin angular momentum, which is a fundamental property, the influence of which permeates into a variety of commonly encountered physical and chemical phenomena. A material is said to be diamagnetic if all its electrons are paired, and paramagnetic if there are unpaired electrons present. It is these unpaired electrons, for example, that are responsible for the colorful absorption features observed for organic radicals. If a system contains multiple paramagnetic centers these are able to interact. This interaction is known as electronic exchange coupling or spin exchange coupling, and it has the potential to cause large perturbations to the electronic structure of a system. Consequently, spin coupled systems might display unique properties, as will be discussed later.

A wide range of extremely important chemical reactions occur ubiquitously in our world, and many of them involve biological processes where electrons interact with metal centers known to contain transition metal centers or clusters (photosynthesis, respiration, etc.), which due to the open d-orbital manifolds common in transition metal ions usually contain unpaired electrons with an associated spin angular momentum. It is therefore relevant to investigate any possible effects of unpaired electrons and their interactions on chemical reactivity to better understand the functioning of these biological and other chemical systems of interest that contain paramagnetic centers.¹

This dissertation chronicles our continuing mission to explore the effects of electronic spin, either in exchange coupled systems or in other paramagnetic systems, on the chemical dynamics of molecular systems. This is afforded either through the direct study of electron and energy transfer dynamics in the aforementioned systems, or via theoretical studies that are used to gain an understanding of how this electronic spin can affect chemical reactivity in previously or yet to be studied molecular systems. This chapter will provide a brief theoretical overview of the spin exchange coupling interaction, theoretical methods used to model said interaction, electron and energy transfer, and the concept of spin conservation in these reactions. Previous work from our group and other groups will also be discussed as it pertains to the understanding of the effects of electronic spin on chemical reactivity.

1.2 Spin Exchange Coupling

Spin exchange coupling has been observed to cause a variety of recognized effects on the spectroscopic, magnetic and electronic properties, all in the absence of applied electric or magnetic fields.² Often times spin forbidden d-d bands have their intensities greatly amplified as a consequence of spin coupling. Another change brought about by spin exchange coupling are changes in the bulk magnetic properties of a system. In a hypothetical system where there are two unpaired electrons present in the complete absence of coupling, there should only be one observed

value for the magnetic moment. If exchange coupling is present in a similar hypothetical system, this single value will transform into a range of values possible for the same number of unpaired electrons. It is in fact this distinction that enables the use of magnetic measurements in the acquisition of parameters used to model this interaction.³

In any chemical system, in order for spin coupling to occur the unpaired electrons must be localized in different parts of the molecule and there must be a thermodynamically favorable pathway to facilitate the interaction leading to spin exchange.⁴ While weak intermolecular spin coupling is possible,⁵ in most cases electron exchange coupling occurs intramolecularly. The interaction between the two spin bearing centers can occur via direct overlap of the spin centers (direct exchange) or through the mutual interaction with a diamagnetic bridge in what is termed a superexchange mechanism.^{4,6,7}

The unpaired electrons on each spin center can interact via exchange coupling in either a ferromagnetic or an antiferromagnetic manner when there is sufficient electronic interaction between the orbitals containing the unpaired electrons.⁴ It is also true that both types of intramolecular spin coupling can be ferromagnetic or antiferromagnetic. Both types of coupling are commonly seen in direct exchange coupled systems. In the binuclear metal complexes studied in this dissertation, the superexchange coupling pathway is predominant. Even in a superexchange mechanism, where antiferromagnetic coupling is common, Ferromagnetic interactions can occur, usually when the interacting unpaired electrons are housed in centers that are 90 degrees to each other relative to the diamagnetic bridge. Since superexchange is usually mediated between porbitals on the diamagnetic bridges, this results in the spin centers interacting via orthogonal p orbitals on the diamagnetic ligand and these interactions are typically rather weak.⁶

An antiferromagnetic interaction occurs commonly in superexchange coupled systems. This spin interaction can be thought of an extension of the more logical direct exchange where in interaction between non-orthogonal orbitals is mediated through the electron hopping between the ligand and the spin centers.⁶ The antiferromagnetic stabilization occurs as a result of the interacting unpaired electrons being stabilized by adopting the lowest possible spin state due to the necessity of the spins being antisymmetric to get efficient hopping between the diamagnetic bridge and the spin centers. The non-orthogonality of the interacting orbitals means that the electrons can be thought to have the opportunity to freely mingle between the two spin centers. As a consequence of the anti-symmetry requirement of the Pauli Exclusion Principle, this means the electrons can more effectively delocalize if they have opposite spins on each spin center.

This spin exchange interaction can be written as the scalar product of the spin operators of atoms in molecules and solids. Thus, the net spin coupling between two spin bearing centers in a molecule can be represented and quantified quantum mechanically with single-ion spin operators S_1 and S_2 for each of the metal centers in the form of the Heisenberg-Dirac-Van Vleck Spin Hamiltonian as defined in Equation 1.^{7,8}

$$H^{\rm HB} = J \,\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{1}$$

If one makes the assumption that the total spin operator is the sum of the spin operators of each spin center, one can obtain the eigenvalues of the spin exchange operator which have energies given by Equation 2, which describes the energy displacement of an individual spin state *S* from the spin barycenter of an exchange-coupled binuclear system in terms of the coupling constant *J*.

$$E_{2S+1}^{\rm HB} = \frac{J}{2} \{ S(S+1) - S_1(S_1+1) - S_2(S_2+1) \}$$
(2)

The exchange interaction removes the degeneracy of the various total spin values possible for the exchange-coupled clusters. The result of this loss of degeneracy is that the spins are ordered into parallel (ferromagnetic) and antiparallel (antiferromagnetic) configurations to form an energetic spin ladder whose energy separations can be expressed as a function of *J*, which is shown in figure 1-1 for an interacting pair of S=1/2 spin centers.

It is possible to use Heisenberg exchange-coupled metal clusters as a way to vary spin without affecting other gross properties of the system. By changing the temperature of the sample, one controls the access to spin states thermally accessible to the complex, which in turn will change the spin of the cluster. This property makes spin exchange coupling in binuclear metal clusters an ideal tool for varying the quantity of spin.





For all of the exchange coupled dimers studied in this thesis, both transition metal ions are high spin with d⁵ occupation, Fe^{III}(OH)Fe^{III} in one case and Mn^{II}₂ in the other. This means that for the ground states of these molecules we have two S=5/2 centers participating in spin exchange. In both cases the spin coupling is antiferromagnetic as determined via variable temperature magnetic susceptibility measurements. This results in a spin ladder which is portrayed in figure 1-2. The energy difference between each spin level depends on the value of the coupling constant, which is unique for each system studied.



Figure 1-2: The spin ladder for two $S = \frac{5}{2}$ spin centers in a bimetallic exchange coupled complex.

1.3 Theoretical Methods for the Modeling of Spin Exchange

Since the energy separations of the individual spin states in a Heisenberg exchange coupled cluster depend on the value of J, it is important to determine the value of said constant in order to understand the intricacies of how thermal population of states in a Heisenberg spin ladder can control spin. Although the constant can be determined experimentally via variable temperature magnetic susceptibility and the Evans NMR methods,³ it is also beneficial to determine the value of J using theoretical methods, 9,10 as these are a powerful diagnostic tool. These theoretical methods offer not only the advantage of providing information on the electronic structure of these complexes, but by comparing the calculated values of the coupling constant to experimentally obtained values and determining the theoretically determined values to be accurate, one can then use theory to determine the coupling in synthetically unobtainable molecules, such as the excited states of spin exchanged systems where bulk magnetization methods are not typically available. Exchange coupled molecules have been modeled for many years,^{7b} and while there are more thorough methods for theoretically determining the Heisenberg coupling element such as techniques employing Green's functions or spin projection,¹¹ the easiest and one of the most prominent in the chemical literature is the broken symmetry formalism for density functional theory (DFT), as developed by Noodleman⁹ and Yamaguchi,¹⁰ which was chosen for our research. This method is prized for its ease in implementation as well as its accuracy in predicting the coupling of complicated systems when the proper theoretical procedures are used.

In the broken symmetry treatment, two individual DFT calculations are carried out on a particular chemical system which exhibits exchange coupling. The first is a high-spin single point energy calculation to determine the energy of the highest possible spin electronic state, which in the case of our spin coupled systems is a spin-pure electronic configuration described by a single determinant wavefunction. The second is a single point energy calculation of a special low spin electronic state corresponding to the lowest possible spin state and generated by the broken symmetry formalism. This low spin state, which in the case of our systems in this thesis is a singlet, is often termed the broken symmetry electronic state or the broken symmetry wavefunction.¹²

A broken symmetry electronic state is generated by disturbing the symmetry of the electronic spin density across a system consisting of more than one paramagnetic site. This is accomplished by creating an initial guess that has sufficient lack of spin symmetry. In practice, this is achievable by mixing HOMO and LUMO orbital guesses at the onset of the DFT calculation,¹³ or in other cases the guess may have to be manually generated.¹⁴ In recent years, new methods to systematically generate guesses with appropriate broken symmetry across a molecule have been developed. These methods create a broken symmetry guess by either flipping the spin density of one of the spin centers in a spin coupled molecule¹⁵ (such as one of the transition metal centers in the compounds studied in this thesis) or by using fragment based guessing¹⁶ which allows for the generation of wavefunction guesses for molecular fragments in isolation of the rest of the fragments in the molecule that can have their individual charge and multiplicity relative to the rest of the molecule specified; with fragment based guessing, a broken symmetry guess is generated by specifying at least one fragment to have negative multiplicity. The broken symmetry state is not a true electronic state of the system studied but rather is a linear combination of spin states that places heavy emphasis on the actual singlet state.^{9b,12} It is for this reason that the spin expectation values for the broken symmetry singlet states are not the ideal value of zero, but are instead spin contaminated with spin expectation values usually in the range of 4.5 to 5.

This broken symmetry state, while not being an actual electronic state of the system studied, is used to determine the Heisenberg coupling constant according to Equation 3 developed by Yamaguchi and coworkers.¹⁰

$$J = 2 \frac{E_{S=S_{max}}^{U-DFT} - E_{S=S_{min}}^{U-DFT}}{\langle S^2 \rangle_{S=S_{max}}^{U-DFT} - \langle S^2 \rangle_{S=S_{min}}^{U-DFT}}$$
(3)

In this equation, E^{U-DFT} values are the high-spin ($S=S_{max}$) and broken symmetry ($S=S_{min}$) energies as obtained from the single point energy unrestricted DFT calculations, and $\langle S^2 \rangle$ are the spin expectation values calculated for the aforementioned states in the single point energy calculations. Once the required values have been found from the two single point calculations, the Heisenberg coupling constant can be obtained, providing valuable information about the energy levels of the spin states in the Heisenberg coupled system.

It is often times possible to perform the actions necessary to generate a guess that should subsequently generate a broken symmetry electronic state, but the DFT procedure will not converge to the proper low spin electronic wavefunction. It is therefore necessary to identify the properties of an adequate broken symmetry state and be able to distinguish them from inadequate broken symmetry states. It is fortunate that over a long research career the author has many opportunities to identify the hallmarks of a good broken symmetry state.

In an unrestricted electronic structure calculation, the electrons are modeled as two sets of individually optimized one-electron eigenfunctions of the energy operator where the spin operator is essentially decoupled from the calculation. In a paramagnetic system, there will be more electrons of one spin than the other. By convention the spin with a majority of the electrons is labeled alpha (α) and the minority spin is labeled beta (β). Spin density is defined as the difference

between alpha and beta electron population at a given point in space.¹⁷ By tracking spin density in a broken symmetry calculation, one can make sure the wavefunction is behaving properly.



Figure 1-3: Spin density plot for the $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+$ exchange coupled system. The plot shows alpha density on one Fe^{III} center (left) and beta spin density on the other (right). This is an example of a good broken symmetry state.

In a proper broken symmetry state for a bimetallic spin exchange coupled system, there should be unpaired spins located on both spin centers, with an equal and opposite magnitude of spin on each spin center, as can be seen in figure 1-3.¹⁸ This results in spin density that is close to but slightly less in magnitude than that present in the high spin electronic state on both metal centers, and most importantly the spin densities oppose each other. This means that there is a preponderance of alpha spin density on one of the metal centers, and an equal amount of beta spin density on the other metal center.

In improperly converged low spin states, the SCF procedure often falls into the trap of attempting to pair up the occupation of the orbitals such that a portion of the spin density on each spin center is lost. This results in lower than expected values for both the spin density on the metal centers and the spin expectation value for the low spin state, as spin contamination depends on the number of open shell orbitals in your low spin state.

Once one obtains a proper broken symmetry electronic state, it is possible to theoretically determine coupling constants for systems of interest. This will prove to be an integral part of the research presented in this thesis.

1.4 Electron and Energy Transfer

Electron and energy transfer processes are an important field of study and justifiably well studied as they are relevant to the understanding of important biological processes¹⁹ and applications to molecular devices with light-induced functionality.²⁰ Electron transfer is a basic chemical event where an electron is transferred between chemical species. As one can imagine, the simplicity and relevance of this reaction has led to countless studies on the dependence of the rate of electron transfer on various parameters.

It has been found that the rate of electron transfer can be described by the semi-classical Marcus equation,^{21a} which describes the rate for nonadiabatic electron transfer between a donor and an acceptor at a fixed distance and orientation as shown in Eq. 1.4, where *h* is Planck's constant, k_b is the Boltzman constant, and T is temperature.

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} e^{-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}}$$
(4)

Parameters that determine the rate of electron transfer are ΔG^0 , which is the free energy driving force for electron transfer, λ , which is the reorganization energy due to inner- and outer-sphere

structural changes associated with the electron transfer, and H_{DA} , which is the measure of electronic coupling between donor and acceptor.

Photo-induced electron transfer occurs as a consequence of the thermodynamics of the photoexcited donor-acceptor pair and functions most often via a through bond mechanism which has been extensively studied.²¹ The advantage of using photo-excited states in the study of electron transfer processes is that allows the use of a well-studied chromophores with defined kinetic properties, such as ruthenium trisbipyridyl complexes,²² such that electron transfer into or out of the complex has measurable effects on these already known kinetics, sometimes allowing for the rate of electron transfer to be elucidated.

Energy Transfer is generally an electronically excited donor transferring its excess energy to an acceptor in its ground state. This process requires energy conservation (thermodynamic viability) and a way for these states to interact. The interaction between donor and acceptor states can occur via a through bond (Dexter) or through space (Förster) mechanism.²³ While these energy donors can be excited in a variety of ways, a common method of exciting energy transfer donors is through photoexcitation. Since this method makes the study of kinetics easier by allowing the use of well characterized chromophores as either donors or acceptors,²² photo-induced energy transfer processes will now be discussed as they were targeted for study in this dissertation.

The through space mechanism is a dipolar coupling of the donor and acceptor states which can function at large distances with a rate dependence of r^{-6} and a dependence on spectral overlap between the donor and acceptor states;²⁴ electrons are not transferred between the donor and acceptor as can be seen in figure 1-4. As Forster transfer is not present in any of the systems studied in this dissertation, it will not be discussed further.



Figure 1-4: An adapted diagram showing the electronic transitions associated with photoinduced electron and energy transfer processes.³¹

The through-bond Dexter energy transfer mechanism can only operate effectively at shorter distances due to its dependence on orbital overlap between the donor and acceptor states.²⁵ The transfer is mediated by the simultaneous exchange of electrons between donor and acceptor. Upon formation of the excited donor state, an excited electron is transferred into an unoccupied orbital on the acceptor. An electron from the acceptor HOMO is concomitantly transferred to the hole in the donor, resulting in an excited acceptor state and a ground donor state, as seen in figure 1-4.⁶ While the above explanation depends on the concept of transferring electrons, this is a distinct process that is differentiated from an electron transfer by the identity of the products formed. Due to the similarities inherent to transferring electrons, much of the theory for electron transfer can be

related to Dexter energy transfer processes,²⁶ with the exception being that the two electron nature of Dexter energy transfer means the rates of energy transfer fall off much more precipitously as a function of distance between donor and acceptor.

To better understand the dynamics of these electron and energy transfer processes, it is beneficial and common practice to synthesize and study covalently bound donor-acceptor complexes.²⁷ These assemblies offer the inherent advantage of not having to contend with diffusion related kinetic phenomena²⁹ when trying to study their photochemistry and photophysics. It is therefore the case that in the course of the research presented in this dissertation covalently bound donor-acceptor complexes were studied. However, distinguishing between energy transfer and electron transfer processes can still be difficult when both are thermodynamically viable.²⁶ As electron transfer creates charge-separated products, any charge separated spectral features observed spectroscopically would confirm the presence of an electron transfer process. As Dexter energy transfer has a smaller outer-sphere reorganization energy, a comparison of kinetic studies in different media can help distinguish between the two processes.²⁵

1.5 Conservation of Spin in Photophysical Processes

One of the primary ways in which we propose spin to effect the reactivity of these systems is through the conservation of spin angular momentum. A good example of this is provided in figure 1-5, where the quenching of the excited state of $[Ru(bpy)_3]^{2+}$ is possible for O₂ because there exists an accessible excited state of O₂ (S=0) that both conserves spin and is thermodynamically downhill. The only spin allowed excited state for N₂ (S=1) is not thermodynamically downhill compared to the energy of the reactants and thus N₂ is not capable of quenching photo-excited $[Ru(bpy)_3]^{2+}$. This concept of a reaction only proceeding if it is both thermodynamically and spin allowed is being proposed as a primary way in which electronic spin affects the reactivity of chemical systems. The possible total spin angular momentum values for a combination of two atoms or compounds $|\mathbf{S}| = \mathbf{S}_1$ and $|\mathbf{S}| = \mathbf{S}_2$ will have the following values:

$$|\mathbf{S}_{\text{total}}| = |\mathbf{S}_1 - \mathbf{S}_2|, |\mathbf{S}_{\text{total}}| = |\mathbf{S}_1 - \mathbf{S}_2| + 1, \dots |\mathbf{S}_{\text{total}}| = \mathbf{S}_1 + \mathbf{S}_2.$$
 (5)

Since in the course of standard chemical reactions, there is no way to convert the spin of an electron, this means that there is no way the total spin of the system can change in the course of the reaction. Therefore, the total spin angular momentum of the reactants remains the same in the products. This conservation of spin angular momentum has important ramifications in the realm of photo-induced chemical reactivity, because it provides an important qualification for whether or not a reaction will occur. One can now add a new condition to the standard requirement of a reaction proceeding only if the process is spontaneous. That condition is that the reaction will only proceed if for all the possible total spin angular momentum values of the reactants and products, there is at least one spin value for which the reaction is thermodynamically downhill. It is through this mechanism that we propose spin will have an easily determined effect and thus photo-induced energy and electron



Figure 1-5: A scheme showing the proposed spin-conserved nature of Ru ${}^{3}MLCT$ quenching by O₂ and the proposed inability of N₂ to quench the excited state of $[Ru(bpy)_{3}]^{2+}$ due to the inaccessibility of a spin-allowed excited state.

transfer reactions should serve as convenient reactions for which the effects of spin on reactivity can be observed.

The previously mentioned donor-acceptor example shows the rudimentary relationship between spin and reactivity, but there are too many hidden variables in these systems for a quantitative relationship to be determined. It can be the case that for a system where more detailed thermodynamic information is available, on can see spin having an effect on the reactivity of a system is when it is the case that the presence of different amounts of spin causes a thermodynamic change in a molecule or changes in the observed reaction of a system. Our group has investigated how changing the amount of spin in a compound affects the observed reactivity in a system. It was via this method that we were able to show the dependence of a Forster energy transfer process on the conservation of spin angular momentum.²⁸

Our research group wishes to study a series of systems that can change spin states without changing any other aspect of the molecular structure of the system, which could allow for a quantitative relationship between spin and reactivity to be determined.

1.6 Contents of Dissertation

To further the goals of establishing the effects of electronic spin on chemical reactivity, a few different studies were performed which are chronicled in this thesis. From these studies, the impact of spin on various aspects of photophysical reactivity is investigated.

Chapter 2 details the acquisition and computational study of variable temperature X-ray crystal structures for the spin coupled $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+$ complex to determine if there were observable structural effects as a result of increasing the thermal occupation of high spin
states, afforded by the small value for the spin coupling constant (34 cm⁻¹). It was the intention that since the effects of changing the energetics of these systems has been linked to changes in reactivity. Specifically it has been found that decreasing the spin coupling between the spin centers results in an increased rate of quenching for analogues of this complex are used as energy and electron acceptors.²⁹ Therefore, density functional theory is used to test if the structural changes had an effect on the electronic structure of these systems. From that conclusion, we should be able to logically extend these results to infer any resulting changes in reactivity that can result from these structural changes.

Chapter 3 reports the variable temperature dynamics of a covalently linked intramolecular donoracceptor assembly consisting of a ruthenium polypyridyl covalently bound to a $Mn^{II}Zn^{II}$ bearing macrocycle. This quenching of the emissive excited state of the Ru donor by the macrocyclic acceptor was determined to have a thermal barrier of 80 ± 20 cm⁻¹ and was found to be proceeding via a Dexter energy transfer mechanism. This rate behavior of quenching by the excited states on the Mn^{II} ion, is compared to previously studied donor-acceptor complexes. Density functional theory was utilized to support the characterization of the mechanism of energy transfer.

Chapter 4 discusses the computational studies on the exchange coupled Mn^{II}_{2} Schiff-base macrocycle that was previously studied in our group³⁰ as the acceptor in a donor-acceptor assembly. Electronic structure calculations were performed to provide insight as to the observed increased quenching rate in Mn_2 compared to the previously mentioned MnZn system. The results of this computational study shows thermodynamic differences in the excited states of a spin coupled molecule when compared to a non-spin coupled analogue that may be due to the exchange coupling interaction.

Finally, future research directions involving the results and techniques discussed in this thesis applied to other potential systems of interest will be briefly outlined and discussed.

APPENDIX

Appendix: Procedure for Broken Symmetry Calculations in ORCA and Gaussian 09

This section is to provide detailed examples of how proper broken symmetry states were obtained in the course of the research presented in this dissertation. The $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+$ exchange coupled system will be used as an example for the purposes of explaining these methods.

General Procedure for ORCA

ORCA has two ways to generate broken Symmetry low spin states. One is to use the spin-flip mechanism to force the spins generated in a high spin electronic state on a single atom to be antisymmetric to the rest of the spin in the system if one starts from a high spin state and knows the final multiplicity of the broken symmetry state. The second is the program will attempt to construct a proper broken symmetry state from a known high spin state if input on the number of unpaired electrons on each spin center is provided. For the purposes of the systems studied in this thesis consisting of two S= $\frac{5}{2}$ metal ions, both methods yielded equivalent results.

Spin Flip Method: In a molecule with two interacting spin centers, you first need to determine which spin center should be flipped. For this guess generation, the following input commands were entered, as shown from this input file excerpt, which is annotated to explain the inputs. See the ORCA manual for more details on other calculation parameters.

#Orca Energy Calculation for Broken Symmetry

! UKS B3LYP/G STO-3G VeryTightSCF Direct Grid4 NoFinalGrid

%pal nprocs 4 Use four processors to expedite calculation

end

%scf

MaxIter 2000	Set a high number for SCF cycle limit, as optimizing the wavefunction is difficult.									
FlipSpin 1	lipSpin 1Flips the spin on the second iron atom									
FinalMs 0	Our broken symmetry state is a singlet									
end										
* xyz 1 11	Based our broken symmetry state on a S=5 high spin state.									
Fe 4.211000	0.298000 4.449000									
Fe 1.650000	2.410000 5.180000									

It should be noted that the smallest possible basis set is being used here to generate the broken symmetry guess, as it is easier to converge to a good broken symmetry wavefunction with a smaller basis set.

After this calculation is complete, the following calculation was run to get the broken symmetry state in the desired basis set.

```
! UKS B3LYP/G 6-311G(d,p) TightSCF Direct Grid4 NoFinalGrid
%pal nprocs 4
end
%scf
MaxIter 2000
Guess=MORead Base the wavefunction on a previously calculated one
MOInp="Fe2_hydroxo_DG_Fe20K.gbw" File name with previous wavefunction guess
end
* xyz 1 1 Now calculating a singlet wavefunction
```

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This results in the desired broken symmetry wavefunction. If a geometry optimization is desired, one should perform the aforementioned single point energy calculation to obtain the full wavefunction and then use this wavefunction as the guess in the geometry optimization.

For those curious, the other "automatic" broken symmetry method would use the following input file header for the first file:

```
! UKS B3LYP/G STO-3G VeryTightSCF Direct Grid4 NoFinalGrid
%pal nprocs 4
end
%scf
MaxIter 2000
BrokenSym 5,5 The two highest spin centers have 5 unpaired electrons each
end
* xyz 1 11
Fe 4.211000 0.298000 4.449000
```

Fe 1.650000 2.410000 5.180000

After calculating a proper guess from this file, the second input example would remain unchanged to get the desired broken symmetry state in the proper basis set.

General Procedure for Gaussian 09

To generate a broken symmetry guess, the spin centers need to be designated as their own fragments. One can choose to make each individual ligand its own fragment as well, but it was not necessary for the system in the example. The fragments were chosen as can be seen in figure A1-1.



Figure A1-1: Color coded diagram of $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+$ with blue corresponding to fragment 1, red to fragment 2, and green to fragment 3.

These fragments and the guess to generate them are integrated into the input for generating the

broken symmetry guess in the following manner:

```
%chk=Fe2_hydroxo_jorge_g09BS_guess.chk
%mem=400MW
%nproc=4
# ub3lyp/6-311G(d,p) guess=(fragment=3,only)
Hydroxo Bridged B3LYP Jorge Optimized g09 BS state BS Guess
1,1 3,6 3,-6 -5,1
                              Charge, Multiplicity for overall molecule and each fragment in order
Fe(Fragment=1) 0.0000000
                                1.75648300
                                             -0.35022500
Fe(Fragment=2)
                 0.00000000
                               -1.75648300
                                             -0.35022500
O(Fragment=3)
                  0.00000000
                               0.00000000
                                             0.59296700
O(Fragment=3)
                 1.43159900 1.12553300
                                             -1.60188500
```

This input specifies that individual guesses for each of the three fragments be run and then just added together to make a guess for the overall molecule. This is why the charge and multiplicity for each fragment is specified.

After this guess is generated, it is incorporated into the checkpoint file, which is copied and used to generate a full wavefunction using the following input:

```
%chk=Fe2_hydroxo_jorge_g09BS_BigLS.chk
%mem=400MW
%nproc=4
# ub3lyp/6-311G(d,p) guess=checkpoint scf=(nosymm,maxcycle=500) stable=opt
Hydroxo Bridged B3LYP Jorge Optimized g09 BS state BS SP
1,1
Fe(Fragment=1)  0.00000000  1.75648300  -0.35022500
Fe(Fragment=2)  0.00000000  -1.75648300  -0.35022500
O(Fragment=3)  0.0000000  0.0000000  0.59296700
O(Fragment=3)  1.43159900  1.12553300  -1.60188500
```

```
•••
```

The resulting wavefunction will provide the proper broken symmetry low spin state. Note that this wavefunction is checked for stability, which is important as it sometimes is the case that the broken symmetry wavefunction is not optimal the first time it is evaluated. For this reason, geometry optimizations should be based on these stable single point energy calculations to ensure the proper wavefunction is used to optimize the geometry.

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Chapter 2: The Magneto-Structural Effects on the Spin Coupling of a Di-iron Hydroxo Complex as Studied with Variable Temperature X-ray Crystal Diffractometry and Density Functional Theory.

2.1 Introduction

Our research group has had a perennial interest in the $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2](CIO_4)^1$ and $Fe_2(\mu-O)(\mu-O_2CCH_3)_2(HBpz_3)_2^2$ complexes first synthesized and studied by Lippard and coworkers in 1984. These bimetallic complexes are interesting to study for a broad range of reasons including their mimicry of the active centers of non-heme oxygen transport proteins,³ but our primary reason for studying complexes of this form is to learn more about the nature of the Heisenberg spin exchange interaction⁴ of the unpaired electrons present in both of the Fe^{III} ions contained in the bimetallic complex.

Previous studies in our research group have focused on the mechanisms of spin exchange in oxo and hydroxo bridged iron dimer complexes,⁵ to deduce how structural changes perturb their electronic structure. It is important to investigate these perturbations, as changes in the magnitude of spin exchange in these complexes have been shown to affect their reactivity in electron and energy transfer reactions. The effects on protonation of the oxo-bridge were studied to understand the changes in the orbital mechanisms of spin exchange brought on by the addition of the proton. It was determined that said proton alters the degree of communication between the two metal centers by stabilizing an orbital on the bridging oxygen that comprised a primary coupling pathway in the oxo bridged dimer. This stabilized orbital reduces the energetic match with the magnetic orbitals on the iron centers, resulting in a reduced ability of the metals to mix with said orbital. This effectively removes one of the key coupling pathways found in the oxo dimer, causing a substantial decrease in coupling constant for the hydroxo bridged dimer compared to that for the oxo. Research also found that the structural changes due to the protonation also acted to a roughly equal extent to reduce the coupling between the two iron centers even in the absence of the proton itself. This reduction was caused by increased Fe-O bond distances with the μ -OH group which act to reduce the coupling between the Fe^{III} centers.

The concept of these magneto-structural effects where conformational changes affect the magnetic communication between the spin bearing centers of a molecule has been observed for many years, with the first studies on bridged di-copper bridged compounds by Hatfield and Hodgson.⁶ In many reported cases of magneto-structural effects, synthetic modifications were used to create geometric changes in the molecule, which were then studied using bulk magnetic characterization methods.⁷ The issue with measuring magneto-structural effects with bulk magnetization studies is that since variations in temperature are used to determine the magnetic properties of the molecules in general, any specific effects of the change in temperature on the structure of the molecule are not considered.



Figure 2-1: Drawings of $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+$ (1) and $[Ga_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+$ (2), excluding the coordinated acetone and ClO₄ cations present in the X-ray crystal structures.



Figure 2-2: The Boltzmann distribution of the spin states for complex I as a function of temperature. This plot was generated using the previously reported value for J of 34 cm⁻¹ by Lippard and coworkers. Vertical lines represent the temperatures at which crystal structure data were obtained.

However, temperature dependent structural changes that are not necessarily a direct consequence of the spin exchange interaction can still result in changes in the communication between the spin centers in question, which can cause magnetic data to indicate that the coupling constant varies as a function of temperature, as has been observed in previous instances.⁸

We wished to further probe which changes in structure could be observed when the total electronic spin of a system changes with temperature. Our primary system studied consists of the $[Fe_2(\mu - OH)(\mu - O_2CCH_3)_2(HBpz_3)_2]^+$ spin coupled system as seen in figure 2-1. Based on the Heisenberg spin exchange creating a ladder of spin states as seen in Chapter 1, one can use the published experimental value of the coupling constant to determine the thermal population for each spin state

in the spin ladder based on the Boltzmann equation, as seen in figure 2-2. The best way to probe structural changes as a function of total spin magnitude is to perform variable temperature X-ray crystal diffraction studies on this spin coupled system, providing us with insight as to what structural changes could be correlated with populating the higher spin states in an otherwise unchanged system. Here it is conceivable that by looking at the crystal structure of the molecule while only the low spin states on the spin ladder are thermally accessible and comparing it to the crystal structure at higher temperature geometries, one should observe how the molecular geometry changes with respect to the thermal population of the higher spin states on the spin ladder. It was therefore determined that structures would be obtained for a series of temperatures, which are indicated in figure 2-2, to sample the different thermal population of spin states and see if there were any observable structural changes.

To differentiate any possible effects of crystal lattice expansion as the temperature is increased from the effects caused by the spin coupling interaction in the iron dimer, the gallium analogue as seen in figure 2-1 was also synthesized and studied. Furthermore, this study sought to correlate these structural changes brought about by thermal population of the higher spin states with changes in the electronic structure of the complexes, with the goal of identifying which magnetic coupling pathways were becoming more or less active as the temperature was increased by using the molecular orbital analysis methods previously used in the computational study of these compounds.^{5,7}

2.2 Experimental

2.2.1 Synthesis of Complexes

 $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2](ClO_4) \cdot CO(CH_3)_2$ (1) was prepared by Dr. Dong Guo using a synthetic procedure previously reported by our research group.⁹ Crystals suitable for X-ray diffraction studies were obtained by ether diffusion into a solution of complex 1 in acetone.

 $[Ga_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2](ClO_4)\cdot CO(CH_3)_2$ (2) was prepared by Dr. Dong Guo as an adaptation on the synthetic procedure used for complex 1, substituting $Ga(ClO_4)_3$ for Fe(ClO₄)₃ with other slight procedural modifications. Crystals suitable for X-ray diffraction studies were obtained by ether diffusion into a solution of complex 2 in acetone.

2.2.2 X-ray Diffraction Crystallographic Studies

The X-ray diffraction crystal diffraction structure determinations for complexes **1** and **2** were performed by our former research group member Dr. Dong Guo with the assistance of Dr. Richard Staples (Michigan State University), Dr. Vladimir V. Zhurov (University of Toledo), and Prof. A. Alan Pinkerton (University of Toledo). Two different instruments were used for the acquisition of X-ray crystal structures. The same mounted single crystals for complex **1** and complex **2** were used on both instrumental setups to maintain consistency between the two X-ray crystal diffraction data collection sessions.

Diffraction data at 20 K and 50 K were collected on a Rigaku diffractometer equipped with a highpower Mo rotating anode generator (18 kW), R-Axis Rapid curved image plate detector, flat graphite monochromator, 0.5 mm collimator, and an open flow helium cryostat for temperature control within 0.3 K of the desired temperatures, which was located at the Instrumentation Center at the University of Toledo.¹⁰ To ensure sufficiently high resolution and redundancy in the collected data, 10 different runs (divided into 5 pairs) ranging from 0 to 180° in ω were collected at different *chi* and *phi* settings. A 4° ω -scan range was taken to avoid significant overlap of reflections in any given image. For each pair of runs, a 2° shift in start angle provided a half-oscillation range overlap for precise scaling and avoided the use of partial reflections. A frame time of 220 s was chosen to maximize the intensity of the Bragg reflections and to avoid saturation of the strongest reflections. The experiment for single structure at a specific temperature was completed in about a day. The reflections were indexed with HKL2000,¹¹ and the collected data were integrated by using the VIIPP¹² data integration program based on the reflection positions predicted from HKL2000. Data were corrected for absorption. The program SORTAV¹³ was used for scaling and averaging of reflections into a reduced data set.

Diffraction data at 100, 173, 234, and 296 K were collected on a Bruker Apex-II diffractometer, equipped with a Bruker CCD (charge coupled device) based detector, and an Oxford Cryostream low-temperature apparatus located in the Department of Chemistry Crystallographic Facilities at Michigan State University. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO¹⁴ where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software¹⁵ and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software¹⁶ which corrects for Lp. Scaling and absorption corrections were applied using SADABS¹⁷ multi-scan technique, supplied by George Sheldrick.

Once reduced diffraction data sets were obtained from each of the different crystallographic facilities, the structures were solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2 , SHELXL-97, which are incorporated in SHELXTL-PC V6.10.¹⁸ Anisotropic thermal parameters were refined for all non-hydrogen atoms, with the exception of the proton on the hydroxo bridge (labeled H50). All other hydrogen atoms were localized in their calculation positions and refined by using the riding model. Crystal structure parameters are reported in table 2-1. Coordinates of the solved crystal structures are available in Appendix 2.2 of this chapter.

2.2.3 Computational Procedure

Unrestricted Density Functional Theory¹⁹ with the Kohn-Sham variational implementation²⁰ was used to determine the electronic structure of the Diiron(III) hydroxo system. Functionals used were the ubiquitous B3LYP²¹ as implemented in the Gaussian 09²² electronic structure package, and the pure GGA BPW91²³ functional. B3LYP offers the advantages of energetic accuracy found for hybrid functionals with regard to calculating the energy differences necessary in the determination of the spin-coupling element in the Heisenberg spin Hamiltonian, based on this and prior research.⁴ BPW91 offers the potential benefit of allowing less ligand mixing with the higher energy metal dorbitals, especially with the low spin electronic states, which allows for better analysis of the mechanisms by which spin coupling can occur. Basis sets employed for relevant computations in this research were used based on prior work in the group, and included 6-31G(d)²⁴ and 6-311G(d,p).²⁵ The 6-31G(d) basis set was used only for geometry optimizations for both the low spin and broken-symmetry states, whereas the 6-311G(d,p) basis set was also used for the aforementioned geometry optimizations in addition to its use for all the high spin and broken-

symmetry single point energy calculations used for the electronic structure analysis of all geometries studied in this dissertation.

Calculations were performed in Gaussian 09²² and to a lesser extent ORCA.^{26,27} It was determined through various comparisons of the electronic wavefunctions generated by these two packages that the resulting low spin and high spin wavefunctions were significantly congruous, having similar compositions as determined by Mulliken population analysis²⁸ and nearly identical energies. The use of Mulliken population analysis is in contrast to previous studies in our group that utilized the Natural Population Analysis of Weinold and coworkers.²⁹ This decision is a consequence of NPA being unavailable in ORCA and this project initially required the use of ORCA for all the low spin calculations. It was determined that the Mulliken and natural population analyses scale accordingly such that comparisons between wavefunctions in either will show similar trending behavior. Therefore, to maintain a consistent analysis of the electronic structure of these systems, Mulliken population analysis was used for this study.

Geometry optimizations were performed on a cornucopia of structural variants of complexes **1** and **2**. These geometries include full C_{2v} symmetrized versions of the di-iron hydroxo cation without the acetone present utilizing different basis sets, functionals and multiplicities, as well as the corresponding gallium analogues. Also optimized was the 296 K crystal structure of complex **1** including the coordinated acetone using a subset of the basis sets and functionals in an attempt to get consistency with the observed X-ray crystal structures in our optimized geometry study. These optimized geometries were also studied without the coordinated acetone molecule to compare between the electronic structures of the di-iron hydroxo with the inclusion or absence of the acetone molecule. The optimization procedures for each of these variants will be discussed below.

The geometry optimizations carried out in full C_{2v} point-group symmetry were performed as a starting point for comparison with previous studies from our group, as well as to establish the basic behavior of the computational geometric modeling of the di-iron hydroxo system independent of the basis sets and functionals used to study them. These optimizations were performed with tight optimization criteria on the cation without the acetone present, based on the previously reported UB3LYP/6-31G(d) S=5 geometry optimization reported from our group, which was in turn based on the published X-ray crystal structure of Lippard and coworkers.¹ This structure was used as a starting point since, at the onset of this project we were interested in replicating the previously published results so as to ensure that the proper electronic states were being obtained and studied. Geometries were optimized in both 6-31G(d) and 6-311G(d,p) basis sets to check the similarity of results between the two basis sets and as a test bed for future work on the system described in Chapter 4, where the desire to compute reorganization energies³⁰ required the optimizations be carried out in the same basis set that was used to calculate the energies of the systems studied. Combined with the different functionals used, this brings the total number of optimized C_{2v} diiron(III) hydroxo geometries studied to eight. The gallium geometries were also optimized in B3LYP and BPW91 using both basis sets to see if similar geometric differences were observed between the X-ray structures and the optimized geometries, as well as to see if the bond distances for 6-31G(d) were shorter than those observed for 6-311G(d,p).

The optimized geometries derived from the X-ray crystal structures were studied in an attempt to model the electronic structure of complex **1** on an optimized geometry while accounting for both the coordinating solvent and the asymmetric character of the diiron coordination environment that is observed in the crystal structures. With this in mind, the optimizations were based on the 296 K X-ray structure of complex **1**, as it had the highest degree of asymmetry in the crystal structure as

is discussed further on in this chapter and as is seen in tables 2-2 and 2-3. By starting with the greatest degree of asymmetry, we can ensure that the asymmetric character of the coordination environment will be preserved in the optimized geometries if it is necessary for the stability of the complex. The Fe 296 K X-ray structure including acetone was imported into Gaussian in the manner described below for the importing of crystal structures, and an initial optimization was performed in the high-spin state using UB3LYP/6-311G(d,p). The resulting structure was a local minimum on the potential energy surface, as there were negative calculated frequencies present. Inspection of this initial optimized geometry revealed that the acetone molecule was far out of the plane consisting of the two iron cations and the hydroxo ion. It was suspected that the acetone molecule needed to rotate a bit to find the global minimum, so the acetone was 'twisted' into the plane by adjusting the dihedral angle between the Fe2-O5 vector and the acetone carbonyl vector to zero, thereby swinging the acetone in line with the diiron hydroxo plane. This modified geometry was then optimized in the high-spin state again using UB3LYP/6-311G(d,p) to obtain the final high spin optimized geometry, which was confirmed by performing a frequency calculation on the obtained geometry and observing an absence of negative frequencies. This high spin geometry was in turn used as a starting point for the low spin optimized geometry in UB3LYP/6-311G(d,p) which was successfully obtained with no additional modification necessary, as confirmed by the lack of negative frequencies in a subsequent frequency calculation. The optimized geometries of the X-ray crystal structures with the acetone excluded were not considered for study, as it is the case that the previously mentioned C_{2v} optimized geometries are a good approximation of the resulting geometry and are studied with much more facility than the slightly asymmetric counterparts that could be obtained by performing said optimizations.

When studying the electronic structure of the obtained crystal structures the geometries were imported from the .cif files. This was done by isolating a single cationic complex in the unit cell of the .cif file using the Mercury crystallographic software,³¹ which was then saved as a .pdb file and subsequently opened in the ChemBioDraw 3D software³² to save the structure as a Gaussian formatted input file or as Cartesian coordinates suitable for inserting into an ORCA input file. In studies where the O5-H50 bond distance was manipulated to be a constant value across the temperature series, the X-ray structure Gaussian input files were opened in GaussView,³³ and the O5-H50 bond was selected and set to the desired value with careful attention given to ensure only the proton position was shifted while extending the bond. The O5-H50 bond distance was the only parameter altered, which preserves the bond angles and dihedral angles associated with the O5-H50 bond. Studies on the electronic properties of the cation-acetone hydrogen bound complex were also performed, with the geometries being imported in a similar fashion with the exception of the associated acetone molecule not being removed from the crystal structure as was the case for the isolated cation.

When assigning the orbital designations and discussing certain aspects of the molecular geometries of complexes **1** and **2**, it is useful to designate a Cartesian axis system for the sake of clarity. The Cartesian axis system used throughout this chapter had the z-axis primarily oriented toward the bridging hydroxo group, with the y axis in the same plane as the *trans*-pyrazole and the x-axis being perpendicular to the *trans*-pyrazole, as depicted in figure 2-3.



Figure 2-3: A Simple diagram explaining the axis system used to assign the orbital labels for orbitals involved with coupling on the Fe^{III} ions and μ -OH. The *x* axis for both the Fe and OH centers is going into and out of the plane of the paper.

2.2.4 Systems Studied

The primary focus of this study were the variable temperature X-ray crystal structures solved by Dr. Dong Guo. These structures consisted of the Fe-hydroxo complex at 20, 50, 100, 173, 234, and 296 K, and the corresponding structures of the gallium(III) analogue. The Fe-OH crystal structures had their low and high spin wavefunctions evaluated with UB3LYP/6-311G(d,p) which allowed for the determination of the spin coupling constant at each crystal structure geometry studied. When considering what changes to expect in these VT X-ray structures as a function of temperature, one can expect that there could be effects on the geometry that are solely due to the change in temperature. In the case of complex 1 we expect that there could be additional geometric changes due to the thermal population of additional spin states as the temperature changes. To determine if the thermal induced changes would have an effect on the communication between the

spin centers on its own, the X-ray structures of the gallium analogue were also studied, with the gallium(III) centers replaced with iron(III), to determine the coupling constants. For the sake of clarity, these theoretical structures will be subsequently referred to as the Fe @ Ga geometries in this work. These Fe @ Ga coupling constants allowed us to discern if any observed changes in coupling constants in complex **1** X-ray structures are unique to the changing electronic structure in the Heisenberg spin coupled diiron hydroxo complex as a function of temperature.

Our previous studies where the coupling constant was determined via theoretical methods reported the values resulting from energy calculations using the UMPW1PW91 functional developed by Barone and coworkers⁴² along with a 6-311G(d) basis set. This functional was not used in this work as suitable values for coupling constants were obtainable with B3LYP, which is also a hybrid density functional and had the benefit of being the function which obtained better geometry optimizations in our earlier work.

The high and low spin wavefunctions of C_{2v} geometries optimized with B3LYP and BPW91 were also studied to check for consistency of results between the different functionals and basis sets used, as well as to establish the expected changes in geometry between a low spin state and a high spin state based on the optimized geometries obtained for those states. The optimized geometries derived from the X-ray crystal structures had their high and low spin wavefunctions evaluated only with B3LYP, as it was determined from the results of calculated coupling constants as discussed further on in this chapter suggested this was the best choice.

Coupling constants were determined using the method of Yamaguchi and coworkers,³⁴ were the spin expectation values as determined by the electronic structure program are used in the determination of the coupling constant as discussed in Chapter 1. This methodology offers the advantage of offsetting any destabilization of the low spin broken symmetry state, which is

typically spin contaminated, while incurring minimal costs in effort. There exist other methods for determining the coupling constant,³⁵ but they are typically used in cases where more is known about the electronic structure ahead of time and are usually more specific in application. The Yamaguchi formalism used herein is relatively accurate over a broad range of applications and thus is preferred for the studies performed in this dissertation.

2.3 Results and Discussion

2.3.1 Crystal Structures

The solved crystal structures are pictured in figure 2-4. The crystal data for all twelve X-ray crystal structures obtained by Dr. Dong Guo are summarized in table 2-1. It is noteworthy that the cell dimensions for both the gallium and iron compounds unit cells did increase with temperature, as would be expected due to the thermal expansion of the material.

$[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2](0)$	$CIO_4) \cdot CO(CH_3)_2$ (1)
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 $[Ga_{2}(\mu-OH)(\mu-O_{2}CCH_{3})_{2}(HBpz_{3})_{2}](ClO_{4})\cdot CO(CH_{3})_{2}$ (2)

Temp.	20K	50K	100K	173K	234K	296K	20K	50K	100K	173K	234K	296K
a (Å)	11.503 (2)	11.514 (2)	11.5257(1)	11.5649 (2)	11.6837 (3)	11.7305(1)	11.467 (2)	11.471 (2)	11.4833 (1)	11.5146(1)	11.6007 (2)	11.6591(4)
b (Å)	20.069 (4)	20.119 (4)	20.1447 (3)	20.2059 (4)	20.1318(5)	20.1813(2)	20.007 (4)	20.032 (4)	20.0776 (2)	20.1492 (2)	20.1207 (4)	20.1725 (8)
c (Å)	15.318 (3)	15.339 (3)	15.3714(2)	15.4616(3)	15.5891(4)	15.6982 (2)	15.324 (3)	15.346 (3)	15.3943 (2)	15.4819 (2)	15.6020(3)	15.7192 (7)
ቤ (°)	90.52 (3)	90.59 (3)	90.638 (1)	90.820 (1)	91.741 (1)	92.000 (1)	90.21 (3)	90.14 (3)	90.057 (1)	90.107 (1)	90.910 (10)	91.394 (2)
V (ų)	3536.1 (12)	3553.1 (12)	3568.74 (8)	3612.68 (12)	3665.08(16)	3714.08(7)	3515.7 (12)	3526.3 (12)	3549.26(7)	3591.95(7)	3641.27 (12)	3696.0 (3)
θmax (°)	30.5	30.5	30.5	30.5	30.5	30.5	30.5	30.5	30.5	30.5	30.5	30.5
R1	0.02	0.021	0.024	0.027	0.04	0.039	0.02	0.02	0.024	0.026	0.036	0.034

Table 2-1: X-ray	crystal structure	parameters for	complexes 1	and 2 at all	temperatures
studied.					



Figure 2-4: (*Left*) X-ray crystal structure of complex 1 at 20 K, with the atom in the coordination environment labeled. (*Right*) X-ray crystal structure of complex 2 at 20 K, with the atom in the coordination environment labeled. For both structures, non-hydrogen atoms are displayed as thermal ellipsoids, and the perchlorate anions are omitted for clarity. These atom labels are consistently used for all complex 1 and 2 crystal structures reported herein, and were determined based on the relative orientation of the bridging acetone molecule in the crystal lattice.

Each crystal structure was analyzed and the major bond distances and angles present within the coordination environment of the Iron and Gallium centers were tabulated to show changes in said environment of the metal centers that could correlate to changes in the calculated properties of the complexes. The bond distances are reported in table 2-2 and the bond distances are reported in table 2-3.

	$[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+ \cdot CO(CH_3)_2$ Bond Distances							$[Ga_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+ \cdot CO(CH_3)_2 \text{ Bond Distances}$						
Temp.	20 K	50 K	100 K	173 K	234 K	296 K	20 K	50 K	100 K	173 K	234 K	296 K		
M1-05	1.9412(7)	1.9421(8)	1.9422(8)	1.9422(9)	1.936(1)	1.935(1)	1.9091(9)	1.9091(9)	1.908(1)	1.907(1)	1.902(2)	1.902(1)		
M2-05	1.9418(8)	1.9426(9)	1.9418(8)	1.9430(9)	1.944(1)	1.944(2)	1.9085(9)	1.9086(9)	1.907(1)	1.907(1)	1.909(2)	1.909(2)		
O5-H50	0.83(2)	0.83(2)	0.81(2)	0.78(2)	0.71(3)	0.59(3)	0.76(2)	0.76(2)	0.73(2)	0.69(2)	0.69(3)	0.68(2)		
H50-O100	1.95(2)	1.94(2)	1.96(2)	2.00(2)	2.02(3)	2.15(3)	2.05(2)	2.05(2)	2.10(2)	2.14(2)	2.10(3)	2.11(2)		
M1-01	2.0115(8)	2.0105(9)	2.0096(8)	2.001(1)	2.001(2)	1.999(1)	1.9836(9)	1.9838(9)	1.990(1)	1.982(1)	1.986(2)	1.985(2)		
M1-03	2.0012(8)	2.0007(9)	2.0015(9)	2.011(1)	2.012(2)	2.011(2)	1.9897(9)	1.9896(9)	1.984(1)	1.987(1)	1.989(2)	1.990(2)		
M2-02	2.0119(7)	2.0113(9)	2.0091(8)	2.0033(9)	2.008(1)	2.006(1)	1.9887(9)	1.9882(9)	1.989(1)	1.987(1)	1.989(2)	1.986(1)		
M2-04	2.0044(8)	2.0047(9)	2.0047(8)	2.007(1)	2.003(1)	2.006(1)	1.9902(8)	1.9899(8)	1.9876(9)	1.989(1)	1.988(2)	1.991(2)		
M1-N1	2.0954(9)	2.0955(9)	2.096(1)	2.106(1)	2.114(2)	2.116(2)	2.055(1)	2.055(1)	2.044(1)	2.056(1)	2.062(2)	2.066(2)		
M1-N3	2.1230(9)	2.1226(9)	2.122(1)	2.123(1)	2.117(2)	2.117(2)	2.065(1)	2.064(1)	2.065(1)	2.064(1)	2.059(2)	2.057(2)		
M1-N5	2.105(1)	2.104(1)	2.1058(9)	2.097(1)	2.098(2)	2.100(2)	2.0441(9)	2.044(1)	2.054(1)	2.046(1)	2.048(2)	2.051(2)		
M2-N7	2.1237(9)	2.1238(9)	2.1253(9)	2.095(1)	2.099(2)	2.101(2)	2.0466(9)	2.0464(9)	2.073(1)	2.046(1)	2.045(2)	2.049(2)		
M2-N9	2.1251(9)	2.1251(9)	2.125(1)	2.126(1)	2.123(2)	2.122(2)	2.061(1)	2.062(1)	2.064(1)	2.063(1)	2.065(2)	2.062(2)		
M2-N11	2.0956(9)	2.0952(9)	2.096(1)	2.124(1)	2.112(2)	2.110(2)	2.073(1)	2.073(1)	2.047(1)	2.073(1)	2.058(2)	2.056(2)		
C1-01	1.267(1)	1.266(1)	1.265(1)	1.257(2)	1.254(3)	1.256(2)	1.260(1)	1.258(1)	1.260(2)	1.250(2)	1.248(3)	1.248(3)		
C1-O2	1.268(1)	1.265(1)	1.265(1)	1.261(1)	1.256(2)	1.254(2)	1.259(1)	1.258(1)	1.260(2)	1.251(2)	1.245(3)	1.249(3)		
C3-O3	1.267(1)	1.264(1)	1.260(1)	1.260(2)	1.257(2)	1.255(3)	1.264(1)	1.262(1)	1.253(2)	1.258(2)	1.256(3)	1.254(3)		
C3-O4	1.267(1)	1.265(1)	1.264(1)	1.262(2)	1.258(2)	1.253(2)	1.265(1)	1.265(1)	1.254(2)	1.256(2)	1.251(3)	1.246(3)		

Table 2-2: Bond distances in Angstroms determined by X-ray crystallography for atoms in the coordination environment ofcomplexes 1 (M=Fe) and 2 (M=Ga). Refer to figure 2-4 for atom labels.

	$[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+ \cdot CO(CH_3)_2 \text{ Bond Angles}$							$[Ga_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2]^+ \cdot CO(CH_3)_2 \text{ Bond Angles}$					
Temp.	20K	50K	100K	173K	234K	296K	20K	50K	100K	173K	234K	296K	
M1-05-M2	122.13(3)	122.13(4)	122.24(4)	122.33(5)	122.81(7)	122.92(8)	124.17(4)	124.15(4)	124.28(5)	124.33(6)	124.5(8)	124.56(8)	
01-M1-03	90.26(3)	90.29(3)	90.24(4)	90.32(4)	90.16(6)	90.26(6)	89.90(3)	89.87(3)	89.89(4)	90.02(5)	89.95(7)	89.99(6)	
02-M2-04	90.95(3)	90.96(3)	90.97(3)	91.04(4)	90.94(6)	90.87(6)	90.60(3)	90.63(3)	90.64(4)	90.69(4)	90.63(6)	90.54(6)	
01-C1-O2	124.81(8)	124.81(9)	124.7(1)	124.7(1)	125.3(2)	124.9(2)	125.1(1)	125.1(1)	125.5(1)	124.5(1)	124.9(2)	124.5(2)	
03-C3-O4	124.74(8)	124.71(9)	124.8(1)	124.8(1)	124.6(2)	124.9(2)	125.7(1)	125.6(1)	125.0(1)	125.3(1)	125.5(2)	125.4(2)	
O5-M1-N3	176.38(3)	176.41(3)	176.48(4)	176.51(4)	176.32(6)	176.42(6)	179.27(3)	179.28(4)	179.38(4)	179.37(5)	178.93(7)	178.83(7)	
O5-M2-N9	175.73(3)	175.80(3)	175.86(4)	175.90(4)	175.48(6)	175.40(6)	178.67(3)	178.72(3)	178.81(4)	179.07(5)	178.75(7)	178.50(7)	
N1-M1-N5	86.71(3)	86.79(3)	86.87(4)	86.81(4)	86.47(6)	86.22(6)	88.79(4)	88.80(4)	88.79(4)	88.74(4)	88.43(7)	88.02(7)	
N7-M2-N11	85.80(3)	85.86(3)	85.90(4)	86.05(4)	86.59(6)	86.83(7)	87.52(3)	87.56(4)	87.65(4)	87.81(4)	88.25(7)	88.59(7)	
M1-05-H50	118(1)	118(1)	118(1)	118(1)	123(3)	122(3)	118(2)	118(2)	117(2)	117(2)	119(2)	117(2)	
M2-05-H50	120(1)	120(1)	119(1)	120(1)	113(3)	115(3)	118(2)	118(2)	118(2)	119(2)	116(2)	117(2)	
M1-01-C1	133.99(6)	133.93(7)	133.97(8)	134.92(8)	135.5(1)	135.9(1)	133.86(7)	133.93(8)	133.58(9)	134.9(1)	135.3(2)	135.8(1)	
M1-03-C3	134.00(6)	134.31(7)	134.49(8)	133.84(9)	133.3(1)	133.2(1)	133.51(7)	133.56(7)	134.2(1)	133.7(1)	133.1(2)	133.1(1)	
M2-02-C1	134.13(6)	134.37(7)	134.59(7)	134.43(8)	133.1(1)	133.2(1)	134.36(7)	134.35(8)	133.92(9)	134.6(1)	133.6(1)	133.6(1)	
M2-04-C3	134.72(6)	134.62(7)	134.51(7)	134.94(9)	135.9(1)	135.7(1)	133.52(7)	133.56(7)	134.37(9)	134.3(1)	134.7(1)	134.9(1)	
01-M1-05	93.16(3)	93.11(3)	93.01(3)	93.51(4)	92.97(6)	92.74(6)	93.61(3)	93.56(4)	92.41(4)	93.08(5)	92.57(7)	92.24(6)	
02-M2-05	92.43(3)	92.31(3)	92.23(3)	93.54(4)	93.12(6)	92.91(6)	93.31(3)	93.28(3)	91.95(4)	92.94(5)	92.57(7)	92.4(6)	
03-M1-05	94.07(3)	93.92(3)	93.76(3)	92.87(4)	92.74(6)	92.65(6)	92.57(3)	92.55(3)	93.32(4)	92.24(4)	92.43(7)	92.36(6)	
04-M2-05	93.88(3)	93.85(3)	93.75(3)	92.10(4)	92.04(6)	92.02(6)	92.12(3)	92.11(3)	93.09(4)	91.82(4)	92.12(7)	92.15(6)	
O5-H50- O100	174(2)	174(2)	173(2)	174(2)	174(4)	178(4)	172(2)	172(2)	172(2)	174(2)	171(3)	172(3)	

Table 2-3: Bond angles in degrees determined from X-ray crystallography for atoms in the coordination environment of complex *1* (M=Fe) and *2* (M=Ga). Refer to figure 2-4 for atom labels.

The bond distances with significant trending differences with respect to temperature in the Iron system are the O5-H50 bond distance and the Fe1-O5 bond distance, where O5 is the oxygen and H50 is the proton of the μ -hydroxo group, and the H50-O100 hydrogen bond distance between the μ -hydroxo proton and the associated co-crystallized acetone molecule present in the crystal lattice, as depicted in figure 2-5. Here it can be seen that there is a significant shortening of the O5-Fe1 bond distance at the higher temperatures studied. We can also see that the O5-H50 bond distance shortens at the higher temperature points and there is a complementary lengthening of the H50-O100 hydrogen bond distance in the iron crystal structures. Both of these changes are absent in the gallium(III) analogue.

There is some concern over the validity of bond distances involving hydrogen atoms in X-ray structures, as there are no core electrons that can give a reliable estimate of the location of the proton. It is the case that the reported X-ray determined bond distances are especially shorter for bonds with hydrogen atoms, as the crystal structure looks for the locations of highest electron density, which for bonds involving a hydrogen will be located between the proton and the nucleus of the atom to which it is bound. However, since we are comparing changes in bond distances to a structural model, we feel that any resulting changes in the X-ray determined O5-H50 and H50-O100 bond distances that are not due to the bonds changing in distance in complex **1** relative to complex **2** would be mirrored in both X-ray structures. Therefore, even though the accuracy of the bond distances for these bonds is not to be innately trusted, it is reasonable to conclude that trends in these bond distances due to differences in electronic structure are being faithfully reproduced in their X-ray determined values.

The Fe-N bond distances showed variations amongst individual bond lengths as a function of temperature. However, if one only considers the list of bond lengths as a function of temperature

and does not concern themselves with the identity of each bond distance, there are no significant changes in Fe-N bond distances that are not also present in the Ga-N bond distances found in complex 2, as seen in figure 2-6. The acetate C-O bond distances also showed temperature dependent behavior (refer to supplemental figure A2-1), but a general trending decrease in in the acetate C-O bond distances can still be observed in complex **2**, making this change in bond distance less significant for studying the magneto-structural effects in complex **1**. In fact, apart from the previously mentioned significant changes, the majority of the bond distances that had temperature dependent behavior for the iron exhibited similar changes in the gallium dimer. Examples of this include C-O bond distances along the acetate bridges, as plotted in supplementary figure A2-2.



Figure 2-5: Plots of relevant bond distances concerning the μ -OH bridge in the X-ray crystal structures of complexes *I* and *2* as a function of temperature. The line between data points is added for clarity. Note how complex 1 exhibits significant changes in the O5-H50 bond distance, and that the Fe1-O5 bond distance gets shorter than Fe2 at higher temperatures exceeding the error of the experiment, both of which do not occur for complex 2. Notice also that the H50-O100 bond distance complements the O5-H50 bond distance in complexes 1 and 2. See text for details.



Figure 2-6: Bond distances associated with the metal and Tp capping ligand in complexes *I* and 2. The line between data points is added for clarity. M1 bond distances for both complexes 1 and 2 appear on the left, and M2 bond distances appear on the right. Note how the bond distances appear to swap atom labels for certain temperatures as discussed in the text.

Generally speaking, the bond angles showed few cases where there was a significant change in bond angle value outside the experimental error as one goes from the low to high temperature structures for both complexes. However, but there were more cases of trending differences as a function of temperature in the iron crystal structures that seemed to parallel those found in the gallium crystal structures. It was however the case that the actual values in these parallel bond angle trends routinely were significantly different when comparing equivalent values from complexes **1** and **2**.

A prominent case of differences in observed bond angle as a function of temperature is the M1-O5-M2 bond angle, which for all temperatures is larger for the gallium complex as seen in figure 2-7. The values for the Ga1-O5-Ga2 angle gradually increase over the temperature range studied, but there is no significant difference between the value at 20K and the value at 296 K. In the case of the iron complex, the Fe1-O5-Fe2 angle also increases over the temperature range studied, but in this case there is a significant difference between the lowest and highest temperature values.

Other bond angles which exhibited significant changes in magnitude across the temperature range studied include the O5-Fe-N(*trans*) bond angles, where N is the coordinating nitrogen from the Tp ligand trans to the μ -hydroxo group. There is a parallel trend in the O5-Ga-N(*trans*) bond angles in complex **2**, albeit the change is not of the same magnitude as depicted in figure 2-8. This makes the changes in the O5-Fe-N(*trans*) bond angles unlikely to be a magneto-structural factor in the temperature dependent behavior of complex **1**.



Figure 2-7: M1-O5-M2 bond angle in the X-ray crystal structures as a function of temperature for complexes *1* and *2*. Note the larger change with temperature for complex 1 compared to complex 2.



Figure 2-8: Relevant bond angles involving the Tp cap from the X-ray structures as a function of temperature. On the left, the O5-M-*trans*-N bond angle for complexes 1 and 2 reflecting the linearity of the z axis of the metal. On the right is the *cis*-N-M-*cis*-N bond angles for complexes 1 and 2, reflecting how square the two *cis*-pyrazole rings are to each other. Lines between data points were added for clarity.

Significant changes as a function of temperature were also present in the N(*cis*)-Fe-N(*cis*) bond angles with the nitrogens cis to the μ -hydroxo which give a measure of how well these side groups envelop the metal ions. The temperature dependence of these bond angles is plotted in figure 2-6. It can be seen that there are parallel changes in N(*cis*)-Ga-N(*cis*) bond angles for the gallium analogue, which means this too is not a significant magneto-structural effect.

The Fe-O-C bond angles with the bridging acetate ligands, and the O-Fe-O5 angles between the acetate oxygens and bridging μ -hydroxo oxygen atom exhibited a degree of temperature dependent behavior, but this was not observably different than that observed for complex **2**, as can be observed in the supplemental figures A2-3 and A2-4.

The O1-M1-O3 and O2-M2-O4 angles, which are a measure of the perpendicularity of the two acetate bridges have different values, with the labels on the oxygens appearing to be switched between the gallium and iron complexes and the iron complexes generally having the larger and therefore less perpendicular angles. The O-C-O angles on the acetate bridges show no significant changes across the temperatures studied and no significant difference between the values for the two different complexes.

It is important to note that for many of these trends, most notably the metal Tp nitrogen bond distances and acetate-O-M-O5 bond angles, some of the atoms appear to switch roles in a way as was mentioned above, with atoms assuming bond angles congruous to differently labeled bond angles at different temperatures. These atom labels were meticulously scrutinized and were found to be consistent with the orientation of the hydrogen bound acetone molecule in the X-ray lattice over all temperatures studied for both the Ga₂ and Fe₂ structures. As for an explanation for this role swapping, we can only postulate. Since these crystals were not stored at cryogenic temperatures between the collection of each temperature run, it is possible that much of this role swapping occurred between collection of crystal diffraction data, which implies that at higher temperatures or over time, the ligand environment may fluctuate between two or more stable configurations, which is reflected in the role-swapping observed in the bond distance and angle data obtained by X-ray crystal structures.

For the purposes of isolating which structural changes are potentially a function of the magnetic properties of the Fe-hydroxo system, we can use the gallium structure as a guide to identify changes that are only due to the change in temperature. More specifically, any structural changes in the Fe-hydroxo system that show a corresponding change in the Ga-hydroxo analog must be a consequence on the changes in temperature, and not the unique magnetic properties induced by

the spin-exchange of the Fe-hydroxo system. This allows us to disregard almost all of the changes in bond angles observed as a function of temperature, with the exception of the Fe-O5-Fe bond angle which has much more significant temperature dependent changes than those observed for the Ga analog. By contrast, most of the bond distances with significant changes in the Fe-hydroxo system are likely correlated with magneto-structural effects in the system. In particular, the temperature dependent changes in the Fe – O5 and O5 - H50 bond distances should be investigated for being caused by the magnetic interaction, since we have already established in previous work by the group the importance of the μ -hydroxo bridge to the exchange interaction in this system. Going forward, it is these metrics with changes unique to the Fe-hydroxo system that will be monitored for their possible contributions to changes in the electronic structure of the Fe-hydroxo system.

2.3.2 Comparison of X-ray Structures to Optimized Geometries

A selection of resulting bond distances and angles obtained from the C_{2v} geometry optimizations without acetone present contrasted with X-ray structure values for the same parameters are tabulated in table 2-4. Unlike in the previous studies on this system, both the low spin brokensymmetry state and the high spin state were optimized and studied utilizing both the pure GGA BPW91 functional, and hybrid B3LYP density functional to ensure that the observed trends were not specific to the high spin electronic state. The results of the same bond distances and angles from the B3LYP/6-311G(d,p) optimized X-ray structures compared with the B3LYP derived values from C_{2v} optimized geometries and the values from select X-ray crystal structures are tabulated in table 2-5.
		Fe ₂ 1	B3LYP		Fe ₂ BPW91				
Geometry	6-31G(d) HS	6-31G(d) BS	6-311G** HS	6-311G** BS	6-31G(d) HS	6-31G(d) BS	6-311G** HS	6-311G** BS	
M1-05	1.994	1.983	2.009	1.999	2.010	1.976	2.026	1.994	
M2-O5	1.994	1.983	2.009	1.999	2.010	1.976	2.026	1.994	
O5-H50	0.970	0.970	0.963	0.963	0.977	0.978	0.970	0.971	
M1-01	2.004	2.003	2.014	2.014	2.016	2.016	2.028	2.028	
M1-O3	2.004	2.003	2.014	2.014	2.016	2.016	2.028	2.028	
M2-O2	2.004	2.003	2.014	2.014	2.016	2.016	2.028	2.028	
M2-O4	2.004	2.003	2.014	2.014	2.016	2.016	2.028	2.028	
M1-N1	2.132	2.133	2.136	2.137	2.139	2.143	2.144	2.147	
M1-N3	2.103	2.104	2.106	2.107	2.106	2.099	2.110	2.105	
M1-N5	2.132	2.133	2.136	2.137	2.139	2.143	2.144	2.147	
M2-N7	2.132	2.133	2.136	2.137	2.139	2.143	2.144	2.147	
M2-N9	2.103	2.104	2.106	2.107	2.106	2.099	2.110	2.105	
M2-N11	2.132	2.133	2.136	2.137	2.139	2.143	2.144	2.147	
M1-05-M2	123.5	123.9	124.0	124.3	124.3	124.7	124.7	125.1	
O1-M1-O3	91.2	91.1	90.6	90.5	90.7	90.8	90.0	90.0	
O2-M2-O4	91.2	91.1	90.6	90.5	90.7	90.8	90.0	90.0	
01-M1-05	91.0	91.1	90.4	90.5	90.6	91.3	90.0	90.7	
O2-M2-O5	91.0	91.1	90.4	90.5	90.6	91.3	90.0	90.7	
O3-M1-O5	91.0	91.1	90.4	90.5	90.6	91.3	90.0	90.7	
O4-M2-O5	91.0	91.1	90.4	90.5	90.6	91.3	90.0	90.7	

	Ga ₂ B3LYP		Ga ₂ B	PW91	Fe ₂ X	Fe ₂ X-ray		K-ray
Geometry	6-311G**	6-31G(d)	6-311G**	6-31G(d)	20K	296K	20K	296K
M1-05	1.970	1.970	1.979	1.980	1.9412(7)	1.935(1)	1.9091(9)	1.902(1)
M2-O5	1.970	1.970	1.979	1.980	1.9418(8)	1.944(2)	1.9085(9)	1.909(2)
O5-H50	0.967	0.968	0.969	0.975	0.83(2)	0.59(3)	0.76(2)	0.68(2)
M1-01	2.005	2.004	2.019	2.017	2.0115(8)	1.999(1)	1.9836(9)	1.985(2)
M1-O3	2.005	2.004	2.019	2.017	2.0012(8)	2.011(2)	1.9897(9)	1.990(2)
M2-O2	2.005	2.004	2.019	2.017	2.0119(7)	2.006(1)	1.9887(9)	1.986(1)
M2-O4	2.005	2.004	2.019	2.017	2.0044(8)	2.006(1)	1.9902(8)	1.991(2)
M1-N1	2.092	2.087	2.099	2.093	2.0954(9)	2.116(2)	2.055(1)	2.066(2)
M1-N3	2.057	2.059	2.067	2.068	2.1230(9)	2.117(2)	2.065(1)	2.057(2)
M1-N5	2.092	2.087	2.099	2.093	2.105(1)	2.100(2)	2.0441(9)	2.051(2)
M2-N7	2.092	2.087	2.099	2.093	2.1237(9)	2.101(2)	2.0466(9)	2.049(2)
M2-N9	2.057	2.059	2.067	2.068	2.1251(9)	2.122(2)	2.061(1)	2.062(2)
M2-N11	2.092	2.087	2.099	2.093	2.0956(9)	2.110(2)	2.073(1)	2.056(2)
M1-05-M2	124.9	124.4	124.6	124.2	122.13(3)	122.92(8)	124.17(4)	124.56(8)
O1-M1-O3	91.1	91.1	91.4	91.5	90.26(3)	90.26(6)	89.90(3)	89.99(6)
O2-M2-O4	91.1	91.1	91.4	91.5	90.95(3)	90.87(6)	90.60(3)	90.54(6)
01-M1-05	91.0	91.4	91.3	91.7	93.16(3)	92.74(6)	93.61(3)	92.24(6)
O2-M2-O5	91.0	91.4	91.3	91.7	92.43(3)	92.91(6)	93.31(3)	92.4(6)
O3-M1-O5	91.0	91.4	91.3	91.7	94.07(3)	92.65(6)	92.57(3)	92.36(6)
O4-M2-O5	91.0	91.4	91.3	91.7	93.88(3)	92.02(6)	92.12(3)	92.15(6)

Table 2-4: Selected bond distances (in Angstroms) and angles (in degrees) for atoms in the coordination environment of C_{2v} optimized geometries for all multiplicities, basis sets, and functionals of complex *1* and *2*. Note that these geometry optimizations did not include the acetone molecule. See figure 2-4 for atom labels.

		Fe B3	LYP C _{2v}		Fe B3LYP	X-ray Opt	Fe X-ray	
Geometry	6-31G(d)H	S 6-31G(d) BS	6-311G**HS	5 6-311G**BS	6-311G(d,p)HS	6-311G(d,p)BS	20K	296K
M1-05	1.994	1.983	2.009	1.999	1.990	1.976	1.9412(7)	1.935(1)
M2-05	1.994	1.983	2.009	1.999	1.979	1.965	1.9418(8)	1.944(2)
O5-H50	0.970	0.970	0.963	0.963	0.981	0.983	0.83(2)	0.59(3)
H50-O100	-	-	-	-	1.789	1.773	1.95(2)	2.15(3)
M1-01	2.004	2.003	2.014	2.014	2.019	2.019	2.0115(8)	1.999(1)
M1-O3	2.004	2.003	2.014	2.014	2.027	2.027	2.0012(8)	2.011(2)
M2-O2	2.004	2.003	2.014	2.014	2.023	2.024	2.0119(7)	2.006(1)
M2-O4	2.004	2.003	2.014	2.014	2.013	2.014	2.0044(8)	2.006(1)
M1-N1	2.132	2.133	2.136	2.137	2.135	2.137	2.0954(9)	2.116(2)
M1-N3	2.103	2.104	2.106	2.107	2.121	2.123	2.1230(9)	2.117(2)
M1-N5	2.132	2.133	2.136	2.137	2.132	2.132	2.105(1)	2.100(2)
M2-N7	2.132	2.133	2.136	2.137	2.140	2.141	2.1237(9)	2.101(2)
M2-N9	2.103	2.104	2.106	2.107	2.124	2.126	2.1251(9)	2.122(2)
M2-N11	2.132	2.133	2.136	2.137	2.150	2.151	2.0956(9)	2.110(2)
M1-05-M2	123.5	123.9	124.0	124.3	123.5	123.7	122.13(3)	122.92(8)
01-M1-03	91.2	91.1	90.6	90.5	90.4	90.1	90.26(3)	90.26(6)
O2-M2-O4	91.2	91.1	90.6	90.5	90.8	90.6	90.95(3)	90.87(6)
01-M1-05	91.0	91.1	90.4	90.5	91.0	91.3	93.16(3)	92.74(6)
O2-M2-O5	91.0	91.1	90.4	90.5	91.6	91.8	92.43(3)	92.91(6)
O3-M1-O5	91.0	91.1	90.4	90.5	91.1	91.2	94.07(3)	92.65(6)
O4-M2-O5	91.0	91.1	90.4	90.5	91.1	91.4	93.88(3)	92.02(6)

Table 2-5: Comparison of the optimized X-ray geometries with the analogous C_{2v} optimizations and X-ray structure. Note that $M = Fe^{III}$.

The almost immediate observation that can be made for all structures is that all of the geometry optimizations almost universally over estimate bond distances compared to the X-ray crystal structures. This is not unexpected as the geometry optimizations are calculated in the gas phase as free molecules without accounting for the presence of solvent or neighboring molecules. It goes to follow that a gas phase calculation would not account for the crystal packing stabilization energy that leads to compressed molecular structures in the solid state structures obtained by X-ray crystallography.

Another general trend that is observable across the series of optimized geometries is that for a geometry optimized with a given basis set and multiplicity, the BPW91 optimized geometry will have longer bond distances compared to those obtained with the B3LYP functional. This is attributable to the larger amount of mixing between the metal d-orbitals and the ligand based orbitals in B3LYP, which is an empirical observation in these compounds that will be discussed further in the proceeding discussions on the electronic structure of these complexes. This increased ligand mixing causes stronger interactions between the ligands and metal centers, which results in reduced bond distances as reported in table 2-4. When comparing basis sets, the 6-31G(d) basis set consistently gives smaller bond distances than 6-311G(d,p) for all combinations of functional and electronic state available for study. Finally, just as in the X-ray crystal structures, the bond distances for gallium optimized in a given basis set and functional are universally less than or equal to those of the analogous iron optimized geometryWhen comparing the bond angles around the metal coordination environments for the optimized geometries and X-ray crystal structures, it can be generally stated that the trends in angles are seemingly less significant than the bond distance changes encountered for the optimized geometries when the basis set and functional were varied. This likely has to do with the highly symmetric nature of the optimized geometries offering fewer

degrees of freedom than available in the area of bond distances. This in turn would have the effect of constraining the degree of variance that could be expected when optimizing the different electronic states of a given functional and basis set combination. It should be noted that BPW91 offered larger variance between the different electronic states in the optimized angles of a given basis set and functional.

The most significant amount of variation in the optimized geometries as a whole is the value of the M1-O5-M2 angle, where the general observable trends include that of the larger basis set having larger optimized angle values across all different functionals, systems and electronic states studied, all high spin optimized geometries having smaller angles than their corresponding broken symmetry optimized bond angles, and B3LYP generally having smaller calculated angle values than those with otherwise equivalent electronic states and basis sets but calculated with the BPW91 functional. Most of these trends also apply to the O1-M1-O3 and O2-M2-O4 bond angles, but they are inverted for the other angles mentioned in table 2-4.

The M1-O5-M2 angle was appreciably higher for all the optimized geometries of Iron than was observed in the X-ray crystal structures, and the O-M-O5 angles between the acetate oxygens and the bridging oxygen were larger in all of the X-ray structures than what was optimized. These trends and the previously mentioned differences in bond distances suggest that the X-ray structures has a more compressed structure along the Fe-OH-Fe bond vectors, and a pinching of together of the metal ions as evidenced by the smaller M-OH-M bond angle. The acetate bridges have wider bite angles when referenced to the bridging hydroxo but shorter distances than the optimized geometries, which is consistent with the metals being pinched in by the smaller M-O5-M bond angle. The acetates were similarly close to perpendicular in the optimized and X-ray geometries.

The effect of these differences will be discussed in relation to the differences calculated electronic structure properties of these molecules in the following sections.

When focusing on the optimized crystal structure geometries it can be generally said that the same general statements made concerning the optimized C_{2v} geometries also apply to the optimized crystal structures, with a few differences. An easily observable difference between the optimized X-ray structures and the C_{2v} B3LYP/6-311G(d,p) optimized geometries was the shorter M-O5 bond distances, which surprisingly were more consistent with those obtained for the high spin B3LYP/6-31G(d) geometries. However, it was also the case that the high spin B3LYP/6-31G(d) geometries to our X-ray crystal structures out of the C_{2v} optimized geometries, so this is a welcome result.

The O5-H50 bond distances were also longer for the optimized X-ray structure geometries than in any of the other geometries studied, but this is easily explained by the presence of the hydrogen bonding acetone in the course of the geometry optimization which was absent in the C_{2v} optimized geometries. The fact that this bond distance was longer is also likely to be correlated to the O100-H50 bond distance being substantially shorter in the optimized X-ray structure, likely because the hydrogen bond interaction was allowed to stabilize without the external influences of the crystal lattice that may lengthen the hydrogen bond in our actual crystal structures. This implies that the hydrogen bonding interaction is less significant in the X-ray structures than it could be, given that acetone prefers to be closer in an uninhibited environment as in the geometry optimization.

Apart from the singular differences mentioned before, the most obvious difference between the optimized X-ray geometries and the other geometries studied is that the X-ray and X-ray optimized geometries have asymmetric elements that are symmetric in the C_{2v} geometry. This is not at all surprising since imposing C_{2v} symmetry forces many of the selected bond distances and angles to

be identical by symmetry. What was surprising was that the most prominent asymmetric feature of the X-ray structures, which was the difference between Fe1-O5 and Fe2-O5 bond distances is sort of the reverse of what occurs in the crystal structures relative to the position of the bridging acetone. In the case of the optimized X-ray structures, the O5-Fe2 bond distance is consistently determined to be shorter than the O5-Fe1 bond distance, even though the reverse is true in our obtained crystal structures. The reason for this is unknown at this time.

The same sort of opposite trend is true for the M-O(acetate) bond distances, where M1-O1 and M2-O4 are shorter in the optimized X-ray structure and the opposite is true in our actual X-ray structures. Again this is also observed for the M-N(cis) bond distances where M1-N5 and M2-N7 bond distances are shorter than the M1-N1 and M2-N11 bond distances in the optimized X-ray geometries and longer for the actual X-ray geometries. The odd part about all of these relations is that it seems they are related by a C₂ rotation around the OH bond axis. One can imagine that if the labels were rotated by a C₂ symmetry operation, the bond distance trends would be consistent with the X-ray geometries. It is possible that the coordinated acetone molecule may have flipped over to the other side during the optimization process so that the labels were effectively rotated by a C₂ symmetry optimization, but the optimized geometries have no negative frequencies, so it is not known why this would occur. It is nonetheless an interesting observation.

The bond angles showed much less variation in the optimized X-ray geometries when compared with the X-ray crystal structures. It is noteworthy that the optimized X-ray structures have M1-O5-M2 bond angles intermediate between the X-ray structures and the C_{2v} optimized geometries. This could be due to the optimized X-ray geometries not having the rigid symmetry restrictions that are found in their C_{2v} brethren, but it does not seem likely considering that the acetone was included in the optimized X-ray structures but not the C_{2v} structures. It could just be that since the

 C_{2v} geometries were optimized with tight optimization criteria, the angles were better able to optimize towards their ideal value which were not reached in the X-ray geometry optimizations since they were run with normal optimization criteria. Similar arguments can be made for the O(acetate)-M-O5 bond angles which in the optimized X-ray geometries are intermediate to the C_{2v} optimized geometries and the X-ray crystal structures.

Regardless of these trifling differences between the optimized geometries and the X-ray crystal structure, it was extremely gratifying to obtain an optimized geometry which bore a great resemblance to our observed crystal structures, as it will serve as an effective bridge between our subsequent studies on the X-ray structures and the same studies on the C_{2v} optimized geometries.

2.3.3 Computational Determination of the Spin-coupling Constant as a Function of Temperature.

It is well known that the Heisenberg-Dirac-Van Vleck Spin Hamiltonian is an empirical explanation of the energetic ordering of different spin states in spin coupled systems.⁴ The energetic spacing of these different spin states is determined by the spin coupling constant J. Experimentally, this quantity is determined using bulk temperature dependent magnetic susceptibility measurements or using EPR techniques.⁴³ By performing electronic structure calculations on X-ray structures or optimized geometries, it is also possible to determine the spin-coupling constant using computational chemistry methods. It was our intent that by using electronic structure theory to determine coupling constants for our variable temperature X-ray crystal structures, the resulting values would function as a useful guide for determining the amount of communication between the spin centers as a function of temperature. It may seem nonsensical to determine different coupling constants for different temperatures when in theory this is a

temperature independent property of the systems studied, but it still is an effective indication of the amount of electronic communication between the spin centers, and thus is a useful tool in determining if the observed structural changes have corresponding consequences on the electronic structure of these complexes.

Electronic coupling constants were determined using B3LYP for all temperatures for the Fe₂hydroxo system. This required the high spin energy as determined from a single point energy calculation and the corresponding low spin energy as determined from a broken-symmetry single point energy calculation, as well as the two spin expectation values of those two wavefunction as is required in the Yamaguchi method³³ for the determination of the spin coupling constant.

To ensure the proper broken symmetry state had been obtained by way of either the spin-flip methodology of ORCA or the fragment based guess of Gaussian 09, the spin and charge density on the two iron(III) centers was routinely monitored via the Mulliken population analysis.²⁸ A proper broken symmetry singlet state will have a spin density of with an absolute value over 4 on each metal center, with one center having positive alpha spin density and the other center possessing negative beta spin density. Values less than this result in an inadequate singlet state, which can result in an artificially stabilized singlet state in the case of BPW91, or an artificially destabilized singlet state in the case of B3LYP. This was encountered when the complex 1 X-ray structures sans acetone were studied with the BPW91 functional, resulting in only three of the temperatures studied having adequate spin coupling values when determined with BPW91. The case of the destabilized singlets determined from bad broken symmetry calculations with B3LYP was discussed in Chapter 1.

The spin expectation value has also been found to be a suitably good indicator of the quality of a broken symmetry state. It has been observed in the course of this research that a good broken

symmetry state has a spin expectation value close to 5. This is a high amount of spin contamination considering the theoretical value for a singlet is zero. However this amount of spin contamination is expected due to the large number of unpaired electrons in this molecule. In this way, much like how a good broken-symmetry state will have a high spin density value on the metal centers, it will also have a large amount of spin contamination. Broken symmetry states with lower than expected spin expectation values were consistently found to also lack the required spin density on the metal centers as was previously reported by our group.⁴

In addition to calculating the spin coupling constant for the X-ray structures of complex 1 using the Yamaguchi method as previously mentioned, the theoretical coupling constants of the Fe @ Ga structures including and excluding acetone for all temperatures using the B3LYP functional. This was done as an added control, to the analysis of crystal structures of complex 2, to make sure that any of the temperature dependent changes observed in the gallium crystal structures and inherent in the Iron crystal structures would not greatly influence spin coupling constant and thus the magnetic communication between the spin centers. It should be noted that only the B3LYP functional was employed to determine the coupling constants of the complex 1 X-ray crystal structures when the acetone was included and all of the Fe @ Ga geometries studied. This is due to the complications regarding the instability of the BPW91 broken symmetry state. It was figured that if difficulties were encountered with the simplest system that was closest to the calculated equilibrium geometry for complex 1, that there would be more problems when the acetone was added to the system and when the Fe @ Ga geometries were studied, so BPW91 studies were not attempted for these systems.

The relevant results of the calculations on the high and low spin B3LYP wavefunctions and the calculated coupling constants on the acetone free X-ray structures are shown in table 2-6, and the

results of these calculations including the acetone molecule are shown in table 2-7. Both results are plotted as a function of temperature in figure 2-9.

The prominent result present in all of these calculations on the variable temperature X-ray structures for complex **1** is that as the temperature increases, the calculated coupling constant decreases for both cases with and without the acetone present as seen in figure 2-9. Furthermore, the decrease is non-linear, occurring noticeably above 100 K. It is also easy to see that the calculated coupling constant for the Fe @ Ga geometries is relatively constant for the studies both including and excluding acetone. This can be taken to mean that the geometric changes occurring in the crystal structure of complex **2** as a function of temperature, which should also be inherently present in complex **1**, are not resulting in substantial changes in the communication between the



Figure 2-9: The UB3LYP/6-311G(d,p) determined *J* **values for X-ray crystal structures of complex** *1* **and Fe** @ **Ga.** Both the acetone-omitted and acetone included structures were analyzed and the pertinent data for this analysis is reported in tables 2-6 and 2-7.

		Fe X-r	Fe @ Ga BS Values					
Temperature (K)	S ² ₁	S ² 11	ΔE _{HS-BS} (cm ⁻¹)	<i>J</i> (cm⁻¹)	S ² ₁	S ² 11	ΔE _{HS-BS} (cm ⁻¹)	<i>J</i> (cm⁻¹)
20	4.97	30.01	501.9	40.1	4.97	30.01	579.9	46.3
50	4.97	30.01	500.5	40.0	4.97	30.01	578.0	46.2
100	4.97	30.01	496.8	39.7	4.97	30.01	570.4	45.6
173	4.97	30.01	486.6	38.9	4.97	30.01	562.6	44.9
234	4.97	30.01	483.4	38.6	4.97	30.01	577.5	46.1
296	4.97	30.01	448.2	35.8	4.97	30.01	575.2	45.9
Previous Result*	4.97	30.01	401.4	32.1				

Table 2-6: UB3LYP/6-311G(d,p) values for the determination of J determined at the Xray crystal structure geometry excluding the acetone in the crystal lattice. The previous result was obtained for a B3LYP optimized C_{2v} geometry as will be discussed in the text.

		Fe X-ı	ay BS Values		Fe @ Ga BS Values			
Temperature (K)	S ² ₁	S ² 11	ΔE _{HS-BS} (cm ⁻¹)	<i>J</i> (cm⁻¹)	S ² ₁	S ² 11	ΔE _{Hs-Bs} (cm ⁻¹)	<i>J</i> (cm ⁻¹)
20	4.97	30.01	553.2	44.2	4.96	30.01	579.9	50.2
50	4.97	30.01	552.7	44.1	4.96	30.01	578.0	50.0
100	4.97	30.01	545.5	43.6	4.96	30.01	570.4	49.0
173	4.97	30.01	531.0	42.4	4.96	30.01	562.6	48.1
234	4.97	30.01	518.9	41.4	4.96	30.01	577.5	49.4
296	4.97	30.01	474.5	37.9	4.96	30.01	575.2	48.9

Table 2-7: UB3LYP/6-311G(d,p) values for the determination of J determined at the Xray Crystal structure geometries of complex I and the Fe @ Ga geometries including the acetone in the crystal lattice. Note the roughly 4 cm⁻¹ increase in coupling constant for the Fe @ Ga and low temperature Fe crystal structure geometries when compared to the analogous values with the acetone omitted.

spin centers. To phrase it another way, the observed temperature dependent structural changes in complex 2 do not make a significant impact on the calculated coupling constant value. This substantiates the argument that structural changes in the crystal structures of complex 1 can only be attributed to magneto-structural effects if those same changes are absent in the crystal structures of complex 2. With this conclusion in hand, it was decided to focus the analysis on the changes in

electronic structure solely on the diiron hydroxo crystal structures, as only those structures show meaningful changes in the spin-related properties of the system as a function of temperature. Furthermore, we can now look to rationalize the changes in the spin coupling as a function of temperature in terms of the significant magneto-structural changes listed in the previous section.

An equally important result of this exercise is that the inclusion of the acetone in the electronic structure calculations increases the calculated coupling constant universally for both complex 1 Xray structures and Fe @ Ga structures. This is likely due to the acetone being able to draw some of the H50 electron density away from O5 and towards the O100 when it is included. This has the effect of effectively increasing the O5-H50 bond distance from the perspective of the electron density when compared to the same O5-H50 bond distance without the acetone present in the model. As we have already seen in our previously published results,⁷ the interaction of the H50 proton with the O5 oxygen lowers the coupling constant. It is therefore reasonable to deduce that since the presence of the acetone in the model weakens this O5-H50 interaction by pulling electron density from the bond, it should strengthen the coupling. Indeed the O5-H50 bond distance is one of the most significant temperature dependent structural changes in complex 1 that is absent in complex 2, and we can see that as the bond shortens with temperature, the coupling constant consistently decreases. Therefore, this pseudo-lengthening of the O5-H50 bond from the presence of acetone in the electronic structure calculations seems a reasonable explanation for the inclusion of acetone increasing the calculated coupling constants.

Since the interaction with acetone makes observable changes in the degree of spin coupling in the X-ray structures, one would think that the results with the included acetone would be the correct ones and should be the ones we focus on in the subsequent studies. Certainly this should be the case when thinking about correlating other results to the calculated coupling constants. However,

there are reasons why the omission of acetone in the modeling of certain aspects of complex **1** might not be deleterious. For one, the presence of acetone made it difficult to analyze the broken symmetry wavefunctions as it introduced a good deal of asymmetry to the electronic structure that is not present when the acetone is removed. We also expected the studies on the mechanisms of spin coupling would not be greatly influenced by the absence of the acetone since we are only concerned with d-orbitals on the metals. Initial observation revealed that the calculated coupling constants evaluated in the absence of acetone were closer to the experimental value of 34 cm⁻¹ reported by Lippard and coworkers.¹ Therefore since the trends in calculated coupling constant are the same with and without the inclusion of acetone, and since it allows the facile study of the electronic structure, many subsequent studies of the electronic structure of these complexes will focus on the acetone excluded X-ray structures.

The calculated coupling constant values for the VT X-ray structures using the BPW91 functional suffered problems with the convergence of the broken symmetry state, with half of the temperature values having singlet energies that were excessively low and lower than the expected spin density values on the Fe centers. This resulted in large computed values for the spin-coupling constant, with the relevant data summarized in table 2-8. What is noteworthy is that even for the correctly determined broken symmetry states having spin density values comparable to those obtained in B3LYP, the calculated spin coupling constants are usually two to three times the magnitude of those determined for B3LYP and the experimental value as determined by Lippard and coworkers.¹

		BPW91	B3LYP Derived Values					
Temperature (K)	S ² ₁	S ² ₁₁	ΔE _{Hs-Bs} (cm ⁻¹)	<i>J</i> (cm⁻¹)	S ² ₁	S ² ₁₁	ΔE _{HS-Bs} (cm ⁻¹)	<i>J</i> (cm⁻¹)
20	1.18	30.01	4360.6	302.5	4.97	30.01	501.9	40.1
50	1.18	30.01	4336.4	300.8	4.97	30.01	500.5	40.0
100	4.75	30.01	1584.6	125.5	4.97	30.01	496.8	39.7
173	4.76	30.01	1557.2	123.3	4.97	30.01	486.6	38.9
234	1.17	30.01	4515.1	313.1	4.97	30.01	483.4	38.6
296	4.76	30.01	1495.1	118.4	4.97	30.01	448.2	35.8
Previous Result*					4.97	30.01	401.4	32.1

Table 2-8: Comparison of UBPW91/6-311G(d,p) and UB3LYP/6-311G(d,p) values for the determination of J at the complex I X-ray crystal structure geometries excluding the acetone in the crystal lattice. The values in red highlight the telltale signs of improper broken symmetry states and the corresponding inflated J values that result.

The reasons for this could be the propensity of pure density functionals to over stabilize singlet energies,³⁶ resulting in a larger energy difference and a larger coupling constant. Alternatively, the larger coupling constants could be symptomatic of differences in the modeled electronic structure such as decreased mixing of metal and peripheral ligand electron density that cause a larger amount of spin coupling than the actual electronic structure of the complex or that modeled with the B3LYP density functional.

2.3.4 Calculated *J* for Optimized Geometries

An effective comparison of the geometric differences between the low and high spin optimized C_{2v} structures for both basis sets in each of the two functionals was obtained, the results of which are discussed previously and summarized in table 2-9. It was observed that low spin optimized geometries in both basis sets had higher calculated coupling constants than that calculated for the corresponding high spin optimized geometries. This is consistent with the notion of the bond distances, with M1-O5 and M2-O5 in particular, being shorter in the broken symmetry optimized

geometries. Fortunately, the problem of convergence in the broken symmetry wavefunctions modeled with BPW91 was not encountered on the analysis of the optimized geometries. It was also found that the optimized geometries suffered a similar overestimation of the coupling constant in BPW91. Since the bond distances in the BPW91 optimized geometries are almost universally longer than their counterparts in B3LYP for a given basis set and electronic state, the differences in geometry are not responsible for this large increase in calculated coupling constant. Instead this is likely an intrinsic property of the pure functional to over-stabilize low spin states compared to the hybrid B3LYP density functional.³⁶

	BF	PW91/6-311	IG(d,p) Electron	ic States	B3LYP/6-311G(d,p) Electronic States			
Optimized Geometry	BS S ²	HS S ²	E(HS) - E(BS)	BPW91 <i>J</i> (cm ⁻¹)	BS S ²	HS S ²	E(HS) - E(BS)	B3LYP J (cm ⁻¹)
B3LYP/6-311G(d,p) BS	4.827	30.008	1164.64	92.50	4.975	30.011	387.66	30.97
B3LYP/6-311G(d,p) HS	4.836	30.008	1102.42	87.59	4.977	30.011	364.86	29.15
B3LYP/6-31G(d) BS	4.806	30.008	1294.15	102.70	4.973	30.011	426.92	34.10
B3LYP/6-31G(d) HS	4.817	30.008	1223.53	97.14	4.975	30.011	401.38	32.06
BPW91/6-311G(d,p) BS	4.824	30.008	1192.74	94.72	4.975	30.011	402.03	32.12
BPW91/6-311G(d,p) HS	4.853	30.008	997.05	79.27	4.978	30.011	335.18	26.78
BPW91/6-31G(d) BS	4.800	30.008	1337.54	106.12	4.972	30.011	444.96	35.54
BPW91/6-31G(d) HS	4.837	30.008	1101.85	87.55	4.977	30.011	367.29	29.34

Table 2-9: The UB3LYP/6-311G(d,p) and UBPW91/6-311G(d,p) values for the determination of J at all of the C_{2v} optimized geometries of complex 1 sans acetone. Compare this to the experimentally determined value of 34 cm⁻¹.

		BPW91	Electronic State	es	B3LYP Electronic States			
Optimized Geometry	BS S ²	HS S ²	E(HS) - E(BS)	BPW91 <i>J</i> (cm ⁻¹)	BS S ²	HS S ²	E(HS) - E(BS)	B3LYP J (cm ⁻¹)
B3LYP/6-311G(d,p)	4.750	30.008	1435.15	113.64	4.974	30.011	430.06	34.35
B3LYP/6-31G(d)	4.744	30.008	1457.16	115.35	4.974	30.011	433.77	34.65
BPW91/6-311G(d,p)	4.777	30.008	1326.00	105.11	4.975	30.011	404.18	32.29
BPW91/6-31G(d)	4.773	30.008	1341.98	106.36	4.975	30.011	406.38	32.46

Table 2-10: The UB3LYP/6-311G(d,p) and UBPW91/6-311G(d,p) values for the determination of J for Fe @ Ga at all of the C_{2v} optimized geometries of complex 2 sans acetone.

This was confirmed when the B3LYP optimized geometries were then studied with the necessary BPW91 single point energy calculations to determine BPW91 spin coupling constants at the B3LYP geometries. The converse procedure was used to evaluate B3LYP coupling constants at BPW91 geometries, with the results being very consistent to those obtained with optimized geometries from the same functional as that used for determining the coupling constant.

The coupling constants were also calculated on Fe @ Ga optimized structures for the range of functionals and basis sets already explored. As these were gallium optimized geometries, there was no high or low spin state to optimize. The values used to determine the coupling constants as well as the coupling constants themselves are listed in table 2-10. When looking at the calculated values, one can see that there is very little variation in the calculated coupling constants within any geometry studied with a particular functional. It is also interesting that for B3LYP, the calculated coupling constants are all within the acceptable range when compared to the previously experimentally determined value by Lippard and coworkers. The calculated coupling constants of the Fe @ Ga structures are almost all higher for a given basis set and functional than either the high or low spin optimized Fe geometries. The exception to this rule is that the BPW91/6-31G(d)optimized gallium geometry that does have lower calculated coupling constants than the LS optimized BPW91/6-31G(d) Fe complex when evaluated with the B3LYP functional. The reason for this is unknown, but since this is a case of the energy calculation being triply off equilibrium as it is Fe substituted for Ga, with a changed functional and a changed basis set compared to how the geometry was optimized, one should not read too much into this anomalous result.

These C_{2v} optimized geometries are also helpful in that the variance between high spin and low spin optimized geometries can provide an approximation to the hypothetical range of geometric

distortion for the molecule in an ideal setting void of external forces on the complex. By studying the electronic structure at these two geometries, one can obtain an estimate for determining what constitutes a significant variation in calculated coupling constants, as such a significant variation would be outside the range of coupling constants possible to be determined using optimized geometries. To figure out this so called uncertainty we followed the suggestion of Ruiz and coworkers that an estimate of the uncertainty of the calculated coupling constant could be determined using this possible range in coupling constant values.³⁷ As we have already seen for this system, the smallest coupling constant that one can obtain is calculated using values obtained only from the optimized high spin geometry of the system of interest for a given functional and basis set. Since the coupling constant is directly proportional to the difference between the high spin and low spin energies of the system, by using values to get the largest energy difference between these high spin and low spin energies one should obtain the largest value for the coupling constant. This is achieved by still using the high spin energy values from the optimized high spin geometry, but using the now stabilized low spin energy and its accompanying spin expectation value taken from the low spin optimized geometry. It is suggested that by looking at the variance in the two coupling constants calculated in this way, one can get a reasonable estimate of the overall uncertainty associated with the calculated coupling constants, which in this case is on the order of 2 cm⁻¹.

Spin coupling constants were obtained with UB3LYP/6-311G(d,p) for two sets of input geometries derived from the low spin and high spin X-ray derived optimized geometries as described in the preceding section. The only difference between the two sets is that the acetone molecule was omitted from one of the geometry sets before the electronic structure calculations

were performed to determine the coupling constant. These calculated coupling constants and relevant values for the calculation of said coupling constants are reported in table 2-11.

	B3LYP Electronic States								
Optimized Geometry	BS S ²	HS S ²	E _{HS} - E _{BS}	B3LYP J (cm ⁻¹)					
LS w/ acetone	4.966	30.011	500.99	40.01					
HS w/ acetone	4.968	30.011	455.89	36.41					
LS w/o acetone	4.975	30.011	441.54	35.27					
HS w/o acetone	4.968	30.011	405.17	32.36					

Table 2-11: The UB3LYP/6-311G(d,p) values for the determination of J at all of the optimized X-ray structure geometries of complex 1 both with and without acetone. Compare these to the experimentally determined value of 34 cm⁻¹.

We see similar albeit slightly elevated values for the coupling constant at both low and high spin geometries calculated in the absence of acetone when compared to the analogous UB3LYP/6- $311G(d,p) C_{2v}$ optimized geometries previously reported. This confirms the suspicion that the C_{2v} optimized geometries are an appropriate model of the diiron hydroxo system in the absence of the coordinating acetone. The reason for the slight elevation of the calculated coupling constants for this system compared to the C_{2v} analogous geometry is likely due to the improved orbital overlap afforded by the shorter bond distances in the X-ray based optimized geometries.

The calculated coupling constants have their values increased when the acetone is included in the otherwise identical geometry. It is notable and likely coincidental that the calculated coupling constants for the low and high spin optimized geometries including acetone greatly match the calculated coupling constants of the complex **1** X-ray structures without the acetone at the lowest and highest temperatures studied. The reasons for the inclusion of the acetone increasing the coupling constant have already been discussed for the case of the X-ray structures and the same

logic applies in this case as well. What is noteworthy is that the range of calculated coupling constants between the low and high spin optimized geometries does increase when the acetone is included.

By surveying the changes in coupling constant values determined over the range of geometry distortions afforded by the plethora of optimized geometries studied, and comparing those results to the variable temperature X-ray crystal structure values, we are able to show that the calculated coupling constant is a useful tool to study the changes in the communication between spin centers in the Fe-hydroxo system. However, to gain more insight as to what types of communication are changing in the system than what is possible by examining the geometric changes as a function of temperature, a more detailed analysis of the molecular coupling mechanisms is required, as described below.

2.3.5 Study of the Molecular Orbital Mechanisms of Spin Exchange in the Fe₂ µ-OH System

As was the case in previous studies by our research group, two primary methods were used to elucidate the orbital mechanisms that significantly contribute to the spin coupling within these molecules.

The first is the Hay-Hoffman method^{7,38} wherein pairs of interacting orbitals, one on each of the two spin centers, are found in both symmetric (same orbital phases) and anti-symmetric combinations. The square of this energy difference is proportional to the relative contribution to the spin coupling provided by the orbitals of that type. This methodology has been used in the past as a way to determine electronic coupling constants and assess other forms of electronic communication.³⁹ Since spin coupling constants for these systems depend on electronic

communication between the spin bearing d-orbitals of the metal ions, this concept was used as a justification for studying the relative contributions to spin coupling by the extension of more strongly interacting d-orbitals should have larger contributions to the spin coupling constant. It has the chief disadvantage that the molecule and its electronic state need to be relatively symmetric such that the orbital nature on each spin center is the same. This is why only high spin states can be used for these Hay-Hoffman studies as only they have an approximately symmetric electronic state in these systems. While it is convenient that the Fe₂-hydroxo system does indeed satisfy this requirement for symmetric spin coupled sites, it is still the case that the nature of the interacting orbitals must always be the same for this method. This means that only the contributions between magnetic orbitals of the same type can be assessed. For example, even though previous results found significant contributions to the spin coupling between the two irons from $d_{z^2}-d_{z^2}$, $d_{z^2}-d_{xy}$, and $d_{xy}-d_{z^2}$ interactions, only the contributions of the $d_{z^2}-d_{z^2}$ interaction can be assessed by the Hay-Hoffman method. The flip side of this method is that while spatial position of orbitals is very sensitive to subtle geometric changes, the energy of those orbitals is relatively unaffected by small geometric changes. This means that for the study of the non-optimized geometries that are present in the X-ray crystal structures, the Hay-Hoffman method could have an advantage in accurately assessing the contributions of these homogenous orbital coupling pathways.

The second method for the determination of the spin coupling pathways is the determination of the orbital overlap of Natural Magnetic Orbitals (NMOs) as described by Kahn and coworkers.^{7,40} These natural magnetic orbitals are comprised of occupied molecular orbitals from the broken-symmetry single point energy calculations. Since the spin on one of the Fe centers is alpha (α), and the spin on the opposite Fe center is beta (β), then the magnetic orbitals that can contribute to the spin coupling are the highest occupied molecular orbitals where the orbital is predominantly

based on the metal and is of a d-orbital morphology. These orbitals will occur in pairs where the alpha orbital on one metal will have a partner on the other metal that is usually but not necessarily the same numbered beta orbital (meaning both orbitals are ranked the same by energetic ordering). The contributions of these spin orbitals to the spin coupling have been found to be proportional to the orbital overlap between these natural magnetic orbital pairs.

It is important to note that ideally, molecular orbitals are by definition orthonormal such that the orbital overlap between two spatial molecular orbitals is by definition zero. However, since our calculations employ unrestricted DFT, the (now spin) molecular orbitals are no longer eigenfunctions of the spin operator. To put this in more understandable terms, the energy and corresponding spin orbitals of the alpha electrons are solved completely independently of the beta electrons and the total energetics of the system are determined as the sum of the independently solved alpha and beta electronic systems. This means that there is no requirement for the alpha and beta spin orbitals to be orthogonal to each other, such that if an alpha and beta spin orbital occupy the same space on a molecule, they are likely to have a non-zero value for their overlap. It is this non-zero overlap value that we depend on for the determination of the magnitude of spin coupling contribution between a pair of NMOs.

This method has the advantage that the overlaps can be calculated between any alpha and beta orbital, thus providing for the assessment of the contributions from magnetic orbitals that are not of the same d-orbital character. This allows for the assessment of more potential pathways of magnetic coupling that those studied by the Hay-Hoffman method. The disadvantage of using this method is that the spatial orientation of these natural magnetic orbitals is very sensitive to the small perturbations in geometry that make the X-ray crystal structures less ideal compared to the very ideal C_{2v} symmetric optimized systems studied herein. Hence the inclusion of the C_{2v} optimized

geometries in conjunction with the X-ray crystal structures for our study on the molecular orbital mechanisms for the spin coupling in the Fe-hydroxo system.

2.3.6 Hay-Hoffman Coupling Interaction Studies

The first step in the Hay-Hoffman analysis is the selection of the symmetric and anti-symmetric interacting orbital pairs from the single point energy calculation on the high-spin state. Fortunately, for this study, this is a relatively trivial task as orbital pairs can either be bonding or anti-bonding in nature and still give satisfactory results about the degree of contribution to the spin coupling. The frontier orbital model would suggest that if a simple atomic orbital basis set was used, the occupied orbitals with d-character would be the ten highest occupied molecular orbitals which would all be alpha in character, with each of the five types of d-orbitals having a symmetric and antisymmetric pairing. With the larger 6-311G(d,p) basis set employed for our single point energy calculations, the ten highest occupied molecular orbitals have a large amount of ligand character mixing into our expected d-orbital pairs which makes the identification of the d-orbital character of these molecular orbitals difficult. Fortunately, the antibonding lowest unoccupied beta orbitals possess almost entirely metal d-orbital character. It is thus easy to identify and pair the orbitals together into symmetric and antisymmetric interacting pairs. Since these are unoccupied orbitals, they have more nodes than would be expected for the interacting spin orbitals, but their energy differences are theoretically equivalent to those one would obtain from the alpha orbitals because the energy difference between symmetric and anti-symmetric d-orbital sets is due to the relative amount of interaction between the mixing orbitals, since the d-orbitals are to a rough estimate isoenergetic. Since the stabilization energy of bonding orbitals arising from an interaction is equivalent to the destabilization energy of the antibonding orbitals arising from the same

interaction, the magnitude of the calculated energy differences should be identical for the occupied alpha and unoccupied beta orbitals. Therefore, it was our general procedure for this study to look at the ten lowest unoccupied beta molecular orbitals and establish the symmetric and antisymmetric pairs as the first order of business for this procedure.

While knowing where to find the d-orbital pairs is not difficult, there is potential for the identification of the symmetric and anti-symmetric pairs to be confounding. Fortunately, this is not the case for the Fe-hydroxo system. In all cases the exact character of the d-orbitals was easily assigned due to the orbitals conforming to an easily determined coordinate axes system relative to each metal center, as depicted in figure 2-4. Examples of these orbital pairs are given in figures 2-10 and 2-11 for B3LYP and BPW91 derived orbitals. For both the B3LYP and BPW91 HS single point energy calculations, orbital pairs were able to be obtained for all of the optimized geometries studied and all twelve of the VT X-ray structures studied. The squared energy differences as derived from the orbital pairs were determined as these quantities are proportional to the contributions to spin coupling. These squared energy values are plotted in figure 2-12 for the C_{2v} optimized geometries.



Figure 2-10: Visualizations of the ten lowest unoccupied beta orbitals from the high spin UB3LYP/6-311G(d,p) wavefunction calculated at the UB3LYP/6-311G(d,p) high spin optimized geometry. Symmetric and Antisymmetric combinations of the d-orbitals are paired into each table entry. The orbitals are plotted with an isovalue of 0.02.



Figure 2-11: Visualizations of thet en lowest unoccupied beta orbitals from the high spin UBPW91/6-311G(d,p) wavefunction calculated at the UBPW91/6-311G(d,p) high spin optimized geometry. Symmetric and Antisymmetric combinations of the d-orbitals are paired into each table entry. The orbitals are plotted with an isovalue of 0.02.



Figure 2-12: Hay-Hoffman coupling contributions from UB3LYP/6-311G(d,p) and UBPW91/6-311G(d,p) for geometries optimized with the same functional and the indicated basis set and multiplicity.

2.3.7 Discussion of Hay-Hoffman Results for Optimized Geometries

The Hay-Hoffman relative coupling contributions were determined from the high spin state wavefunctions studied with a 6-311G(d,p) basis set using either the B3LYP or BPW91 functionals and calculated for select C_{2v} optimized geometries. Geometries that were optimized with all permutations of high or low spin state as well as 6-31G(d) or 6-311G(d,p) basis sets were studied; the resulting spin coupling contributions are presented in figures 2-12 which will be considered further on in this discussion.

The first observation that can be made is that for the most part, the relative contributions of all of the coupling pathways determined for the spin coupling in the C_{2v} BPW91/6-31G(d) optimized geometry are consistent with those indicated in our previous work. This is highly gratifying as we have independently verified the relative significance of the symmetric d-orbital interactions on the spin exchange using the Hay-Hoffman method. We know from our calculated coupling constants that the broken symmetry states we obtained in this work are not precisely consistent with those obtained for the same geometries that we previously studied, as is evidenced by our differing calculated exchange coupling values. The similarity in the calculated Hay-Hoffman coupling contributions both generally and in particular with the ordering of the BPW91/6-311G(d,p) High spin orbitals studied at the BPW91/6-31G(d) HS geometry indicates that the calculated high spin electronic wavefunctions are mostly conserved between this work and our former work as the orbitals energy spacing are also similar.

When considering the spin coupling contributions, all combinations of functional and basis set show consistent behavior between low spin and high spin optimized geometries. As a general rule for all B3LYP and BPW91 optimized geometries studied with their corresponding functionals, the largest contribution was from the d_{z2} orbitals. The next significant pathway as determined with B3LYP wavefunctions was the d_{x2-y2} orbital interactions, followed by a lesser contribution from the d_{xz} orbitals. The contributions from d_{x2-y2} and d_{xz} as determined by BPW91 were roughly equivalent. It was then the case that for both functionals the least contributions came from d_{yz} and d_{xy} in descending order. The only time the magnitude of any of these pathways coupling contributions changed relative to other pathways for different geometries was for the d_{x2-y2} and d_{xz} orbital pairs as determined from BPW91, where d_{xz} was less significant at high spin geometries, and more significant at low spin geometries when compared with d_{x2-y2} . When looking for trends in terms of the values of the coupling contributions, we can compare the contributions between low spin and high spin geometries, between basis sets used to optimize the geometry and the functional used to study the wavefunction. When comparing the low spin and high spin optimized geometries, the only significant are increases in contributions from d_{xz} and slight increases in contributions from d_{z2} and d_{yz} . The d_{x2-y2} and d_{xy} orbital contributions remain essentially unchanged between the high spin and low spin optimized geometries. When looking at changes in basis set used for optimizing, it is universally true that coupling contributions are overall larger when a smaller basis set is used for optimizing the structure. This is likely due to the longer bond lengths in the larger basis sets. Finally, when comparing the functionals used to study the geometries, B3LYP gave larger contributions from d_{z2} , d_{x2-y2} , and d_{xz} compared to those obtained with BPW91. Contributions had similar trends but not identical values for geometries studied in the opposite functional from that in which they were optimized.

The optimized X-ray structures were also investigated to determine the d-orbital pathway contributions to the spin coupling using the Hay-Hoffman method. These optimized crystal structure geometries are intermediate between the X-ray structures and the previously discussed C_{2v} optimized geometries. Therefore by obtaining the d-orbital coupling contributions at these geometries, we can be sure there is consistency between results for the C_{2v} optimized geometries and the subsequently discussed X-ray structure results.

The coupling contributions from the d-orbital coupling pathways were determined for both the low spin and high spin B3LYP/6-311G(d,p) optimized geometries. To test as to whether or not the presence of acetone has an effect on the calculated coupling mechanisms, the coupling contributions were determined with the acetone included and omitted from the input geometries. The results of these calculations are presented in figure 2-13.



Figure 2-13: Hay-Hoffman coupling contributions from UB3LYP/6-311G(d,p) for X-ray structure optimized geometries optimized with the same functional and the indicated multiplicity.

When comparing the calculated coupling contributions for the optimized X-ray geometries sans acetone with those obtained for the C_{2v} B3LYP/6-311G(d,p) optimized geometries (see figure 2-14), one can see that the only significant changes in coupling contribution come from the d_{xz} and d_{x2-y2} orbital contributions. Specifically the d_{xz} has increased contributions compared to the analogous symmetric geometry whereas the d_{x2-y2} has decreased coupling contribution. The magnitude of the other coupling contributions remains approximately static. It is not evident as to why the relative contributions of these two orbitals shift, but since the X-ray optimized geometries are closer to the actual X-ray structures, we should expect a similar shift to occur there as well. It is suspected that if analogous studies were performed with the BPW91 functional, one would see a similar increase in the contribution of d_{xz} relative to that for d_{x2-y2}. The changes in the contributions between low spin and high spin geometries in these optimized X-ray geometries are comparable to those that were observed in the B3LYP/6-311G(d,p) C_{2v} optimized geometries.

What is also noteworthy when inspecting the results of the optimized X-ray geometries is that while the actual values of the contributions varied slightly between when the acetone molecule was included or excluded, the relative ordering of the contributions was consistent between the two sets of data. Furthermore, the same trends between LS and HS optimized geometries were observed with and without the acetone present. This suggests that the presence of the acetone molecule, while important when performing the geometry optimization, is not essential to the evaluation of the mechanisms of spin coupling.

We are cataloging these changes in d_{z^2} , d_{xz} , and $d_{x^2-y^2}$ as consequences of the inherent changes in electronic structure between low spin and high spin states in the optimized geometries in the absence of other factors present in the X-ray crystal structure. Since the span of geometric changes in the optimized geometries of a given functional and basis set are small compared to the geometric changes present in the variable temperature X-ray crystal structures, there is the possibility that more pathways are being affected than those merely indicated by the differences in the optimized geometries. Since the d_{xz} and $d_{x^2-y^2}$ pathways showed changes between the C_{2v} and X-ray structure optimized geometries, we can expect the actual values of these contributions to be even more different for the X-ray structures.

2.3.8 Discussion of Hay-Hoffman Results for X-ray structures

As was the case for the optimized geometries, the energy differences for the symmetric and antisymmetric d-orbital pairs as obtained from the ten lowest unoccupied beta orbitals were calculated from both the B3LYP and BPW91 high spin wavefunctions for all of the variable temperature Xray crystal structures. To simplify the analysis, these wavefunctions were determined with acetone excluded. The squares of these energy differences are reported in figure 2-14. One can see that at low temperatures, the coupling contributions for the X-ray structures are similar to those for the optimized geometries discussed earlier. The B3LYP low temperature X-ray values are very close to those obtained for the optimized X-ray structure geometry. The BPW91 X-ray structure values show a similar increase in the contributions of d_{xz} relative to $d_{x^2-y^2}$ compared to the C_{2v} optimized geometries that was present in the B3LYP optimized X-ray structure geometries.



Figure 2-14: Complex 1 Hay-Hoffman analysis of coupling contributions for the symmetric d orbital interactions in X-Ray structures as a function of temperature using B3LYP (left) and BPW91 (right) wavefunctions. Contributions are expressed in units of (cm⁻¹)².

What is immediately noteworthy for the contributions determined via both BPW91 and B3LYP is that there are significant changes are occurring for the d_{z^2} - d_{z^2} and d_{xz} - d_{xz} orbital interactions as the temperature increases, with the d_{z^2} interaction experiencing a larger magnitude change in coupling contribution. All of the other orbital pairings show little change across the temperatures studied. To confirm the variable effect of these two coupling pathways on the amount of overall coupling between the spin centers, plots of the calculated coupling constant in B3LYP versus the squares of the energy differences have been produced. It is evident in these plots that changes in the d_{z^2} - d_{z2} and d_{xz} - d_{xz} orbital interactions appear proportional to changes in the coupling constant, while the magnitude of the other interactions remains static with regards to the coupling constant. We have already established that the spin coupling constant is a good gauge for the total interaction between the unpaired spins in these systems, so we can conclude from these results that changes in temperature are affecting the magnitude of the spin coupling contributions that arise from the d_{z2} - d_{z2} and d_{xz} - d_{xz} spin orbital interactions. As the coupling constant decreases when the temperature increases, this means that the contribution of these pathways decreases as a function of temperature.

As for the asymmetric spin coupling pathways previously mentioned, Information is unavailable from the Hay-Hoffman method so the subsequent NMO analysis will need to be relied on to gain information on these pathways.



Figure 2-15: Fe @ Ga Hay-Hoffman analysis coupling contributions for the symmetric d orbital interactions in X-ray structures as a function of temperature using B3LYP (left) and BPW91 (right) wavefunctions. Contributions are expressed in units of (cm⁻¹)².

Since the coupling constant does not change appreciably across the temperature ranges studied for the Fe @ Ga structures, a similar Hay-Hoffman investigation of coupling pathway contributions would not be expected to yield interesting results. It is however worth noting that the contributions of all the possible symmetric pathways in the couplings between the iron centers at the gallium Xray geometries stay relatively unchanged over the whole temperature range as depicted in figure 2-15. This is consistent with the finding that the coupling constant for the iron hydroxo molecule studied at the gallium X-ray geometries does not appreciably change over the temperature range studied.

In summary, the Hay-Hoffman method for determining the contributions to spin exchange coupling in the variable temperature X-ray crystal structures give consistent results between B3LYP and BPW91 functionals. Both functionals show evidence of temperature changes primarily affecting the magnitude of the d_{z2} - d_{z2} and d_{xz} - d_{xz} spin orbital interaction contributions to the Heisenberg spin exchange, with d_{z2} - d_{z2} having the largest variance as a function of temperature. It shows an inverse relationship between the contributions of these orbital mechanisms for spin exchange and temperature, which is an interesting result as it implies that changes in the Boltzmann population of available spin states act to reduce the efficacy of the primary spin coupling pathways present in the molecule.

2.3.9 Coupling Contributions Determined via Overlap of Natural Magnetic Orbitals

The Hay-Hoffman method was a relatively facile way to study the contributions to spin coupling. However, the necessity of identifying the asymmetric coupling pathways where different types of interacting d-orbitals on each metal center cause meaningful contributions to the spin coupling necessitated the use of the NMO analysis.

For the NMO analysis, instead of relying on the single determinant high spin wavefunctions, one must create the approximate singlet broken symmetry wavefunctions to obtain NMOs. Indeed the identification of the NMOs which are the ten broken symmetry orbitals that have the most d-metal character localized on a single metal center can be an entirely subjective undertaking. What is desired is to find an alpha orbital which is predominantly a metal d-orbital in character on one of the metal centers, and to find a corresponding beta orbital which has the same metal d-orbital character on the opposite metal center. What is subjective is that there can be several broken symmetry orbitals that have similar d-orbital character, and one needs to select orbitals that have a high percentage of metal d-character and do not have excessive ligand character. The orbitals will by necessity have some ligand character, as it is this ligand character that allows the overlap in these complexes which exhibit a super-exchange interaction. However, too much ligand character will result in erroneously high overlap values, which could lead to false interpretations of the importance of certain spin coupling pathways. If given a choice, the orbitals should have ligand character which is located on ligands between the two metal centers, as this is more likely to be relevant as a spin exchange pathway.

The task therefore is to select the orbitals which have the most d-orbital character and also have the correct ligand character, which is certainly a matter of the authors' discretion. Fortunately, a highly relevant previous example was available from work within our research group. The previously selected orbitals in BPW91 as determined from an optimized geometry were readily reproduced in this work, which provided a valuable starting point for the subsequent study of all the other systems discussed herein. Typical BPW91 broken symmetry orbitals are shown in figure 2-16 (see pg. 88). One will note that these orbitals have extremely high metal character and that it is very easy to pick out the d-orbital type based on the Cartesian axes described previously. These BPW91 orbitals in turn were used as a starting point for the subsequent identification of natural magnetic orbitals in B3LYP broken symmetry wavefunctions, examples of which are shown in figure 2-17 (see pg. 89).

It was the case that for almost all the optimized geometries studied, the orbitals looked very similar to those depicted in figure 2-16 when studied with the BPW91 functional. The orbital numbering was also surprisingly consistent for the optimized geometries studied with the BPW91 functional given that geometric changes can have the effect of reordering the orbital energies. When comparing to the orbital assignments and morphologies of the BPW91 broken symmetry orbitals to those obtained with B3LYP broken symmetry single point energy calculations, there are some key differences that can be observed. The most notable difference is that the orbital numbers are completely different. In most cases the primarily metal based orbitals as determined with B3LYP are significantly lower in energy than their BPW91 counterparts.

When a comparison between the morphologies of the BPW91 and B3LYP NMOs is considered, it becomes more obvious why this might be the case. The B3LYP orbitals, while selected by their similarity in appearance to the BPW91 orbitals, have significantly more ligand character mixed in with the metal orbitals. Furthermore this ligand character is often located on the Tp capping ligands, which delocalizes the interacting spins away from each other. This is a reasonable conjecture as to why B3LYP calculates lower values for the coupling constant than what is calculated for BPW91. More peripheral ligand character is mixed into the NMOs for hybrid density functionals than for pure density functionals, which causes the B3LYP orbitals to be lower in energy than the BPW91 orbitals. This is likely the cause for lower numbered orbitals being the ones with the required d-

orbital character for B3LYP. It is also the case that this increased amount of ligand involvement in the selected B3LYP metal d-orbitals will provide different values for the alpha beta orbital overlaps than those obtained with BPW91. It should be noted that since the B3LYP energies provide better calculated coupling constants, it is not unreasonable that their wavefunctions and in particular the properties that depend on their orbitals should also be closer to representing the true nature of the spin coupling interaction.

Once NMOs have been selected for a given system, to ascertain the degree of communication between the orbitals bearing the spin one depends on the anti-symmetric spin distribution of the broken symmetry state so that the analysis of spin coupling contributions can be performed via the evaluation of the alpha beta overlap integrals. This only works because the alpha and beta orbitals are not in fact orthogonal to each other in spin unrestricted calculations and the broken symmetry state conveniently places all of the spin electrons on one iron center in alpha orbitals, and it places all the spin electrons for its partner in beta orbitals. This allows for the evaluation of overlap integrals between the NMOs of the two metal centers. The Multiwfn analysis package⁴¹ was used in these studies to evaluate the overlap between the alpha and beta orbitals obtained in our broken symmetry wavefunctions.
d Orbital Interaction	$d_{z^2} - d_{z^2}$	d _{xy} - d _{xy}	d _{xz} - d _{xz}	$d_{x^2-y^2} - d_{x^2-y^2}$	d _{yz} - d _{yz}
Orbital Numbers	171 α 171 β	172 α 172 β	135 α 135 β	145 α 145 β	144 α 144 β
Side On Images (yz plane)					
Top Down Images (~xz plane)					

Figure 2-16: Visualizations of the ten NMOs from the broken symmetry singlet UBPW91/6-311G(d,p) wavefunction calculated at the UBPW91/6-311G(d,p) low spin optimized geometry. The orbitals are plotted with an isovalue of 0.02.

d Orbital Interaction	d _z ² - d _z ²	d _{xy} - d _{xy}	d _{xz} - d _{xz}	$d_{x^2-y^2} - d_{x^2-y^2}$	d _{yz} - d _{yz}
Orbital Numbers	159 α 159 β	160 α 160 β	155 α 155 β	153 α 153 β	110 α 110 β
Side On Images (yz plane)					
Top Down Images (~xz plane)					

Figure 2-17: Visualizations of the ten NMOs from the broken symmetry singlet UB3LYP/6-311G(d,p) wavefunction calculated at the UB3LYP/6-311G(d,p) low spin optimized geometry. The orbitals are plotted with an isovalue of 0.02.

	BPW91/0	6-31G* HS	BPW91/6	5-31G* BS	BPW91/	6-311G** HS	BPW91/6-	-311G** BS	B3LYP/6-3	31G* HS	B3LYP/6	5-31G*LS	B3LYP/6-	311G** HS	B3LYP/6-	311G** BS
Orbitals	Numbers	Overlaps	Numbers	Overlaps	Numbers	Overlaps	Numbers	Overlaps	Numbers	Overlaps	Numbers	Overlaps	Numbers	Overlaps	Numbers	Overlaps
z²/z²	171/171	0.2149	171/171	0.2150	171/171	0.2168	171/171	0.2179	159/159	0.3410	159/159	0.3473	159/159	0.3167	159/159	0.323166
xz/xz	135/135	0.1674	135/135	0.1460	135/135	0.2124	135/135	0.2020	155/155	0.1686	155/155	0.1438	155/155	0.1385	155/155	0.11321
x²-y²/x²-y²	145/145	0.2275	145/145	0.2178	145/145	0.2674	145/145	0.2625	153/153	0.1664	153/153	0.1490	153/153	0.1052	153/153	0.082062
xy/xy	172/172	0.0936	172/172	0.0950	172/172	0.0994	172/172	0.1019	160/160	0.1017	160/160	0.1011	160/160	0.094	160/160	0.095958
yz/yz	144/144	0.1345	144/144	0.0509	144/144	0.2090	144/144	0.1424	110/110	0.0191	109/109	0.0087	110/110	0.0378	110/110	0.016914
z²/yz	171/144	0.1486	171/144	0.1550	171/144	0.1347	171/144	0.1400	159/110	0.1372	159/109	0.1388	159/110	0.1374	159/110	0.13848
yz/z²	144/171	0.1486	144/171	0.1550	144/171	0.1347	144/171	0.1400	110/159	0.1372	109/159	0.1388	110/159	0.1374	110/159	0.13848
x²-y²/yz	145/144	0.0841	145/144	0.0805	145/144	0.0941	145/144	0.0997	153/110	0.0572	153/109	0.0536	153/110	0.0586	153/110	0.0550
yz/x²-y²	144/145	0.0841	144/145	0.0805	144/145	0.0941	144/145	0.0997	110/153	0.0572	109/153	0.0536	110/153	0.0586	110/153	0.0550
xy/xz	172/135	0.0211	172/135	0	172/135	0.0180	172/135	0.0166	160/155	0.0375	160/155	0.0325	160/155	0.0290	160/155	0.0245
xz/xy	135/172	0.0211	135/172	0	135/172	0.0180	135/172	0.0166	155/160	0.0375	155/160	0.0325	155/160	0.0290	155/160	0.0245
z²/x²-y²	171/145	0.0988	171/145	0.1090	171/145	0.0865	171/145	0.0949	159/153	0.0328	159/153	0.0321	159/153	0.0178	159/153	0.0167
x ² -y ² /z ²	145/171	0.0988	145/171	0.1090	145/171	0.0865	145/171	0.0949	153/159	0.0328	153/159	0.0321	153/159	0.0178	153/159	0.0167
xy/z²	172/171	0	172/171	0	172/171	0	172/171	0	160/159	0	160/159	0	160/159	0	160/159	0
z²/xy	171/172	0	171/172	0	171/172	0	171/172	0	159/160	0	159/160	0	159/160	0	159/160	0
xy/x²-y²	172/145	0	172/145	0	172/145	0	172/145	0	160/153	0	160/153	0	160/153	0	160/153	0
x²-y²/xy	145/172	0	145/172	0	145/172	0	145/172	0	153/160	0	153/160	0	153/160	0	153/160	0
xy/yz	172/144	0	172/144	0	172/144	0	172/144	0	160/110	0	160/109	0	160/110	0	160/110	0
yz/xy	144/172	0	144/172	0	144/172	0	144/172	0	110/160	0	109/160	0	110/160	0	110/160	0
z²/xz	171/135	0	171/135	0.0183	171/135	0	171/135	0	159/155	0	159/155	0	159/155	0	159/155	0
xz/z²	135/171	0	135/171	0.0183	135/171	0	135/171	0	155/159	0	155/159	0	155/159	0	155/159	0
x²-y²/xz	145/135	0	145/135	0	145/135	0	145/135	0	153/155	0	153/155	0	153/155	0	153/155	0
xz/x²-y²	135/145	0	135/145	0	135/145	0	135/145	0	155/153	0	155/153	0	155/153	0	155/153	0
yz/xz	144/135	0	144/135	0	144/135	0	144/135	0	110/155	0	109/155	0	110/155	0	110/155	0
xz/yz	135/144	0	135/144	0	135/144	0	135/144	0	155/110	0	155/109	0	155/110	0	155/110	0

Table 2-12: The alpha beta overlap integrals determined for all possible permutations of the d-orbital like natural magnetic orbitals for select optimized geometries studied sans acetone. The overlap integrals are listed in descending order as determined with B3LYP for both the symmetric d-orbital interactions and the asymmetric d-orbital interactions.

2.3.10 Alpha Beta Orbital Overlap Analysis of Spin Coupling Mechanisms in Optimized Geometries

To start, the overlaps were determined for the same system we previously studied and obtained orbital overlap integrals on to verify that the MultiWavefn program was producing reliable results. A comparison between the previously reported orbital overlap values for the natural magnetic orbitals obtained with a BPW91/6-31G(d) high spin optimized C_{2v} geometry and our new alpha beta overlap values calculated from the same optimized geometry using MultiWavefxn reveals similar overlap values that are nonetheless different from those previously reported. This difference is not alarming however, as we are obtaining our broken symmetry electronic state using the new fragment-based guessing in Gaussian 09 versus a manual manipulation of the guess as was obtained in Gaussian 98 for our previous studies. If the method for generating the broken symmetry electronic state is different, there should be no expectation that the resulting broken symmetry wavefunction should be exactly the same. Based on our differing calculated values for the spin coupling constant for the exact same geometry and functional, it seems that we are working with a different broken symmetry wavefunction. If the broken symmetry wavefunctions are different, so should the orbital overlaps that are determined from those broken symmetry wavefunctions be different.

While there are observable differences from our previous values, the BPW91 alpha beta orbital overlaps for the natural magnetic orbitals do show similar relative contributions to the spin coupling for all the C_{2v} optimized geometries studied, which provides us with a good baseline when evaluating the orbital overlaps of the different optimized geometries and comparing these values to overlap values obtained with the B3LYP functional. The alpha beta overlaps for BPW91

and B3LYP natural magnetic orbitals for the optimized geometries studied are reported in table 2-12.

As was previously reported in work from our research group, the primary spin coupling pathways as determined using this method are Fe1(d_z2): μ -OH(p_{||}):Fe2(d_z2), Fe1(d_x2-y₂):bis- μ -acetato:Fe2(d_x2-y₂), Fe1(d_{xz}): μ -OH(p_x): Fe2(d_{xz}), Fe1(d_{yz}): μ -OH(p[⊥]): Fe2(d_z2), and Fe1(d_z2): μ -OH(p[⊥]): Fe2(d_{yz}). These are reflected in the high alpha beta overlap values derived for the BPW91 broken symmetry wavefunction. The results for the overlap integrals evaluated for the high spin 6-31G(d) optimized geometry show good consistency with the previously reported overlap integral values.

It is important to note that it was by evaluating all of the possible 25 permutations of overlap integrals between the natural magnetic orbitals and determining which ones were significant that the assignments of the relevant coupling pathways in our previous work were made. This is the reason all 25 orbital permutations are represented in table 2-12 (see pg. 90). The cutoff for what is reported as significant seems arbitrary at best, given that there are a few more overlap integral values with nearly the same magnitude that were not mentioned as significant in our previous results. However, one can also see in table 2-12 that we are getting agreement in the overlap values of the important coupling pathways. While it is debatable to classify what is truly significant, for the sake of consistency and the ease of presentation, we will confine our discussion to the same set of significant pathways that was previously determined since their overlap values are similar for all of the optimized geometries studied.

When looking for trends between the different C_{2v} optimized geometries in both functionals, it is helpful to plot the overlap values in bar graph form, as depicted in figure 2-18.







Figure 2-18: The calculated α - β overlap integral absolute values for the significant spin coupling pathways calculated from broken symmetry orbitals generated with BPW91 (A) and B3LYP (B) density functionals. Our previously reported result is also included for comparison. See text for details.

From these plots, a few general trends can be observed. The first is that generally speaking, the overlaps in the significant pathways are larger for the broken symmetry optimized geometry than

for the high spin optimized geometry of a given basis set and functional. This is logical since the broken symmetry optimized geometry will depend on these spin exchange interactions to properly model the low spin state. This means that these exchange interactions should be emphasized more in the broken symmetry ground state than in the high spin state, which results in increased overlap values due to these interactions being stabilized in the broken symmetry state. It is also the case that for the geometries optimized with the 6-31G(d) basis set the overlap values are typically larger than those obtained for geometries optimized with the 6-311G(d,p) basis set. This is a simple consequence of the optimized bond distances being shorter for the 6-31G(d) basis set, which results in the increased overlap values based on increased spatial overlap when the interacting orbitals that are having their overlaps computed are closer together.



Figure 2-19: The calculated α - β overlap integral absolute values for the significant spin coupling pathways calculated from broken symmetry orbitals generated with BPW91 density functional at the optimized B3LYP geometries. Our previously reported result is also included for comparison. Compare to figure 2-18: see text for details.

When generally comparing the results of the B3LYP and BPW91 natural magnetic orbital overlaps, the effects of the increased ligand character in the NMOs is on clear display. To study these

differences without the possible influence of similar but nonetheless different geometries, the alpha beta orbital overlap values were compared for the B3LYP optimized geometries using both the B3LYP and BPW91 broken symmetry wavefunctions. The plot of BPW91 overlaps at the B3LYP geometry is found in figure 2-19, and they can be compared to the second plot in figure 2-18 for the B3LYP overlaps at B3LYP geometry. It can be clearly seen that the B3LYP broken symmetry wavefunction has significantly higher calculated alpha beta overlap integral values for the d_{z2} natural magnetic orbitals. This is no doubt due to the high amount of bridging ligand character in these orbitals, even those generated with the BPW91 pure density functional. The other alpha beta orbital overlaps between the natural magnetic orbitals with the same d-orbital assignments was overall consistent for the BPW91 and B3LYP functionals, with the values in some cases being slightly lower than those determined with BPW91. The trends for differences in geometry are similar for overlaps evaluated from broken symmetry wavefunctions determined with both functionals.

The similar trends in the results of the B3LYP and BPW91 orbital overlaps between high and low spin optimized geometries is encouraging since it suggests that B3LYP orbital overlap integrals have the potential to provide meaningful insight on the changes in the spin exchange pathways in the variable temperature X-ray crystal structures. This is important because as has been mentioned previously, the BPW91 broken-symmetry electronic state suffered convergence issues for the X-ray crystal structures. This was not the case for the B3LYP broken symmetry wavefunctions, making the B3LYP derived natural magnetic orbitals an ideal target for the study of the contributing orbital pathways to spin exchange in the X-ray crystal structures.

As a further test of the NMO analysis before studying the X-ray structures, the alpha beta overlap integrals were evaluated from the broken symmetry B3LYP/6-311G(d,p) wavefunction evaluated

on the optimized X-ray structure geometries both with and without acetone included. The results of this analysis for all 25 possible orbital interactions are tabulated in the supplementary information.

The symmetric overlap values obtained for the optimized X-ray geometries with the acetone omitted should have been similar to those obtained for the B3LYP/6-311G(d,p) optimized C_{2v} geometries that were previously discussed, as both these geometries were optimized with the same functional and basis set. However, the presence of the acetone in the X-ray optimized geometry had some observable effects on the calculated overlap values, even when the acetone was removed before the orbitals were generated.

The X-ray optimized geometry symmetric pathway overlap values had some key similarities with their C_{2v} counterparts along with some key differences. The calculated overlap values of the d_{z^2} d_{z^2} , and d_{xy} - d_{xy} of the optimized X-ray geometries were similar to those obtained for their C_{2v} optimized counterparts. Smaller overlap values were observed for the d_{xz} - d_{xz} compared to the C_{2v} values while there were larger values observed for d_{yz} - d_{yz} and especially for $d_{x^2-y^2}$ - $d_{x^2-y^2}$. Besides these differences, the observed trends between low spin and high spin geometries were consistent with those reported for the C_{2v} geometries as was discussed previously.

When comparing these changes relative to the C_{2v} geometry with the changes in coupling contributions calculated via the Hay-Hoffman method, we can see that most of the changes are consistent between the two. The d_{z2} and d_{xy} contributions are unchanged in both, and there are increases in the contributions from d_{yz} and even more increases in the d_{x2-y2} contributions. However, while the contributions from d_{xz} increase substantially for the Hay-Hoffman method, they decrease substantially for the NMO contributions. The reason for this is not understood, but since there is a high degree of ligand character on the other side of the molecule for the d_{xz} broken symmetry orbitals, we can postulate that this was enhanced in the asymmetric optimized geometry and let to a cancellation of the overlap between the two metals as the phases were opposite for the wavefunctions on each side of the molecule. Therefore, since the wavefunctions appear less influenced by small geometric changes for the Hay-Hoffman method, we will follow those results as more telling of the situation than those obtained for the NMO method.

The number of significant asymmetric coupling pathways in the X-ray optimized geometries was substantially increased in the optimized X-ray geometries with the acetone removed (after optimization) for the generation of the orbitals when compared to the C_{2v} optimized counterparts. This was to be expected because the presence of the acetone in the X-ray structure optimization forced a degree of asymmetry on the structure. This asymmetry causes the d-orbitals of each metal center to not line up exactly, which has the effect of increasing the communication between d-orbitals of different symmetry. Since the overall value of the coupling constant is not substantially altered, one can presume that the electronic communication responsible for the spin coupling is now divided amongst the higher number of pathways, making each overlap integral value less significant to the overall coupling than it was for the equivalent C_{2v} optimized geometry. It is interesting to note that the identity of the orbitals in these asymmetric pathways is consistent, with the dyz and dz² orbitals showing significant asymmetric coupling contributions being joined by contributions involving the d_{xz} and d_{x²-y²} orbitals.

When the acetone is kept in place for the calculations that generate the broken symmetry orbitals used for the NMO orbital overlap analysis, we observe a few changes in the values for the overlap integrals. With the exception of the d_{xz} - d_{xz} orbital overlap, we see increases roughly between 60% and 100% for the remaining symmetric overlap integrals with the $d_{x^2-y^2}$ - $d_{x^2-y^2}$ showing the largest increase. The d_{xz} - d_{xz} overlap showed an increase by over an order of magnitude. These increased

overlaps apart from d_{xz} - d_{xz} are all able to be explained with the earlier explanation of the acetone drawing the electron density away from the O5 hydroxo bridge allowing for increased energetic overlap with the metal d orbitals. However, it is also the case that the overlaps can be increased because the acetone molecule polarizes the electron density on the bridging ligands. This results in the portions of the NMOs with ligand character being localized on the one side of the molecule resulting in increased overlap as the alpha and beta orbitals are more concentrated in the same space.

The d_{xz} - d_{xz} overlap increase with the inclusion of acetone is more puzzling since it appears that it is now ascribing too much contributions to the spin coupling whereas the omission of acetone resulted in too small a contribution. It has been observed in all our C_{2v} optimized geometries that the d_{xz} orbital overlaps are sensitive to geometric changes, but this hypersensitivity to the acetone presence may be due to the acetone lining up approximately with the node of the d_{xz} -hydroxo molecular orbital while being not in the nodal plane, which could have the effect of skewing these orbitals when it is present allowing for the huge increase in observed overlap.

The number of significant asymmetric overlap pathways is reduced with the inclusion of acetone, with the previously mentioned $d_{z^2}-d_{xy}$ and $d_{xy}-d_{z^2}$ pathways no longer being of the same magnitude as they were in the C_{2v} optimized geometries. Significant asymmetric pathways involved the d_{x^2} y^2 and d_{z^2} orbitals, as well as single pathways involving the d_{xz} and d_{xy} in combination with the aforementioned orbitals. It is not known why the number of pathways decreases, but it may be due to the electronic wavefunction being able to adopt their equilibrium conformations when the acetone is included since these geometries were optimized with the acetone present.

Conclusions that we can draw from studying these optimized X-ray structures with the NMO method are that most of the symmetric coupling pathways show similar trends between the

wavefunctions calculated with and without acetone present. The asymmetric pathways show changed behavior between the two systems, and the NMO analysis on these optimized geometries all showed inconsistent results with regards to d_{xz} - d_{xz} coupling contributions when compared to the Hay-Hoffman results. This inconsistency combined with the extreme variability of the NMO method means that going forward with the actual X-ray structures, we will be focusing on the Hay-Hoffman results with less emphasis on the NMO analysis going forward.

2.3.11 Spin Exchange Contribution Analysis via Alpha Beta Orbital Overlap Integrals in The Broken Symmetry Wavefunctions of VT X-ray crystal structures.

It was decided through the course of these studies that the coordinating acetone molecule was not necessary for the accurate modeling of the spin exchange pathways, and this was supported by Hay-Hoffman results being consistent between the inclusion and exclusion of acetone. It also made the systems easier to study, as the NMOs had more consistent morphologies when the acetone was omitted.

Even without the acetone, the asymmetry of the X-ray structures was problematic for the implementation of the NMO method to study these structures. While the BPW91 orbitals showed consistency between the C_{2v} optimized geometries and the X-ray structures having a similar appearance and energies, there were some differences. Where the optimized C_{2v} geometries offered the natural magnetic orbitals in the same numbered alpha beta pairs, the lack of similar symmetric constraints in the X-ray crystal structures led to some of the alpha and beta natural magnetic orbital pairs having different orbital numbers, as was observed in the optimized X-ray structures when acetone was present. What happened more frequently was that the orbitals were

less symmetrically distributed on the ligands, with alpha and beta at times having disparate amounts of ligand character, or having ligand character on only one side of the molecule as was seen in the optimized X-ray crystal structures. It also meant that the asymmetric mixing pathways could and did have different values for the overlap integrals between the two possible sets of alpha beta overlaps. Regardless, since only half of the structures for complex **1** were able to converge to a broken symmetry state, the results were less than conclusive.

The issues previously discussed for studies with BPW91 were exacerbated with the B3LYP broken symmetry orbitals. It seemed in general that the d-orbital shapes for the B3LYP derived natural magnetic orbitals suffered from the geometric distortions compared to the equilibrium geometries encountered in the previous section. This resulted in apparently smaller d-orbitals when compared to those obtained for the optimized geometries, which led to smaller overlap values for certain d-orbital coupling pathways than were found for the optimized geometries, as can be seen in the data for figure 2-20.

The resulting overlap integrals from these less well defined natural magnetic orbitals obtained for the X-ray crystal structures, particularly in the case of B3LYP where there were already concerns with the proper orbital spatial distributions for the broken-symmetry wavefunctions determined for the optimized geometries, had a high degree of variance as seen in figure 2-20.

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Figure 2-20: The calculated α - β overlap integral absolute values for the significant spin coupling pathways calculated from broken symmetry orbitals generated with B3LYP for the X-ray crystal structures of complex *1*. Note the inconsistency of contributions, especially at 173 K.

In particular, the B3LYP NMO alpha beta overlaps show such high variance for all of the coupling pathways studied that any information on the change in contribution to spin coupling as a function of temperature is essentially lost in the noise. This was a disappointing result, as the B3LYP broken symmetry wavefunction had a much better success rate in obtaining the correct broken symmetry states, not to mention that the energetics of the B3LYP determined spin coupling constants are much closer to the experimentally reported value. However, the irregularity of the natural magnetic orbitals obtained with B3LYP essentially doomed these alpha beta orbital overlap results to be unreliable. Unfortunately, the limited BPW91 results also showed a fair degree of variance, which was makes drawing conclusions from their differences as a function of temperature difficult if not impossible. This means that for the purposes of looking at coupling pathways in the X-ray crystal

structures, the Hay-Hoffman method will be relied upon to provide us with conclusions concerning how the contributions to spin coupling are changing with temperature.

2.3.12 Magneto-Structural Effects Discussion

So far, we have observed the changing nature of the coordination environment of the spinexchanged iron centers in complex **1**, particularly changes associated with the μ -hydroxo bridging ligand, in the variable temperature X-ray crystal structures. We have also seen that the changes as a whole have resulted in systematic changes to the contributions to spin exchange coupling from the individual d-orbitals on each iron center. However, we wanted to pinpoint which changes were having these effects. It was already suspected that the variable bond distances associated with the H50 μ -hydroxo proton were primarily responsible for these variable contributions, so a few tests were devised to determine if this was the case.

The main test that was proposed was to set the O5 - H50 bond distance at a constant value without changing any other structural parameter of the X-ray structures for complex **1** and to see if similar changes in the spin exchange coupling were observed. To this end, the O5 - H50 bond distance was shifted to the same 0.827 Å value (observed for the iron structure at 20K) for all of the higher temperatures. A similar procedure was used to modify the crystal structures such that the O5-H50 bond distance was held constant at its 296 K value of 0.58853 Å. For these modified geometries, the acetone was omitted.

It is worth mentioning again that the O5-H50 bond distance is shorter in the X-ray structures than the optimized geometries and it is likely the case that the optimized geometries are much closer to the actual bond distances, since the geometry optimizations tracks the nuclear position of the proton and the X-ray structure only tracks the electron density, which for protons is situated close to the atom to which it is bound. One might think that it is just the increased thermal motion of the acetone that causes the average electron density position associated with H50 to get closer to O5 in complex **1** as the temperature increases. However, this phenomenon should have also been observed in the crystal structures for complex **2**, and the fact that it is not leads us to believe that even though the bond distances determined via the X-ray structures are not accurate, this trend is likely based in what is really happening in the X-ray structures as the temperature increases.

When the Hay-Hoffman contributions for the optimized geometries are compared to those for the crystal structure, one can see that they are similar (refer to figure 2-13 and 2-14). It is based on this assessment and the fact that we should still expect this trend of bond shortening to occur in complex **1** based on a lack of similar results in complex **2**, that we feel it is valid to investigate how changes in the X-ray structure bond length will affect the orbital mechanisms of spin coupling, as we should expect similar trends to occur, albeit with more muted responses to bond distance changes as the O5-H50 bond is being studied at geometries distorted from their equilibrium value by using the distances from the X-ray structures.

For the study on the O5-H50 bond distance dependence, the coupling constants were theoretically evaluated via the Yamaguchi method using the B3LYP functional in the manner described previously. These modified geometry results contrasted with those obtained for the actual crystal structures of complex **1**, all of which are presented in figure 2-21. It is evident from these results that when the O5 – H50 bond distance is held constant, the degree of spin interaction becomes almost static. While it appears that the two highest temperature points have increased coupling in these modified geometries which can be correlated to the decreasing Fe1-O5 bond distance at these temperatures, the degree of change is within the estimated 2 cm⁻¹ uncertainty described earlier. It



Figure 2-21: Plot of the UB3LYP/6-311G(d,p) calculated J values for the unaltered X-ray crystal structures of complex 1, the aforementioned X-ray structures altered such that the O5-H50 bond distance was fixed at the 20 K value of 0.82707 A, and the X-ray structures altered such that the O5-H50 bond distance was fixed at the 296 K value of 0.58853 Å. All of these calculated values used geometries that did not include the acetone molecule.

can therefore be stated that the only significant change in the electronic structure and thus the spin coupling constants brought about by the changing temperature is a shift in this single bond distance.

To determine if the relative mechanistic contributions to the spin coupling were also held static with a fixed O5 – H50 bond distance, the Hay-Hoffman spin exchange orbital contributions were evaluated for these modified crystal structures. The NMO alpha beta overlap method was not used, due to it being too variable for use in studying the X-ray crystal structures as was demonstrated previously. The results of the Hay-Hoffman spin exchange contribution analysis on the 20 K and 296 K O5-H50 bond altered X-ray structures are shown in figure 2-22.



Figure 2-22: Relative contributions to the spin coupling determined with UB3LYP/6-311G(d,p) in modified complex *1* X-ray crystal structures as determined via the Hay-Hoffman method. The modifications involved holding the O5-H50 bond distance constant for all temperatures. On the left, the O5-H50 bond distance is set at the 20 K value of 0.82707 Å. On the right, the O5-H50 bond distance is set at the 296 K value of 0.58853 Å. These contributions are expressed in units of $(cm^{-1})^2$. See text for more details.

Again, it is easily seen that the coupling pathway contributions are generally lower at the 296 K bond distance compared to the 20 K bond distance. What is clearly demonstrated however is that there is no apparent change in the orbital contributions to the spin exchange when all other structural parameters are allowed to change with temperature but the O5-H50 bond distance is held constant. This is strong confirmation of the singular importance of the O5-H50 bond distance to the spin interaction in this system.

It is possible that the O-H bond shortening observed in the μ -hydroxo bridge is correlated with a concomitant destabilization of the hydrogen bonding interaction between H50 and O100 that is observed in the lower temperature crystal structures. While this change is not observed in the VT X-ray structures of complex **2**, it could be merely attributed to the differences in the Lewis acidity of gallium compared to iron. It may be the case that the weaker Lewis acid would make it possible for the O-H bond distance in the iron complex to be shorter than that in the gallium since it would

accept less electron density from the hydroxo bridge. This could mean that while the O-H bond distance and subsequent hydrogen bonding nature with acetone could vary for complex **1**, it would be unable to do so in complex **2**. This was one of the main justifications used to study the crystal structures with acetone included. It is possible that if the hydrogen bonding was the driving influence for the longer O-H bond distance at low temperatures, there would be a visible difference in the trending behavior of the changes in absolute energy values as a function of temperature since the hydrogen bonding constant behavior seemed less likely, as the acetone provided no communication pathway for the spin interaction. A comparison of the changes in absolute electronic energy as a function of temperature and the calculated coupling constant for the VT X-ray structures of complex **1** with and without the associated acetone molecule are shown in graphical form in figure 2-23.

As was already discussed, the trends in the calculated coupling constant as a function of temperature are very similar for complex 1 with and without the acetone, even though the values are slightly offset as seen in figure 2-7. When the changes in absolute energy of the wavefunctions used to determine said coupling constants as a function of temperature are inspected for the crystal structures with and without acetone, one can notice that there is a deviation of the energies of the two systems. Even though we are looking at the changes in the absolute energy value, we should not expect identical changes in the two systems as energy does not scale linearly with the number of atoms in the system, so the energy differences are not guaranteed to be identical in the absence of the interaction between the acetone and complex **1**. This seems to be the case as seen in figure 2-23.



Figure 2-23: Energy diagram of the absolute energy of the broken symmetry electronic states of the complex *1* crystal structures relative to the energy value at 20 K for structures both including and excluding the acetone. The difference between with and without the acetone is always positive yet variable, indicating that there is a non-negligible interaction between the acetone and the energetics of the system independent of the differing electron count of the two systems.

We can see that the difference in absolute energy varies significantly more at the 100 through 234 K temperatures than it does at the other temperature points. However, the differences between the two systems do not seem to correlate with the changes in the hydrogen bonding distance, so it cannot be concluded that variation in the hydrogen bonding nature of the acetone is affecting our observed structural and electronic differences as a function of temperature in complex 1. Given that the crystal structures of both complexes 1 and 2 have an acetone molecule in the same relative position to the μ -hydroxo bridge, and there are no changes in the bond distance in complex 2, it seems that this change in bond distance has to be due to the unique electronic properties of the iron

centers present in complex **1** and that suggests that the spin coupling is responsible for this behavior without conclusively proving that it is the cause of this dynamic behavior.

This leads us to the situation of having to decide whether the differences in O5-H50 bond distance are causing the observed perturbations in the mechanisms of the spin exchange coupling or if the opposite is true and temperature induced changes in the spin states of the spin coupling mechanisms are manifesting themselves in this shifting bond distance. Since the contributions from d_{z2} and d_{xz} are the ones that change the most as a function of temperature, one would have thought that the coupling constant and orbital mechanisms of spin exchange would have been disturbed as a function of temperature even with the O-H bond distance being held constant, as there are still significant changes in the Fe-O5 bond distance as a function of temperature. While we can see a slight increase in the calculated coupling constants for the two highest temperature values that correlates nicely with the shortening of the Fe1-O5 bond distances, we cannot be sure if this is a real difference in the calculated coupling constant because it fits within the determined error of the calculated coupling constant as was discussed previously. Since the Fe1-O5 bond distance is much more difficult to alter in the crystal structure since the Fe1 is bonded to many more parts of the molecule, an analogous study of holding the Fe1-O5 bond distant at a constant value was not attempted. It is almost certain that the Fe1-O5 bond shortening has an effect on the spin coupling, as the shorter Ga-O5 bond distances in complex 2 are what is presumed to be at least partially responsible for the increased calculated coupling constant values for the Fe @ Ga structures. However, we cannot determine if this bond shortening has a significant effect on the electronic structure of complex 1 at this time based on the uncertainty of our evaluation methods for the coupling constant.

Since the changes in the Fe1-O5 bond distance are not greatly influencing the coupling constant and orbital mechanism contributions to the spin exchange, one can draw the shocking conclusion that these observed changes in the orbital coupling mechanisms and their contribution to the spin exchange coupling as a function of temperature is likely due to the changing O5-H50 bond distance. The change in this bond distance is certainly unique to complex **1**, but it is not known at this time if the spin exchange is responsible for this behavior or if it is merely due to the presence of iron and the spin exchange is just a circumstantial side effect of the irons being present.

2.4 Conclusion

We have obtained detailed variable temperature X-ray crystal structures of complex 1 and complex 2. Through comparative analysis of the crystal structures, it was determined that the significant changes in the structures unique to complex 1 involved the shortening of the Fe1-O5 and O5-H50 bonds with increasing temperature. The coupling constant was calculated for a plethora of optimized geometries and the VT X-ray structures and it was found that the calculated coupling constant for the complex 1 X-ray structures decreases significantly at higher temperatures wile coupling constants determined for Fe @ Ga geometries do not change. These coupling constants were compared and found to be consistent with values obtained for the optimized geometries. The coupling pathways were analyzed via the Hay-Hoffman and NMO methods for the optimized geometries to gain an understanding of how geometric changes effect the coupling pathways. This same analysis was then performed on the X-ray structures, with the results indicating that the significant geometric changes in the complex 1 X-ray structures correlated with a reduction in the d_{z2} and d_{xz} related coupling pathways. A series of calculations on crystal structures with modified O5-H50 bond distances showed that the change in coupling behavior for complex one is primarily

correlated with the O5-H50 bond distance change. However, we cannot determine if it is the changes in the electronic structure of complex **1** due to the thermal population of higher spin states that cause the changes in this bond distance, or if it is a thermal effect of the weakened hydrogen bond between H50-O100 at higher temperatures that results in these geometric changes. Therefore, we cannot confidently say from this set of studies if populating the higher spin states of complex **1** has an effect on its geometry, but it can be reported that a correlation exists.

APPENDICES

Appendix 2.1: Supplementary Figures



Figure A2-1: Acetate C-O bond distances in the X-ray structures as a function of temperature. Distances for complex *1* are on the left and distances for complex *2* are on the right. Note that in both complexes the bond distance shows a general decreasing trend.



Figure A2-2: Bond distances for the M-O bond distances for the acetate bridges for complexes *1* and *2* as a function of temperature.



Figure A2-3: The M-O(acetate)-C(acetate) bond angles for complexes *1* and *2* as a function of temperature.



Figure A2-4: The O(acetate)-M-O5 bond angles for complexes 1 and 2 as a function of temperature.

Appendix 2.2: Cartesian Coordinates of Variable Temperature X-ray Structures

Notes: These input geometries were taken from the X-ray crystal structure results. The perchlorate anion is omitted but the coordinated acetone is included. The .cif files will be made available at a later time.

Fe 20 K:

Fe	4.211000	0.298000	4.449000
Fe	1.650000	2.410000	5.180000
Ν	3.629000	-1.320000	3.252000
Ν	4.555000	-1.979000	2.492000
Ν	5.924000	-0.869000	4.907000
Ν	6.566000	-1.544000	3.910000
Ν	5.399000	0.916000	2.825000
N	6.039000	-0.003000	2.044000
N	-0.238000	1.857000	4.380000
N	-1.154000	2.834000	4.108000
N	0 506000	3 674000	6 449000
N	-0 549000	4 370000	5 934000
N	1 583000	4 008000	3 826000
N	0.429000	4 714000	3.652000
$\hat{\mathbf{n}}$	1.535000	0.800000	5.052000 6.492000
0	3 268000	0.890000	6.051000
0	3.208000	2 125000	6 100000
0	3.282000	5.125000	5.500000
0	4.981000	1.731000	3.390000
0	2.669000	1.348000	3.913000
Н	2.437000	1.311000	3.120000
C	2.213000	-0.165000	6.683000
C	1.749000	-1.115000	7.752000
Н	0.898000	-0.937000	8.022000
Н	1.807000	-1.993000	7.443000
Н	2.286000	-1.048000	8.471000
С	4.495000	2.767000	6.168000
С	5.429000	3.603000	6.996000
Η	5.934000	4.170000	6.406000
Н	6.050000	3.022000	7.460000
Н	4.923000	4.154000	7.602000
С	2.472000	-1.985000	3.119000
Η	1.696000	-1.710000	3.570000
С	2.637000	-3.085000	2.272000
Η	1.993000	-3.731000	2.036000
С	3.973000	-3.045000	1.904000
Н	4.478000	-3.606000	1.357000
С	6.666000	-1.018000	6.015000
Н	6.381000	-0.624000	6.824000
С	7.792000	-1.798000	5.743000
Н	8.483000	-2.029000	6.341000
С	7.690000	-2.107000	4.392000
Н	8.260000	-2.597000	3.831000
C	5,770000	2.129000	2.387000
н	5,446000	2.922000	2.838000
C	6 650000	2 002000	1 310000
н	7.067000	2.685000	0.853000
\hat{C}	6 795000	0.635000	1 125000
н	7 30/000	0.035000	0.516000
C	0.845000	0.684000	4 132000
ц	0.385000	0.084000	4.132000
С	2 157000	-0.142000	4.270000
	-2.13/000	0.900000	3.702000
П	-2.800000	0.273000	3.403000
С	-2.311000	2.279000	3.703000
п	-3.041000	2.040000	3.409000

С	0.504000	3.894000	7.774000
Н	1.177000	3.496000	8.325000
С	-0.562000	4.726000	8.124000
Н	-0.791000	5.019000	8.987000
С	-1.207000	5.003000	6.927000
Н	-1.974000	5.525000	6.735000
С	2.496000	4.544000	3.005000
Н	3.380000	4.202000	3.033000
С	1.940000	5.605000	2.287000
Н	2.358000	6.145000	1.680000
С	0.627000	5.675000	2.728000
Η	-0.082000	6.254000	2.491000
Н	6.629000	-2.091000	1.809000
Н	-1.684000	4.923000	4.143000
В	6.014000	-1.494000	2.458000
В	-0.848000	4.313000	4.422000
0	2.052000	1.109000	1.222000
С	1.234000	1.547000	0.426000
С	1.173000	1.035000	-0.985000
Н	1.697000	0.245000	-1.101000
Η	0.279000	0.859000	-1.254000
Н	1.490000	1.706000	-1.565000
С	0.255000	2.624000	0.791000
Н	0.352000	2.902000	1.702000
Η	-0.646000	2.334000	0.622000
Н	0.409000	3.370000	0.211000

Fe 50 K:

Fe	9.965000	0.303000	4.453000
0	9.041000	3.138000	6.096000
В	11.771000	-1.490000	2.467000
Н	12.376000	-2.082000	1.816000
Ν	9.385000	-1.316000	3.257000
С	7.966000	-0.155000	6.683000
Fe	7.408000	2.422000	5.181000
0	10.731000	1.755000	5.597000
В	4.908000	4.320000	4.422000
Н	4.080000	4.923000	4.151000
Ν	10.312000	-1.976000	2.498000
С	7.494000	-1.104000	7.748000
Н	6.667000	-0.925000	8.042000
Н	7.534000	-1.966000	7.457000
Н	8.019000	-1.105000	8.419000
0	7.297000	0.902000	6.494000
Ν	11.677000	-0.866000	4.914000
С	10.251000	2.776000	6.167000
0	9.017000	-0.468000	6.050000
Ν	12.319000	-1.541000	3.918000
С	11.189000	3.610000	6.990000
Н	10.680000	4.157000	7.597000
Н	11.812000	3.046000	7.437000
Н	11.695000	4.173000	6.430000

0	8.426000	1.356000	3.914000
н	8.189000	1.316000	3.115000
N	11.156000	0.922000	2.832000
C	8 229000	-1 983000	3 122000
н	7 458000	-1 706000	3.572000
N	11 707000	0.000000	2.052000
C	8 205000	2 080000	2.052000
U U	a.393000	-3.080000	2.277000
H	7.758000	-3.724000	2.040000
N	5.521000	1.865000	4.382000
C	9.732000	-3.041000	1.909000
Н	10.238000	-3.593000	1.370000
Ν	4.602000	2.840000	4.111000
С	12.416000	-1.018000	6.022000
Η	12.132000	-0.620000	6.821000
Ν	6.261000	3.683000	6.448000
С	13.541000	-1.800000	5.751000
Н	14.224000	-2.022000	6.341000
Ν	5.207000	4.380000	5.933000
C	13.442000	-2.106000	4.403000
й	14 009000	-2 607000	3 825000
N	7 339000	4 020000	3 828000
$\hat{\mathbf{C}}$	11 524000	2 132000	2 301000
с ц	11.107000	2.132000	2.391000
п N	6 192000	4.722000	2.855000
N	0.182000	4.725000	3.031000
C.	12.403000	2.004000	1.316000
Н	12.825000	2.672000	0.842000
С	12.550000	0.640000	1.134000
Н	13.059000	0.123000	0.529000
С	4.917000	0.691000	4.136000
Η	5.377000	-0.143000	4.270000
С	3.605000	0.905000	3.708000
Н	2.966000	0.284000	3.471000
С	3.447000	2.278000	3.708000
Н	2.714000	2.837000	3.485000
C	6.257000	3.904000	7.770000
н	6 918000	3 509000	8 327000
C	5 190000	4 734000	8 121000
ц	4 952000	5.020000	8 971000
C	4.932000	5.020000	6.971000
U U	4.347000	5.010000	0.924000
П	3.778000	5.555000	6.726000
C .	8.252000	4.564000	3.014000
Н	9.134000	4.221000	3.038000
С	7.694000	5.623000	2.296000
Н	8.109000	6.160000	1.686000
С	6.380000	5.687000	2.733000
Н	5.669000	6.257000	2.496000
0	7.813000	1.119000	1.224000
С	6.996000	1.556000	0.428000
С	6.017000	2.626000	0.792000
Н	5.124000	2.364000	0.606000
н	6.112000	2,895000	1.683000
н	6.174000	3 368000	0.247000
$\hat{\mathbf{C}}$	6 939000	1 042000	-0.981000
й	7 248000	1 710000	-1 563000
н	6.056000	0.855000	-1.238000
11 11	7.460000	0.055000	1 101000
н	7.400000	0.251000	-1.101000

Fe 100 K:

4.122000	10.376000	12.146000
5.930000	8.586000	10.161000
6.547000	7.979000	9.525000
3.169000	9.607000	13.740000
3.542000	8.756000	10.950000
2.121000	9.923000	14.374000
1.566000	12.500000	12.871000
-0.936000	14.391000	12.107000
	4.122000 5.930000 6.547000 3.169000 3.542000 2.121000 1.566000 -0.936000	4.12200010.3760005.9300008.5860006.5470007.9790003.1690009.6070003.5420008.7560002.1210009.9230001.56600012.500000-0.93600014.391000

	1 77 (000	15 00 1000	11.00.4000
н	-1.//6000	15.004000	11.824000
0	1.458000	10.984000	14.185000
Ν	4.470000	8.097000	10.190000
С	1 647000	8 976000	15 437000
ц	0.885000	0.202000	15 770000
11	0.885000	9.202000	15.770000
Н	2.126000	8.966000	16.128000
Н	1.549000	8.171000	15.101000
0	4.884000	11.829000	13.293000
Ň	5 832000	9 209000	12 609000
0	4.402000	12.952000	12.007000
C	4.408000	12.852000	13.834000
0	3.201000	13.218000	13./82000
Ν	6.475000	8.533000	11.615000
С	5.348000	13.690000	14.673000
Н	4.804000	14.208000	15.306000
н	5 810000	14 254000	14 121000
и Ц	5.071000	12 100000	15 160000
п	3.971000	13.100000	13.100000
0	2.583000	11.432000	11.608000
Н	2.346000	11.398000	10.832000
Ν	5.315000	10.997000	10.527000
С	2.389000	8.088000	10.811000
н	1 626000	8 342000	11 219000
N	5.056000	10.075000	0.749000
IN C	3.930000	10.073000	9.748000
C	2.559000	6.996000	9.968000
Н	1.933000	6.323000	9.713000
Ν	-0.322000	11.939000	12.073000
С	3.891000	7.036000	9.603000
й	4 391000	6.485000	9.065000
N	4.371000	12 011000	11 901000
N	-1.242000	12.911000	11.801000
C	6.569000	9.052000	13.719000
Н	6.277000	9.462000	14.519000
Ν	0.416000	13.761000	14.137000
С	7.691000	8.271000	13 449000
й	8 367000	8.042000	14.056000
11	0.307000	14 455000	12 (20000
NT	11 2 21 11 11 11		
N	-0.639000	14.455000	13.620000
N C	-0.639000 7.597000	7.966000	13.620000
N C H	-0.639000 7.597000 8.183000	7.966000 7.468000	13.620000 12.103000 11.546000
N C H N	-0.639000 7.597000 8.183000 1.495000	7.966000 7.468000 14.097000	13.620000 12.103000 11.546000 11.516000
N C H N C	-0.639000 7.597000 8.183000 1.495000 5.677000	$\begin{array}{c} 14.433000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\end{array}$	$13.620000 \\12.103000 \\11.546000 \\11.516000 \\10.081000$
N C H N C H	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000	7.468000 7.468000 14.097000 12.205000 12.991000	$13.620000 \\12.103000 \\11.546000 \\11.516000 \\10.081000 \\10.483000$
N C H N C H N	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.227000	$\begin{array}{c} 14.435000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\\ 12.991000\\ 14.796000\end{array}$	$\begin{array}{c} 13.620000\\ 12.103000\\ 11.546000\\ 11.516000\\ 10.081000\\ 10.483000\\ 11.226000 \end{array}$
N C H N C H N	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000	14.433000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000	13.620000 12.103000 11.546000 11.516000 10.081000 10.483000 11.336000
N C H N C H N C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000	$\begin{array}{c} 14.435000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\\ 12.991000\\ 14.796000\\ 12.076000\end{array}$	13.620000 12.103000 11.546000 11.516000 10.081000 10.483000 11.336000 9.008000
N C H N C H N C H	$\begin{array}{c} -0.639000\\ 7.597000\\ 8.183000\\ 1.495000\\ 5.677000\\ 5.357000\\ 0.337000\\ 6.554000\\ 6.995000\end{array}$	7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000	$\begin{array}{c} 13.620000\\ 12.103000\\ 11.546000\\ 11.516000\\ 10.081000\\ 10.483000\\ 11.336000\\ 9.008000\\ 8.575000 \end{array}$
N C H N C H N C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000	$\begin{array}{c} 14.433000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\\ 12.991000\\ 14.796000\\ 12.076000\\ 12.742000\\ 10.715000\end{array}$	$\begin{array}{c} 13.620000\\ 12.103000\\ 11.546000\\ 11.516000\\ 10.081000\\ 10.483000\\ 11.336000\\ 9.008000\\ 8.575000\\ 8.828000 \end{array}$
N C H N C H N C H C H C H C H	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 6.554000 6.554000 6.995000 6.707000 7.201000	14.453000 7.966000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000 10.715000 10.205000	13.620000 12.103000 11.546000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000
N C H N C H N C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 7.201000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000 10.275000 10.205000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000
N C H N C H N C H C H C H C H	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 0.464000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.742000 10.715000 10.766000 10.766000 0.9001000	13.620000 12.103000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000	14.435000 7.966000 7.468000 14.097000 12.205000 12.991000 12.742000 10.715000 10.205000 10.766000 9.901000	13.620000 12.103000 11.546000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.952000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.594000 6.595000 6.707000 7.201000 -0.923000 -0.464000 -2.234000	14.433000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.742000 10.715000 10.205000 10.766000 9.901000 10.974000	13.620000 12.103000 11.546000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.952000 11.403000
N C H N C H N C H C H C H C H C H	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 6.554000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.871000	$\begin{array}{c} 14.35000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\\ 12.991000\\ 14.796000\\ 12.076000\\ 12.076000\\ 10.715000\\ 10.205000\\ 10.766000\\ 9.901000\\ 10.974000\\ 10.356000\\ \end{array}$	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.206000 11.831000 11.952000 11.952000 11.174000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.871000 -2.395000	$\begin{array}{l} 14.35000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\\ 12.991000\\ 14.796000\\ 12.076000\\ 12.076000\\ 12.742000\\ 10.276000\\ 10.205000\\ 10.205000\\ 9.901000\\ 10.356000\\ 10.356000\\ 12.347000\\ \end{array}$	13.620000 12.103000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.952000 11.403000 11.174000 11.400000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 5.677000 5.357000 6.554000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -3.166000	14.435000 7.966000 7.468000 14.097000 12.205000 12.205000 12.742000 10.715000 10.766000 9.901000 10.974000 10.356000 12.347000 12.909000	13.620000 12.103000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.952000 11.403000 11.174000 11.179000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -3.166000 0.409000	14.453000 7.966000 7.468000 14.097000 12.205000 12.2991000 14.796000 12.742000 10.715000 10.205000 10.766000 9.901000 10.356000 12.347000 12.909000 13.981000	13.620000 12.103000 11.546000 11.516000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.952000 11.403000 11.403000 11.174000 11.174000 11.174000 11.174000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.554000 6.595000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.871000 -2.395000 -3.166000 0.409000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 12.76000 12.742000 10.715000 10.766000 9.901000 10.356000 12.347000 12.347000 13.981000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.275000 8.28000 8.206000 11.831000 11.952000 11.403000 11.174000 11.174000 11.179000 15.642000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.871000 -2.395000 -3.166000 0.409000 1.066000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000 10.276000 10.276000 10.26000 9.901000 10.356000 12.347000 12.909000 13.981000 13.981000	13.620000 12.103000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.28000 8.206000 11.952000 11.403000 11.174000 11.174000 11.179000 15.458000 16.942000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.871000 -2.871000 -2.871000 -3.166000 0.409000 1.066000 -0.657000	14.435000 7.966000 7.468000 14.097000 12.205000 12.991000 12.742000 12.742000 10.715000 10.766000 9.901000 10.376000 10.376000 12.347000 12.347000 12.399000 13.981000 13.596000 14.808000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.280000 11.952000 11.403000 11.952000 11.403000 11.174000 11.174000 11.179000 15.458000 16.042000 15.805000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 5.677000 5.357000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.855000	14.35000 7.966000 7.468000 14.097000 12.205000 12.205000 12.742000 10.715000 10.715000 10.205000 10.766000 9.901000 10.356000 12.347000 12.347000 13.981000 13.596000 14.808000 15.098000	13.620000 12.103000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.92000 11.403000 11.174000 11.174000 11.179000 15.458000 16.042000 15.805000 16.688000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.855000 -1.299000	14.435000 7.966000 7.468000 14.097000 12.205000 12.991000 12.742000 10.715000 10.766000 9.901000 10.766000 9.901000 10.766000 10.356000 12.347000 12.347000 13.596000 13.596000 15.098000 15.098000	13.620000 12.103000 11.546000 11.516000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.403000 11.403000 11.403000 11.174000 11.174000 11.179000 15.458000 16.642000 15.805000 16.688000 14.612000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.855000 -1.299000 -2.074000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000 10.276000 10.276000 10.26000 10.26000 10.356000 12.347000 12.999000 13.981000 13.981000 15.083000 15.634000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.28000 8.28000 11.831000 11.952000 11.403000 11.403000 11.174000 11.174000 11.179000 15.458000 16.042000 16.688000 14.612000 14.428000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.855000 -2.074000 2.405000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000 10.276000 10.276000 10.276000 10.266000 9.901000 10.356000 12.347000 12.909000 13.981000 13.981000 15.083000 15.634000 15.634000 14.647000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.282000 8.282000 11.331000 11.952000 11.403000 11.174000 11.174000 11.174000 11.179000 15.458000 16.042000 15.805000 16.688000 14.612000 14.428000 10.708000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.855000 -1.299000 2.405000 2.405000	14.35000 7.96600 7.46800 14.097000 12.205000 12.205000 12.991000 12.742000 10.715000 10.715000 10.766000 9.901000 10.356000 12.347000 12.347000 12.3981000 13.596000 14.808000 15.098000 15.083000 15.634000 14.647000	13.620000 12.103000 11.516000 11.516000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.831000 11.403000 11.403000 11.174000 11.179000 15.458000 16.042000 15.805000 16.688000 14.612000 14.612000 14.612000 10.716000
N C H N C H C H C H C H C H C H C H C H	-0.639000 7.597000 8.183000 5.677000 5.357000 6.554000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -2.395000 -3.166000 -0.657000 -0.657000 -0.855000 -1.299000 2.074000 2.405000 3.284000 1.847000	14.35000 7.966000 7.468000 14.097000 12.205000 12.205000 12.991000 12.742000 10.715000 10.205000 10.766000 9.901000 10.356000 12.347000 12.347000 12.909000 13.596000 14.808000 15.083000 15.634000 14.647000 14.293000	13.620000 12.103000 11.516000 11.516000 10.483000 11.336000 9.008000 8.575000 8.28000 8.206000 11.831000 11.403000 11.403000 11.403000 11.474000 11.474000 15.458000 16.642000 15.458000 16.688000 14.612000 14.612000 14.428000 10.716000 9.992000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.995000 6.707000 7.201000 7.201000 7.201000 -0.464000 -2.234000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 0.657000 -0.855000 -1.299000 2.074000 2.405000 3.284000 1.847000	14.435000 7.966000 7.468000 14.097000 12.205000 12.991000 12.742000 10.715000 10.766000 9.901000 10.356000 12.347000 13.396000 13.996000 13.996000 15.098000 15.098000 15.634000 14.647000 14.647000 15.703000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.28000 8.206000 11.831000 11.952000 11.952000 11.952000 11.403000 11.974000 11.174000 11.174000 11.174000 15.458000 16.688000 16.688000 14.612000 14.612000 14.428000 10.716000 9.992000 0.306000
N O H N O H O H O H O H O H O H O H O H	-0.639000 7.597000 8.183000 1.495000 5.357000 0.337000 6.554000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.395000 -3.166000 -0.457000 -0.855000 -1.299000 -2.074000 2.405000 3.284000 1.847000 2.265000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000 10.276000 10.276000 10.266000 9.901000 10.356000 12.347000 12.909000 13.981000 13.981000 13.981000 15.083000 15.634000 14.647000 14.293000 15.703000 16.241000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.282000 8.282000 11.331000 11.952000 11.403000 11.403000 11.174000 11.400000 11.179000 15.458000 16.042000 16.688000 14.612000 14.428000 10.716000 9.992000 9.396000
N C H N C H N C H C H C H C H C H C H C	-0.639000 7.597000 8.183000 1.495000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.871000 -2.871000 -2.871000 -2.871000 -2.871000 -2.871000 -2.875000 -0.657000 -2.074000 2.405000 3.284000 1.847000 2.265000 0.536000	$\begin{array}{l} 14.35000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\\ 12.205000\\ 12.991000\\ 14.796000\\ 12.076000\\ 12.076000\\ 12.076000\\ 10.2742000\\ 10.205000\\ 10.205000\\ 10.376000\\ 10.376000\\ 10.356000\\ 10.356000\\ 12.347000\\ 12.347000\\ 12.399000\\ 13.596000\\ 13.596000\\ 13.596000\\ 14.808000\\ 15.083000\\ 15.083000\\ 15.634000\\ 15.634000\\ 15.634000\\ 15.634000\\ 15.703000\\ 16.241000\\ 15.760000\\ \end{array}$	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.28000 11.331000 11.952000 11.403000 11.403000 11.174000 11.174000 11.174000 11.179000 15.458000 16.642000 16.688000 14.428000 14.428000 10.716000 9.992000 9.396000 10.424000
N С H N C H O H C H C H C H C H C H C H C H C H	-0.639000 7.597000 8.183000 5.677000 5.357000 6.554000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.855000 -1.299000 2.405000 3.284000 1.847000 2.265000 0.536000 -0.184000	14.35000 7.96600 7.46800 14.097000 12.205000 12.205000 12.076000 12.742000 10.715000 10.715000 10.766000 9.901000 10.356000 12.347000 12.347000 12.347000 12.347000 13.596000 14.808000 15.083000 15.083000 15.634000 14.647000 15.703000 16.241000 15.760000 16.327000	13.620000 12.103000 11.516000 11.516000 10.483000 11.336000 9.008000 8.575000 8.28000 8.206000 11.831000 11.403000 11.403000 11.474000 11.479000 15.458000 16.648000 16.688000 14.612000 16.688000 14.612000 14.612000 10.716000 9.992000 9.396000 10.424000 10.209000
N O H N O H O H O H O H O H O H O H O H	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.234000 -2.234000 -2.395000 -3.166000 0.466000 0.657000 -0.657000 -0.855000 -1.299000 2.2074000 2.405000 3.284000 1.847000 2.265000 0.536000 -0.184000 1.974000	14.433000 7.966000 7.468000 14.097000 12.205000 12.991000 12.742000 12.742000 10.715000 10.766000 9.901000 10.766000 9.901000 10.356000 12.347000 13.981000 13.996000 14.808000 15.098000 15.083000 15.634000 14.647000 14.647000 15.760000 16.327000 11.198000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.28000 8.206000 11.831000 11.952000 11.952000 11.952000 11.403000 11.974000 11.174000 11.174000 11.174000 11.400000 15.458000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.708000 10.716000 9.396000 9.396000 10.424000 10.209000 8.913000
N O H N O H O H O H O H O H O H O H O H	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.395000 -3.166000 -0.457000 -0.455000 -0.855000 -1.299000 -2.074000 2.405000 3.284000 1.847000 2.265000 0.184000 -0.184000	14.35000 7.966000 7.468000 14.097000 12.205000 12.991000 14.796000 12.076000 12.742000 10.276000 10.276000 10.205000 10.766000 9.901000 10.356000 12.347000 12.999000 13.981000 13.981000 13.981000 15.083000 15.634000 14.647000 14.647000 14.647000 15.703000 15.703000 16.221000 11.198000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.28000 8.28000 11.331000 11.952000 11.403000 11.403000 11.403000 11.400000 11.179000 15.458000 16.042000 16.688000 14.612000 14.428000 10.716000 9.992000 9.396000 10.42400
И О Н И О Н О Н О Н О Н О Н О Н О Н О Н	-0.639000 7.597000 8.183000 1.495000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.657000 -2.074000 2.405000 3.284000 1.847000 2.265000 0.536000 -0.184000 1.163000 0.181000	$\begin{array}{c} 14.35000\\ 7.966000\\ 7.468000\\ 14.097000\\ 12.205000\\ 12.991000\\ 14.096000\\ 12.076000\\ 12.076000\\ 12.076000\\ 12.076000\\ 10.2742000\\ 10.205000\\ 10.205000\\ 10.766000\\ 9.901000\\ 10.356000\\ 12.347000\\ 12.909000\\ 13.981000\\ 13.981000\\ 13.981000\\ 13.981000\\ 13.98000\\ 15.083000\\ 15.083000\\ 15.634000\\ 15.634000\\ 15.634000\\ 15.634000\\ 15.634000\\ 15.634000\\ 15.760000\\ 16.327000\\ 11.637000\\ 11.637000\\ 12.696000\\ \end{array}$	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.206000 11.403000 11.952000 11.403000 11.474000 11.174000 11.174000 11.174000 11.174000 11.174000 11.179000 15.458000 16.042000 16.042000 16.042000 10.716000 9.992000 9.396000 10.424000 10.209000 8.111000 8.476000
N C H N C H O H C H C H C H C H C H C H C H C H	-0.639000 7.597000 8.183000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -2.657000 -2.074000 2.405000 2.405000 0.536000 -0.184000 1.847000 2.265000 0.536000 -0.184000 1.974000 1.163000 0.777000	14.35000 7.96600 7.468000 14.097000 12.205000 12.205000 12.991000 14.796000 12.076000 12.742000 10.276000 10.276000 10.376000 10.376000 10.376000 12.347000 12.347000 13.981000 13.596000 14.808000 15.098000 15.634000 15.634000 15.763000 15.760000 16.241000 15.760000 16.327000 11.198000 11.637000 12.64000	13.620000 12.103000 11.516000 11.516000 10.483000 11.336000 9.008000 8.575000 8.828000 8.28000 11.331000 11.952000 11.403000 11.174000 11.174000 11.174000 11.174000 11.174000 11.179000 15.458000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 10.716000 9.992000 9.992000 9.396000 10.424000 10.209000 8.913000 8.111000 8.720000
ИОНИОНОНОНОНОНОНОНОНОНОНОНОНОНООООН;	-0.639000 7.597000 8.183000 1.495000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.395000 -2.395000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -0.657000 -2.074000 2.405000 0.536000 -0.184000 1.974000 1.163000 0.181000 -0.737000	14,35000 7.966000 7.468000 14.097000 12.205000 12.991000 12.742000 12.742000 10.715000 10.766000 9.901000 10.766000 9.901000 10.766000 10.356000 12.347000 13.596000 13.596000 15.098000 15.098000 15.634000 14.647000 14.647000 15.760000 16.327000 11.198000 11.198000 11.637000 12.696000 12.441000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.275000 8.28000 8.206000 11.831000 11.952000 11.403000 11.952000 11.403000 11.174000 11.174000 11.400000 15.805000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.688000 16.76000 9.396000 10.229000 8.913000 8.111000 8.476000 8.239000
N O H N O H O H O H O H O H O H O H O H	-0.639000 7.597000 8.183000 1.495000 5.677000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.395000 -3.166000 0.409000 1.299000 -0.657000 0.855000 -1.299000 2.074000 2.405000 3.284000 1.847000 2.265000 0.536000 -0.184000 1.974000 1.163000 0.181000 -0.737000 0.207000	14.4,35000 7.966000 7.468000 14.097000 12.205000 12.295000 12.991000 12.742000 10.715000 10.766000 9.901000 10.356000 12.347000 13.981000 13.981000 13.981000 13.981000 15.083000 15.634000 15.634000 15.703000 15.703000 16.327000 11.198000 11.637000 12.696000 12.441000 12.941000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.28000 8.28000 11.831000 11.952000 11.403000 11.952000 11.403000 11.174000 11.403000 11.174000 11.403000 11.403000 11.403000 11.403000 14.612000 14.612000 14.612000 14.612000 14.612000 14.612000 14.62000 10.716000 9.992000 9.396000 8.111000 8.111000 8.476000 8.239000 9.333000
И О Н И О Н О Н О Н О Н О Н О Н О Н О Н	-0.639000 7.597000 8.183000 1.495000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.234000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -2.074000 2.405000 3.284000 1.847000 2.265000 0.536000 -0.184000 1.163000 0.181000 -0.737000 0.207000 0.227000 0.246000	14.33000 7.966000 7.468000 14.097000 12.205000 12.295000 12.076000 12.076000 12.742000 10.276000 10.276000 10.26000 10.766000 9.901000 10.356000 12.347000 12.909000 13.981000 13.981000 15.034000 15.634000 15.634000 15.634000 15.7703000 16.241000 15.7703000 16.241000 12.296000 12.441000 12.494000 12.494000 12.494000 13.386000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.28000 11.331000 11.952000 11.403000 11.403000 11.174000 11.403000 11.174000 11.400000 11.179000 15.458000 16.042000 16.042000 16.042000 16.042000 16.042000 10.716000 9.992000 9.396000 10.424000 10.746000 8.239000 9.333000 7.913000
N C H N C H O H C H C H C H C H C H C H C H C H	-0.639000 7.597000 8.183000 1.495000 5.357000 0.337000 6.554000 6.995000 6.707000 7.201000 -0.923000 -0.464000 -2.234000 -2.234000 -2.395000 -2.395000 -3.166000 0.409000 1.066000 -0.657000 -2.074000 2.405000 3.284000 1.847000 2.265000 0.536000 -0.184000 1.974000 1.163000 0.227000 0.226000 1.110000	14.435000 7.966000 7.468000 14.097000 12.205000 12.295000 12.991000 12.076000 12.076000 12.742000 10.276000 10.276000 10.376000 10.376000 10.376000 12.347000 12.347000 13.981000 13.981000 13.981000 13.596000 14.647000 14.647000 14.647000 15.703000 16.241000 15.760000 12.441000 12.696000 12.441000 12.696000 12.441000 12.696000 12.441000	13.620000 12.103000 11.516000 11.516000 10.081000 10.483000 11.336000 9.008000 8.575000 8.828000 8.28000 11.331000 11.952000 11.403000 11.952000 11.403000 11.174000 11.174000 11.174000 11.174000 11.179000 15.458000 16.688000 14.612000 14.428000 16.688000 14.612000 14.428000 10.716000 9.992000 9.992000 9.396000 10.424000 10.209000 8.913000 8.176000 8.239000 9.330000 7.913000 6.707000

Η	1.655000	10.306000	6.605000
Н	1.375000	11.726000	6.145000

Fe 173 K:

Fe	4.198000	9.801000	4.489000
0	4.949000	8.347000	5.639000
В	6.018000	11.583000	2.511000
н	6.674000	12.180000	1.863000
Ν	5 395000	9 175000	2 874000
C	4 483000	7 311000	6 178000
E	1 644000	7.660000	5 202000
re O	2 281000	6.040000	5.203000
D D	3.281000	6.940000	0.099000
в	-0.86/000	5.798000	4.424000
Н	-1./05000	5.21/000	4.132000
Ν	6.046000	10.096000	2.097000
С	5.426000	6.468000	6.981000
Η	4.887000	5.918000	7.634000
Η	6.058000	7.018000	7.433000
Η	5.945000	5.949000	6.411000
0	3.232000	10.573000	6.074000
Ν	5.908000	10.970000	4.958000
C	2 195000	10.243000	6 709000
õ	1 547000	9 176000	6 525000
N	6 557000	11 639000	3 964000
$\hat{\mathbf{C}}$	1 714000	11 170000	7 777000
U U	1.714000	10.001000	8.222000
н	1.074000	10.901000	8.222000
н	1.559000	11.998000	7.421000
Н	2.277000	11.538000	8.194000
0	2.663000	8.742000	3.945000
Η	2.445000	8.779000	3.199000
Ν	3.628000	11.421000	3.285000
С	5.745000	7.969000	2.418000
Η	5.426000	7.193000	2.838000
Ν	4.560000	12.073000	2.527000
С	6.619000	8.097000	1.345000
Н	7.050000	7 426000	0.904000
N	1 568000	6.075000	3 845000
\hat{C}	6 783000	9.449000	1 173000
с ц	7 202000	0.086000	0.552000
п N	7.293000	5.201000	2 655000
N	0.403000	3.391000	5.055000
C .	6.634000	11.133000	6.069000
Н	6.306000	10.776000	6.883000
Ν	0.484000	6.408000	6.462000
С	7.753000	11.915000	5.800000
Η	8.457000	12.156000	6.390000
Ν	-0.571000	5.724000	5.937000
С	7.668000	12.211000	4.462000
Η	8.257000	12.695000	3.919000
Ν	-0.239000	8.244000	4.407000
С	2.482000	12.094000	3.138000
Н	1.721000	11.847000	3,488000
N	-1 163000	7 278000	4 126000
C	2 657000	13 182000	2 294000
ц	2.037000	13 831000	2.224000
C	2.040000	12 125000	2.010000
U U	3.987000	13.133000	1.950000
П	4.481000	13.098000	1.398000
5	2.477000	3.509000	3.045000
Н	3.329000	5.811000	3.086000
С	1.912000	4.462000	2.333000
Н	2.345000	3.906000	1.784000
С	0.604000	4.421000	2.747000
LT			
п	-0.114000	3.851000	2.505000
п С	-0.114000 0.472000	3.851000 6.185000	2.505000 7.781000
п С Н	-0.114000 0.472000 1.139000	3.851000 6.185000 6.537000	2.505000 7.781000 8.336000
п С Н С	-0.114000 0.472000 1.139000 -0.598000	3.851000 6.185000 6.537000 5.358000	2.505000 7.781000 8.336000 8.115000

С	-1.236000	5.094000	6.923000
Н	-2.021000	4.562000	6.720000
С	-0.836000	9.420000	4.170000
Η	-0.378000	10.224000	4.296000
С	-2.142000	9.214000	3.742000
Н	-2.801000	9.834000	3.528000
С	-2.309000	7.853000	3.728000
Н	-3.072000	7.300000	3.516000
0	2.065000	8.961000	1.240000
С	1.269000	8.519000	0.435000
С	1.250000	9.029000	-0.977000
Н	0.342000	9.157000	-1.266000
Н	1.490000	8.394000	-1.507000
Η	1.797000	9.893000	-1.090000
С	0.268000	7.487000	0.781000
Η	-0.642000	7.870000	0.427000
Н	0.346000	7.201000	1.670000
Η	0.206000	6.828000	0.124000

Fe 234 K:

Fe	1.451000	19.903000	3.226000
В	-0.438000	21.649000	5.171000
Н	-1.057000	22.248000	5.831000
0	0.754000	18.425000	2.071000
Ν	0.241000	19.254000	4.833000
С	1.214000	17.349000	1.619000
Fe	4.032000	17.775000	2.585000
В	6.590000	16.043000	3.477000
Н	7.416000	15.469000	3.694000
0	2.405000	16.964000	1.733000
Ν	-0.448000	20.163000	5.583000
С	0.262000	16.454000	0.871000
Н	0.747000	15.725000	0.421000
Н	-0.374000	16.935000	0.374000
Н	-0.338000	16.045000	1.496000
0	2.442000	20.672000	1.652000
Ν	-0.261000	21.044000	2.726000
С	3.455000	20.303000	1.008000
0	4.073000	19.225000	1.204000
Ν	-0.938000	21.709000	3.705000
С	3.941000	21.197000	-0.095000
Н	3.297000	21.823000	-0.467000
Н	4.482000	20.816000	-0.608000
Н	4.516000	21.762000	0.577000
0	2.982000	18.868000	3.802000
Н	3.277000	18.934000	4.441000
Ν	1.972000	21.530000	4.444000
С	-0.057000	18.049000	5.323000
Н	0.296000	17.285000	4.874000
Ν	1.013000	22.159000	5.188000
С	-0.934000	18.165000	6.385000
Н	-1.274000	17.493000	6.950000
Ν	4.136000	16.216000	3.987000
С	-1.155000	19.513000	6.523000
Н	-1.722000	19.926000	7.051000
Ν	5.321000	15.597000	4.233000
С	-0.958000	21.219000	1.600000
Н	-0.726000	20.844000	0.832000
Ν	5.260000	16.522000	1.390000
C	-2.074000	21.996000	1.838000
Н	-2.686000	22.221000	1.103000
N	6.326000	15.890000	1.962000
C	-2.031000	22.279000	3.179000
H	-2.601000	22.707000	3.708000
N	5.869000	18.446000	3.383000
С	3.098000	22.221000	4.622000

Н	3.833000	21.964000	4.195000
Ν	6.818000	17.530000	3.726000
С	2.882000	23.294000	5.471000
Н	3.480000	23.963000	5.815000
С	1.559000	23.219000	5.800000
Н	1.084000	23.687000	6.228000
С	3.228000	15.601000	4.745000
Н	2.308000	15.816000	4.799000
С	3.815000	14.595000	5.485000
Н	3.436000	14.124000	6.108000
С	5.124000	14.622000	5.127000
Н	5.761000	14.139000	5.345000
С	5.315000	16.238000	0.089000
Н	4.700000	16.639000	-0.502000
С	6.409000	15.433000	-0.192000
Н	6.774000	15.165000	-1.060000
С	7.025000	15.247000	1.024000
Н	7.837000	14.650000	1.256000
С	6.393000	19.649000	3.612000
Н	5.914000	20.367000	3.386000
С	7.681000	19.500000	4.103000
Н	7.987000	20.011000	4.394000
С	7.910000	18.179000	4.171000
Н	8.651000	17.577000	4.441000
С	4.329000	18.455000	7.233000
0	3.942000	19.077000	6.347000
С	3.563000	18.191000	8.246000
Н	2.647000	18.352000	8.006000
Н	3.804000	18.753000	8.986000
Н	3.670000	17.269000	8.497000
С	5.632000	17.901000	7.367000
Н	6.090000	17.954000	6.526000
Η	5.563000	16.983000	7.637000
Н	6.121000	18.394000	8.031000

Fe 296 K:

Fe	1.443000	19.952000	3.242000
0	0.762000	18.469000	2.088000
В	-0.467000	21.692000	5.169000
Η	-1.098000	22.310000	5.806000
С	1.220000	17.385000	1.649000
Ν	0.229000	19.298000	4.846000
Fe	4.032000	17.825000	2.620000
0	2.409000	17.005000	1.774000
В	6.597000	16.126000	3.538000
Н	7.444000	15.582000	3.845000
С	0.274000	16.484000	0.910000
Η	-0.329000	16.892000	0.361000
Η	-0.249000	16.226000	1.412000
Η	0.746000	15.764000	0.471000
Ν	-0.473000	20.201000	5.589000
0	2.444000	20.723000	1.677000
С	3.455000	20.346000	1.035000
Ν	-0.267000	21.089000	2.729000
0	4.066000	19.269000	1.227000
С	3.952000	21.240000	-0.067000
Η	4.432000	20.716000	-0.712000
Η	4.535000	21.909000	0.301000
Η	3.206000	21.669000	-0.494000
Ν	-0.956000	21.747000	3.702000
С	-0.052000	18.095000	5.342000
Η	0.286000	17.312000	4.923000
Ν	1.948000	21.580000	4.470000
0	2.972000	18.920000	3.827000
Н	3.179000	18.952000	4.377000
С	-0.933000	18.209000	6.407000

Н	-1.261000	17.552000	6.892000
Ν	0.979000	22.203000	5.206000
Ν	4.139000	16.270000	4.028000
С	-1.171000	19.555000	6.532000
Н	-1.681000	20.004000	7.148000
Ν	5.329000	15.672000	4.288000
С	-0.944000	21.271000	1.597000
Н	-0.650000	20.906000	0.822000
Ν	5.277000	16.577000	1.438000
С	-2.060000	22.049000	1.820000
Н	-2.680000	22.173000	1.174000
Ν	6.344000	15.961000	2.028000
С	-2.039000	22.323000	3.163000
Н	-2.642000	22.720000	3.772000
Ν	5.855000	18.521000	3.423000
С	3.071000	22.272000	4.667000
Н	3.830000	22.066000	4.192000
С	2.843000	23.336000	5.516000
Н	3.353000	24.052000	5.769000
Ν	6.811000	17.615000	3.779000
С	1.520000	23.261000	5.833000
Н	1.017000	23.770000	6.382000
C	3.238000	15.639000	4.770000
Н	2.428000	15.915000	4.714000
С	3.825000	14.639000	5.513000
Н	3.432000	14.127000	6.197000
С	5.131000	14.684000	5.177000
Н	5.793000	14.119000	5.428000
С	5.342000	16.288000	0.145000
Н	4.719000	16.637000	-0.444000
С	6.442000	15.489000	-0.118000
Н	6.763000	15.164000	-0.860000
С	7.052000	15.319000	1.096000
Н	7.835000	14.833000	1.371000
С	6.354000	19.737000	3.651000
Н	5.897000	20.452000	3.456000
С	7.645000	19.602000	4.151000
Н	8.075000	20.080000	4.565000
С	7.890000	18.284000	4.230000
Н	8.699000	17.723000	4.518000
0	3.999000	19.112000	6.357000
С	4.300000	18.460000	7.261000
С	5.658000	18.058000	7.516000
H	6.243000	18.494000	6.892000
Н	5.734000	17.108000	7.416000
Н	5.902000	18.306000	8.411000
С	3.314000	17.927000	8.083000
Н	2.455000	18.250000	7.804000
Н	3.476000	18.193000	8.991000
Н	3.332000	16.970000	8.023000

Ga 20 K:

Ga	4.181000	0.309000	10.946000
В	5.940000	-1.466000	12.895000
Н	6.545000	-2.081000	13.533000
0	4.961000	1.734000	9.807000
Ν	5.339000	0.940000	12.522000
С	4.485000	2.747000	9.228000
Ga	1.659000	2.421000	10.199000
В	-0.794000	4.312000	10.884000
Н	-1.632000	4.938000	11.137000
0	3.287000	3.125000	9.300000
Ν	5.972000	0.023000	13.311000
С	5.425000	3.564000	8.401000
Н	6.063000	2.977000	7.955000
Η	4.932000	4.067000	7.780000
Н	5.923000	4.139000	8.951000

0	3.262000	-0.454000	9.355000
Ν	5.833000	-0.826000	10.449000
С	2.236000	-0.117000	8.697000
0	1.552000	0.931000	8.884000
Ň	6 480000	-1 505000	11 439000
C	1 810000	1.031000	7 588000
п	0.014000	-1.031000	7.388000
н	0.914000	-0.856000	7.305000
Н	2.348000	-0.940000	6.896000
Н	1.932000	-1.921000	7.821000
0	2.661000	1.359000	11.428000
Η	2.425000	1.338000	12.155000
Ν	3.572000	-1.276000	12.084000
С	5.736000	2.153000	12.925000
Ĥ	5 422000	2 923000	12 494000
N	4 479000	-1.942000	12.855000
C	6 620000	2 022000	12.002000
U U	0.029000	2.033000	13.993000
H	/.066000	2.739000	14.443000
Ν	1.618000	3.999000	11.502000
С	6.754000	0.668000	14.204000
Н	7.266000	0.152000	14.804000
Ν	0.472000	4.714000	11.668000
С	6.555000	-0.983000	9.331000
Н	6.264000	-0.596000	8.529000
N	0 589000	3 607000	8 896000
C	7 677000	1 774000	0.590000
п	8 227000	-1.774000	9.389000
H	8.327000	-2.025000	8.983000
N	-0.458000	4.336000	9.379000
С	7.593000	-2.082000	10.938000
Н	8.141000	-2.573000	11.482000
Ν	-0.188000	1.864000	10.958000
С	2.410000	-1.933000	12.186000
Н	1.666000	-1.639000	11.700000
Н	0.135000	0.880000	16.590000
Ν	-1.111000	2.838000	11.214000
C	2 553000	-3.037000	13 030000
н	1 923000	-3 673000	13 235000
C	2 880000	2 008000	12 426000
U U	3.880000	-3.008000	13.420000
П	4.376000	-5.589000	13.962000
C	2.533000	4.522000	12.327000
Н	3.405000	4.165000	12.317000
С	1.983000	5.587000	13.043000
Н	2.403000	6.116000	13.660000
С	0.673000	5.672000	12.595000
Н	-0.015000	6.262000	12.838000
С	0.611000	3,788000	7 569000
Ĥ	1 252000	3 381000	7.035000
C	-0.432000	4 632000	7 182000
ц	0.622000	4.896000	6 313000
	-0.022000	4.890000	0.313000
U U	-1.091000	4.951000	8.359000
Н	-1.850000	5.490000	8.523000
С	-0.794000	0.688000	11.193000
Н	-0.346000	-0.138000	11.082000
Η	1.402000	1.689000	16.944000
С	-2.115000	0.904000	11.602000
Н	-2.780000	0.250000	11.810000
С	-2.274000	2.280000	11.599000
й	-3.011000	2 803000	11 790000
ц	0.367000	2.000000	13 667000
11 17	0.307000	2.931000	15.00/000
п	0.510000	3.39/000	13.164000
U	2.010000	1.124000	14.152000
С	1.179000	1.558000	14.936000
С	1.072000	1.017000	16.335000
Н	1.563000	0.188000	16.459000
С	0.226000	2.657000	14.571000
н	-0.665000	2,359000	14.662000

Ga	4.197000	0.312000	10.963000
0	4.974000	1.739000	9.824000
В Ц	5.950000	-1.405000	12.907000
N	5 355000	0.941000	12 539000
C	4.500000	2.753000	9.249000
Ga	1.675000	2.427000	10.221000
0	3.304000	3.133000	9.325000
В	-0.780000	4.314000	10.907000
Н	-1.615000	4.932000	11.161000
N	5.990000	0.023000	13.326000
с ц	5.440000	3.570000	8.423000
н	6.066000	2 987000	7.958000
н	5.940000	4.131000	8.973000
0	3.274000	-0.448000	9.372000
Ν	5.847000	-0.823000	10.463000
С	2.250000	-0.109000	8.716000
0	1.569000	0.939000	8.903000
N	6.495000	-1.503000	11.451000
C	1.818000	-1.025000	7.610000
н н	2 380000	-0.833000	7.294000
Н	1.919000	-1.897000	7.848000
0	2.678000	1.363000	11.447000
Н	2.445000	1.344000	12.172000
Ν	3.589000	-1.275000	12.098000
С	5.750000	2.153000	12.947000
Н	5.431000	2.923000	12.521000
N	4.496000	-1.942000	12.870000
С П	0.041000 7.070000	2.031000	14.015000
п	1.63/000	2.752000	14.464000
C	6 770000	0.666000	14 222000
Н	7.288000	0.144000	14.815000
Ν	0.485000	4.717000	11.692000
С	6.567000	-0.980000	9.344000
Н	6.278000	-0.585000	8.542000
N	0.605000	3.614000	8.918000
С	/.688000	-1.//3000	9.600000
H N	8.338000	-2.021000	8.990000 9.402000
C	7 605000	-2 080000	10 948000
Н	8.153000	-2.576000	11.480000
Ν	-0.171000	1.866000	10.978000
С	2.427000	-1.932000	12.201000
Η	1.681000	-1.643000	11.717000
N	-1.096000	2.840000	11.234000
С	2.5/1000	-3.03/000	13.045000
С	3 897000	-3.070000	13.248000
н	4.391000	-3.580000	13.972000
C	2.548000	4.531000	12.346000
Н	3.418000	4.181000	12.332000
С	1.997000	5.595000	13.062000
Η	2.424000	6.136000	13.678000
C	0.687000	5.677000	12.617000
H	-0.005000	6.268000	12.861000
ц	1 260000	3.797000	7.392000
C	-0.418000	4.640000	7.206000
H	-0.612000	4.898000	6.350000
Ċ	-1.078000	4.955000	8.382000
Η	-1.830000	5.481000	8.552000
С	-0.775000	0.691000	11.210000
H	-0.331000	-0.132000	11.089000
C	-2.096000	0.905000	11.618000
н С	-2.158000	0.248000 2.278000	11.620000
Н	-2.993000	2.806000	11.800000
	•		

0	2.030000	1.128000	14.173000
С	1.200000	1.561000	14.959000
С	0.247000	2.656000	14.595000
Н	-0.632000	2.372000	14.701000
Η	0.380000	2.937000	13.689000
Н	0.330000	3.403000	15.208000
С	1.098000	1.020000	16.357000
Н	1.582000	0.182000	16.474000
Η	0.165000	0.889000	16.610000
Н	1.422000	1.703000	16.971000

Ga 100 K:

Ga	-4.222000	9.725000	-3.302000
В	-5.988000	11.503000	-5.240000
Н	-6.583000	12.127000	-5.876000
0	-3.293000	10.483000	-1.714000
Ν	-3.617000	11.313000	-4.437000
С	-2.274000	10.139000	-1.057000
Ga	-1.703000	7.605000	-2.565000
B	0.756000	5 728000	-3 257000
ц	1 613000	5 106000	3.521000
0	1.602000	0.000000	1 245000
N	-1.003000	9.090000	-1.245000
N	-4.526000	11.981000	-5.209000
C H	-1.85/000	11.052000	0.047000
Н	-1.011000	10.888000	0.394000
н	-1.906000	11.906000	-0.200000
Н	-2.343000	11.043000	0.724000
0	-4.994000	8.296000	-2.163000
Ν	-5.872000	10.860000	-2.797000
С	-4.526000	7.280000	-1.599000
0	-3.335000	6.897000	-1.678000
Ν	-6.522000	11.542000	-3.784000
С	-5.464000	6.459000	-0.778000
Н	-4.950000	5.923000	-0.180000
Н	-5.947000	5.899000	-1.259000
н	-6.086000	7.013000	-0.326000
0	-2.706000	8.673000	-3.787000
н	-2 464000	8 730000	-4 471000
N	-5 382000	9.097000	-4 877000
C	2 4 5 9 0 0 0	11 07/000	4.545000
ц	1 700000	11.574000	4 120000
п N	-1.709000	10.017000	-4.120000
IN C	-0.021000	12.077000	-3.003000
C H	-2.606000	13.077000	-5.584000
Н	-1.9/3000	13./35000	-5.610000
Ν	0.143000	8.172000	-3.319000
С	-3.928000	13.046000	-5.777000
Н	-4.430000	13.601000	-6.312000
Ν	1.070000	7.200000	-3.577000
С	-6.586000	11.020000	-1.681000
Н	-6.290000	10.651000	-0.873000
Ν	-0.630000	6.415000	-1.265000
С	-7.702000	11.815000	-1.935000
Н	-8.355000	12.043000	-1.347000
Ν	0.421000	5.694000	-1.752000
С	-7.625000	12.119000	-3.271000
Ĥ	-8.163000	12.587000	-3.795000
N	-1 659000	6.030000	-3 872000
Ĉ	-5 772000	7 886000	-5 294000
н	-5.459000	7.138000	-4 875000
N	0.508000	5 321000	4.043000
C	6 657000	8 010000	6 362000
U U	7.002000	0.010000	-0.302000
П	-1.092000	1.330000	-0.800000
U T	-0./91000	9.3/3000	-0.302000
H	-/.310000	9.922000	-/.185000
C	0.746000	9.346000	-3.547000
H	0.303000	10.155000	-3.430000
С	2.064000	9.134000	-3.950000

Н	2.741000	9.786000	-4.146000
С	2.228000	7.770000	-3.957000
Н	2.957000	7.228000	-4.170000
С	-0.650000	6.228000	0.058000
Н	-1.286000	6.616000	0.571000
С	0.394000	5.390000	0.439000
Н	0.592000	5.146000	1.298000
С	1.051000	5.081000	-0.730000
Н	1.801000	4.580000	-0.910000
С	-2.569000	5.492000	-4.687000
Н	-3.440000	5.847000	-4.658000
С	-2.015000	4.433000	-5.400000
Н	-2.464000	3.889000	-6.011000
С	-0.708000	4.360000	-4.965000
Н	-0.015000	3.763000	-5.211000
0	-2.061000	8.902000	-6.521000
С	-1.238000	8.468000	-7.310000
С	-0.277000	7.388000	-6.947000
Н	0.581000	7.615000	-7.083000
Н	-0.430000	7.126000	-6.008000
Н	-0.291000	6.690000	-7.569000
С	-1.147000	9.004000	-8.709000
Н	-0.246000	9.175000	-8.932000
Н	-1.661000	9.846000	-8.855000
Н	-1.447000	8.336000	-9.327000

Ga 173 K:

Ga	7.282000	9.765000	3.320000
0	6.518000	8.332000	2.182000
Ν	6.121000	9.132000	4.894000
С	6.973000	7.306000	1.632000
В	5.506000	11.537000	5.252000
Н	4.909000	12.140000	5.892000
Ga	9.796000	7.638000	2.593000
0	8.161000	6.923000	1.719000
Ν	5.473000	10.051000	5.673000
В	12.262000	5.777000	3.297000
Н	13.095000	5.166000	3.569000
С	6.032000	6.479000	0.831000
Н	6.528000	5.990000	0.248000
Н	5.434000	7.040000	0.344000
Н	5.444000	5.888000	1.308000
С	9.231000	10.169000	1.079000
0	8.220000	10.521000	1.740000
Ν	5.635000	10.901000	2.811000
0	9.888000	9.115000	1.265000
С	9.666000	11.072000	-0.025000
Н	9.063000	11.539000	-0.387000
Н	10.318000	10.752000	-0.495000
Н	9.856000	11.807000	0.279000
Ν	4.979000	11.578000	3.793000
Ν	7.879000	11.356000	4.459000
0	8.795000	8.712000	3.809000
Н	8.988000	8.727000	4.471000
С	5.741000	7.929000	5.320000
Н	6.067000	7.183000	4.915000
Ν	6.967000	12.017000	5.229000
С	4.860000	8.051000	6.385000
Н	4.440000	7.387000	6.837000
Ν	9.845000	6.066000	3.902000
С	4.715000	9.399000	6.575000
Н	4.203000	9.885000	7.150000
Ν	11.003000	5.368000	4.083000
С	4.928000	11.066000	1.692000
Н	5.244000	10.687000	0.873000
Ν	10.877000	6.450000	1.299000
С	3.819000	11.856000	1.938000

Н	3.209000	12.102000	1.331000
Ν	11.926000	5.733000	1.788000
С	3.882000	12.154000	3.275000
Н	3.354000	12.660000	3.785000
Ν	11.639000	8.217000	3.343000
С	9.031000	12.016000	4.576000
Н	9.775000	11.701000	4.132000
С	8.877000	13.114000	5.414000
Н	9.460000	13.746000	5.643000
Ν	12.569000	7.250000	3.607000
С	7.560000	13.078000	5.802000
Н	7.071000	13.637000	6.324000
С	8.939000	5.514000	4.705000
Н	8.042000	5.859000	4.694000
С	9.498000	4.460000	5.418000
Н	9.063000	3.927000	6.033000
С	10.798000	4.404000	4.998000
Н	11.529000	3.810000	5.245000
С	10.861000	6.249000	-0.019000
Н	10.198000	6.655000	-0.528000
С	11.904000	5.420000	-0.391000
Н	12.104000	5.180000	-1.211000
С	12.557000	5.120000	0.776000
Н	13.334000	4.638000	0.947000
С	12.233000	9.391000	3.564000
Н	11.757000	10.187000	3.434000
С	13.549000	9.183000	3.972000
Н	14.175000	9.807000	4.185000
С	13.723000	7.829000	3.984000
Н	14.468000	7.288000	4.203000
0	9.438000	8.921000	6.551000
С	10.239000	8.484000	7.348000
С	11.211000	7.435000	6.997000
Н	12.134000	7.741000	7.338000
Η	11.215000	7.234000	6.100000
Н	11.247000	6.730000	7.571000
С	10.292000	9.010000	8.754000
Н	9.748000	9.865000	8.961000
Н	11.256000	9.091000	9.029000
Н	10.023000	8.273000	9.385000

Ga 234 K:

Ga	4.173000	9.817000	4.487000
В	6.006000	11.566000	2.589000
Η	6.585000	12.147000	1.955000
0	4.894000	8.362000	5.630000
Ν	5.344000	9.174000	2.916000
С	4.440000	7.302000	6.108000
Ga	1.638000	7.694000	5.150000
В	-0.863000	5.930000	4.352000
Н	-1.677000	5.386000	4.029000
0	3.262000	6.916000	5.995000
Ν	6.025000	10.078000	2.160000
С	5.384000	6.437000	6.876000
Н	4.859000	5.815000	7.410000
Η	6.008000	7.002000	7.348000
Н	5.873000	5.895000	6.412000
0	3.212000	10.572000	6.056000
Ν	5.823000	10.926000	5.026000
С	2.217000	10.187000	6.719000
0	1.581000	9.127000	6.526000
Ν	6.500000	11.605000	4.058000
С	1.786000	11.064000	7.855000
Н	2.467000	11.650000	8.299000
Η	1.178000	10.664000	8.362000
Н	1.450000	11.590000	7.285000
0	2.670000	8.777000	3.963000

Н	2.395000	8.881000	3.338000
Ν	3.617000	11.421000	3.342000
С	5.673000	7.971000	2.459000
Н	5 279000	7 197000	2,855000
N	4.552000	12.061000	2.582000
C	6 553000	8 084000	1 400000
н	6 957000	7 493000	0.952000
N	1 568000	6 156000	3 805000
C	6 753000	9.427000	1 240000
ч	7 321000	9.427000	0.675000
N	0.326000	5.502000	3 576000
C	6.407000	11 008000	5.570000
U U	6.497000	10.74(000	6.100000
H N	0.1/0000	10.746000	6.998000
N	0.511000	0.497000	6.398000
C	7.612000	11.883000	5.932000
Н	8.202000	12.113000	6.552000
N	-0.555000	5.828000	5.867000
С	7.582000	12.176000	4.60/000
Н	8.124000	12.612000	4.168000
Ν	-0.168000	8.343000	4.406000
С	2.482000	12.099000	3.201000
Н	1.753000	11.825000	3.568000
Ν	-1.120000	7.416000	4.090000
С	2.672000	13.184000	2.358000
Н	2.136000	13.883000	2.122000
С	3.980000	13.127000	1.990000
Η	4.467000	13.650000	1.441000
С	2.466000	5.560000	3.033000
Н	3.259000	5.847000	2.989000
С	1.890000	4.542000	2.298000
Н	2.293000	3.998000	1.700000
С	0.587000	4.537000	2.676000
Н	-0.086000	3.986000	2.510000
С	0.505000	6.254000	7.704000
Н	1.122000	6.642000	8.237000
С	-0.566000	5.431000	8.030000
Ĥ	-0.837000	5 139000	8 848000
C	-1.213000	5,202000	6.845000
н	-1.961000	4 660000	6 627000
C	-0.717000	9 544000	4 195000
н	-0.266000	10 243000	4 352000
C	-2 019000	9 370000	3 742000
н	-2 479000	10.068000	3 432000
C	-2 238000	8 046000	3 678000
н	-2.955000	7 435000	3 479000
C	1 261000	8 403000	0.491000
õ	1 79/000	8 986000	1 334000
č	0.037000	7 712000	0.532000
н	-0.265000	7 650000	1 441000
н	0.15/000	6.831000	0.172000
ц	-0.616000	8 187000	0.011000
С	1 7/0000	0.10/000 0.10/000	0.011000
ч	1.740000	0.302000	0.724000
п	2.220000	2.122000	1 251000
п	1.01/000	0.308000	-1.331000
п	2.327000	7.050000	-0.022000

Ga 296 K:

Ga	1.486000	19.940000	3.328000
0	0.789000	18.477000	2.182000
Ν	0.306000	19.291000	4.895000
С	1.238000	17.406000	1.726000
В	-0.382000	21.680000	5.202000
Η	-0.951000	22.266000	5.829000
Ga	4.034000	17.822000	2.693000
0	2.420000	17.025000	1.853000
С	0.304000	16.530000	0.988000
Н	-0.374000	17.066000	0.570000

Η	-0.107000	15.914000	1.600000
Η	0.786000	16.041000	0.317000
В	6.549000	16.107000	3.536000
Н	7.368000	15.537000	3.853000
N	-0.392000	20.193000	5.632000
0	2.463000	20.696000	1.768000
N	-0.162000	21.038000	2.770000
C	3.451000	20.302000	1.104000
0	4.079000	19.244000	1.301000
C II	3.896000	21.1/5000	-0.030000
H	4.231000	21.86/000	0.550000
н	3.210000	21.806000	-0.409000
H N	4.501000	20.737000	-0.503000
IN N	-0.830000	21.713000	5.727000
C	2.019000	18 085000	4.487000 5.370000
с ц	0.382000	17 324000	4 908000
$\hat{0}$	2 987000	18 904000	3 867000
н	3 237000	19.023000	4 485000
\hat{C}	-0.883000	18 205000	6 426000
н	-1.276000	17.552000	6.914000
N	1.070000	22.180000	5.231000
C	-1.112000	19.536000	6.558000
H	-1.689000	20.013000	7.108000
Ν	4.111000	16.284000	4.045000
N	5.297000	15.665000	4.295000
С	-0.816000	21.217000	1.634000
Н	-0.546000	20.887000	0.878000
С	-1.927000	22.006000	1.831000
Н	-2.512000	22.305000	1.164000
Ν	5.185000	16.627000	1.468000
С	-1.922000	22.293000	3.155000
Η	-2.443000	22.686000	3.595000
Ν	6.253000	15.981000	2.016000
Ν	5.820000	18.507000	3.447000
С	3.146000	22.229000	4.645000
Η	3.920000	21.970000	4.205000
Ν	6.783000	17.601000	3.780000
С	2.933000	23.313000	5.494000
Η	3.475000	24.019000	5.744000
С	1.627000	23.240000	5.830000
Η	1.187000	23.709000	6.317000
С	3.210000	15.666000	4.795000
Н	2.287000	15.843000	4.714000
C	3.792000	14.662000	5.535000
Н	3.349000	14.022000	6.097000
C	5.092000	14.692000	5.192000
Н	5.791000	14.088000	5.415000
	5.211000	16.364000	0.164000
п	4.379000	15.715000	-0.505000
п	6.290000	15.330000	-0.143000
п	6.036000	15.214000	-1.057000
п	7 700000	13.340000	1.043000
п С	6 337000	14.831000	3 650000
с ц	5 783000	20 447000	3.050000
C	7 628000	19 592000	4 128000
н	7.020000	20 277000	4 463000
C	7.879000	18 272000	4 197000
н	8.650000	17.673000	4.356000
0	3,982000	19,098000	6.457000
č	4.357000	18,450000	7.326000
č	3.507000	18.006000	8.233000
й	2.633000	18.357000	8.051000
н	3.791000	18.290000	9.105000
Н	3,479000	17.046000	8.203000
C	5.709000	17.994000	7,499000
Ĥ	6.261000	18.359000	6.801000
Н	5.732000	17.036000	7.455000
н	6.039000	18 284000	8 352000

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Chapter 3: Investigations into the Energy Acceptor Reactivity of a Manganese(II) Ligand Field State in a Covalently Linked Donor-Acceptor Assembly

3.1 Introduction

To better understand the dynamics of electron and energy transfer, it is common to synthesize and study covalently bound donor-acceptor complexes.¹ These donor-acceptor systems offer the inherent advantage of not having to contend with diffusion related kinetic phenomena^{2a} when studying their photochemistry and photophysics. In spite of this benefit, studying the exact mechanism at work in these donor-acceptor complexes can still be challenging, as it is difficult to distinguish between electron transfer and energy transfer processes.³

Our group has previously explored how to differentiate between different types of electron and energy transfer in a well characterized series of covalently linked donor-acceptor complexes such that the mechanism of the electron and/or energy transfer can be easily determined.² Of particular interest were studies from our group on a series of donor-acceptor systems, consisting of a ruthenium polypyridyl complex covalently appended di-manganese Schiff base macrocycle,⁴ which includes the $[Mn_2(L)(mcb)Ru((CF_3)_2-bpy)_2]^{3+}$ (4) complex as seen in figure 3-1, where (L) is a Schiff base macrocycle, (mcb) is 4-carboxy,-4'-methyl-2,2'-bipyridine, and (CF₃)₂-bpy is 4,4'bistrifluoromethyl-2,2'-bipyridine. The ruthenium polypyridyl moiety is used as an extremely well characterized chromophore which exhibits emission from a triplet metal-to-ligand charge transfer state (³MLCT).⁵ As ruthenium polypyridyls are known to participate as photo-induced electron or energy donors or acceptors,⁶ the ³MLCT emission allows the ruthenium polypyridyl to function as a kinetic handle by which the rates of energy or electron transfer can be measured. The energetics of the ligands also allow for the directed localization of the ³MLCT either closer or in the case of complex **4** farther from the binuclear macrocycle.^{1a} The Mn^{II} macrocycle was chosen for its extremely small ligand field absorptions to limit the possible mechanism of energy transfer (by eliminating the Förster mechanism)^{7,8} while still allowing for the study of possible reactivity with a transition metal dimer. In our previous work, we observed the quenching of the ³MLCT in these previously studied systems and it was determined that this quenching was caused by a Dexter energy transfer mechanism.^{4,9}

In this work, the Schiff base macrocycle present in complex **4** has been replaced by an analogue with a single manganese which will enable the probing of the possible interaction of the ³MLCT with a single transition metal ion. This results in the design of complex **3**, which is drawn in figure 3-1. If quenching due to a single Mn^{II} is present in complex **3**, this will profoundly enhance our understanding of the temperature dependence of the energy transfer rate in complex **4**, where the Heisenberg spin exchange coupled macrocyclic core opens up a host of electronic states responsible for the observed quenching of the Ru ³MLCT.



Figure 3-1: Chemical drawings of systems studied.

3.2 Experimental

GENERAL: Commercially available reagents were procured and used as received unless otherwise indicated. Solvents were acquired from Fisher Scientific, Sigma-Aldrich, Acros, or Alfa Aesar and were distilled and degassed prior to use, except when "E.D." anhydrous grade solvents, packaged under an inert gas, in which case they were used as received. The ligands H(mcb),¹⁰ $(CF_3)_2$ -bpy,¹¹ as well as the complexes $Ru((CF_3)_2$ -bpy)₂Cl₂,¹² and the macrocycle precursor (L')Zn¹³ were prepared using literature methods. The syntheses of [Mn(L)Mn(mcb)Ru((CF₃)₂ $bpy_{2}](PF_{6})_{3}$ (4), $[Zn(L)Zn(mcb)Ru((CF_{3})_{2}-bpy)_{2}](PF_{6})_{3}$ (5), were previously reported.⁴ Na(mcb) was obtained by addition of NaOH (aq) to an aqueous solution of H(mcb) as previously reported.⁴ Na(OAc) was purified by hot recrystallization from hot glacial acetic acid and dried under vacuum. Mn(SO₄)·4H₂O was obtained from recrystallization of the commercially available monohydrate from hot water with subsequent evaporation under a stream of nitrogen. The resulting transparent pink metastable crystals were confirmed to be the tetrahydrate with the aid of elemental analysis. Elemental Analyses were performed by the analytical facilities at Michigan State University or by Midwest Microlab. ESI-MS were acquired either by Prof. Gavin Reid (currently at University of Melbourne) or by the Michigan State University Mass Spectrometry facility. ¹H NMR spectra were obtained at the MSU Chemistry NMR facilities on either 300 MHz or 500 MHz Varian/Agilent spectrometers.

3.2.1 Syntheses

[Pb(L')Zn](ClO₄)₂: This complex was prepared using an adapted synthetic procedure previously reported by Okawa and coworkers for an analogous compound.¹³ Zn(L') (0.913 g) was suspended

in a relatively small amount of methanol (20 mL) under nitrogen, and a methanol solution of Pb(ClO₄)₂·3H₂O (1.012 g in 15 mL of MeOH) was added slowly into the aforementioned stirring suspension under nitrogen and allowed to stir for an hour. To this, a solution of 1 equivalent (0.258 g / 0.283 mL in 10 mL of MeOH) of N,N-bisaminoethyl-N-methylamine ('triamine') in methanol was added slowly, and the mixture was then heated using an oil bath to reflux under nitrogen and allowed to stir for an hour. During this time the suspended solid mostly dissolved. Afterwards the solution was allowed to cool and any remaining solids were removed via vacuum filtration and the filtrate was evaporated to dryness under nitrogen flow to yield a yellow powder, which is the desired product in 94% yield. ¹H-NMR (*d*⁶-DMSO): δ 2.27ppm (s, 6H), 2.48 (s, 3H), 2.98 (m, 2H), 3.25 (m, 2H), 3.89 (m broad, 6H), 4.18 (t, 2H), 7.42 (dd, 4H), 8.58 (d, 4H). Elemental Analysis found (*calculated*) for Pb(L')Zn(ClO₄)₂·2H₂O: %C: 31.59 (31.98) %H: 3.465 (3.54) %N: 7.345 (7.46) ESI-MS: (*m*/z) = 802.1 (M-ClO₄) UV/Vis peaks in MeOH: 215, 252, 378 nm.

[Mn(L')Zn](ClO₄)₂: This complex was prepared in a nitrogen glovebox by suspending 0.200 g (0.221 mmol) of the Pb(L')Zn in 10 mL of methanol under nitrogen, and adding a solution of 1 equivalent (0.049 g) of Mn(SO₄)·4H₂O in 10 mL of MeOH dropwise to the stirring suspension. After two hours of stirring the suspension was filtered through a celite pad to remove the yellow-stained white PbSO₄ precipitate, resulting in a filtrate that is evaporated under nitrogen to dryness. This yellow powder was then dissolved in 40 mL of dichloromethane under nitrogen and the insoluble portions were removed via vacuum filtration under nitrogen and discarded. The desired product was crashed out of solution under nitrogen by addition of approximately 60 mL of diethyl ether to the aforementioned filtrate, and the precipitate was separated via vacuum filtration under nitrogen and dried in a vacuum desiccator to yield the desired product in 54% yield. Note: The unbridged complex is especially susceptible to complexation with any residual carboxylates

present in the mass spectrometer, and since formate and acetate salts are typically used as standards in of ESI-MS, the desired complex is likely to pick up any of these spare carboxylates present. This was the case for our ESI-MS results, which mirrored those obtained for the complex with an acetate bridge due to the acetate present in the mass spectrometer. ESI-MS (m/z) = 609.1 (M+OAc-2CIO₄) UV/Vis peaks in MeOH: 215, 252, 370 nm.

[Zn(L')Zn](ClO₄)₂: This complex was synthesized in an analogous fashion as the [Mn(L')Zn](ClO₄)₂ complex, substituting an equivalent of Zn(SO₄)·7H₂O for the Mn(SO₄)·4H₂O in the added methanol solution. Yield 42%. ¹H-NMR (MeOH- d^4): δ 2.34 ppm (s, 6H), 2.39 (s, 3H), 2.99 (t, 4H) 4.03 (s, broad, 8H), 7.49 (d, 4H), 8.52 (s, 2H), 8.64 (s, 2H). UV/Vis peaks in MeOH: 214, 252, 372 nm.

[Mn(L')Zn(OAc)](ClO₄) (1): This compound was prepared by slow addition of a methanol solution (15mL) of Na(OAc) (1 eq., 0.0094 g) to a concentrated stirring solution of 0.0862 g of [Mn(L')Zn](ClO₄)₂ in 25 mL of methanol under nitrogen. Gradual formation of a yellow precipitate was observed, which after stirring for 3 hours was separated via vacuum filtration to yield the reported product as a yellow microcrystalline powder in 64% yield. Single crystals suitable for crystallography were obtained via ether diffusion into a solution of the compound in methanol with a few drops of acetonitrile under nitrogen. ESI-MS: m/z 609.1 (M-ClO₄). Elemental Analysis found (*calculated*) for [Mn(L')Zn(OAc)](ClO₄) \cdot 0.2 NaClO₄: %C: 43.78 (44.13), %H: (4.39), %N: 9.88 (9.53). UV/Vis peaks in MeOH: 215, 252, 374 nm.

 $[Zn(L')Zn(OAc)](ClO_4)$ (2): This compound was prepared in an analogous fashion to the preparation of $[Mn(L')Zn(OAc)](ClO_4)$, with the substitution of $[Zn(L')Zn](ClO_4)_2$ for the $[Mn(L')Zn](ClO_4)_2$ in the procedure above. Yield 44%. Single crystals suitable for crystallography were obtained from slow evaporation of a solution of the compound in methanol. ESI-MS m/z:

620.1 (M-ClO₄), Elemental Analysis found (*calculated*) for $[Zn(L')Zn(OAc)](ClO_4) + 0.2$ NaClO₄: %C: 43.41 (43.51), %H: 4.38 (4.33), %N: 9.21 (9.40). ¹H-NMR (MeOH- d^4): δ 1.95 ppm (s, 3H), 2.30 (s, 6H), 2.51 (s, 3H), 3.03 (t, 4H), 3.54 (s, broad, 2H), 3.76 (s, broad, 2H), 4.22 (s, broad, 4H), 7.38 (dd, 4H), 8.50 (d, 4H). UV/Vis Peaks in MeOH: 215, 252, 375 nm.

[Ru((CF₃)₂-bpy)₂(mcb)](PF₆): The synthesis of this intermediate complex was developed and performed by previous group member Dr. Monica Soler via a modification of previous literature methods.^{14,15} 0.4311 g (1.0 eq.) Ru((CF₃)₂-bpy)₂Cl₂, 0.1149 g (mcb)H (1.15 eq.), and 0.1031 g (3.0 eq.) NaHCO₃ were dissolved in a mixture of 15 mL of water and 10 mL methanol under nitrogen. The solution was allowed to reflux under nitrogen for 2 to 3 hours in the dark, after which 20 eq. of NaPF₆ dissolved in water were added to the hot solution and impure crystals of the product were obtained by allowing the reaction mixture to cool overnight in the refrigerator. Solid precipitate was isolated via vacuum filtration and the solid was dissolved in acetonitrile, filtered through celite and the filtrate purified via an alumina column. The column was initially loaded with acetonitrile, and after impurities had run through the column, methanol was added to the eluent until a 1:1 mixture of acetonitrile to methanol was eluting through the column, after which the fractions containing the desired product were collected, identified via NMR, and subsequently used in the following reaction without further characterization. ¹H-NMR (MeCN- d^3): δ 2.52 ppm (s, 3H), 7.24 (d, 2H), 7.48 (d, 1H), 7.60 (d, 1H), 7.68 (t, 4H), 7.80 (dd, 1H), 8.05 (m broad, 4H), 8.59 (s, H) 8.96 (s, 2H) 9.04 (s, 2H).

 $[Mn(L')Zn(mcb)Ru((CF_3)_2-bpy)_2](ClO_4)_2(PF_6)$ (3): The synthesis of this complex was developed and performed by Dr. Monica Soler and is roughly analogous to that of $[Mn(L')Zn(OAc)](ClO_4)$, with the substitution of $[Ru((CF_3)_2-bpy)_2(mcb)](PF_6)$ for sodium acetate.¹⁵ 0.1093 g of $[Ru((CF_3)_2-bpy)_2(mcb)](PF_6)$ was dissolved under nitrogen in 15 mL of

distilled and degassed acetonitrile. After the solid was completely dissolved, 0.0783 g (1 eq.) of $[Mn(L')Zn](ClO_4)_2$ was added to the stirring solution and the mixture was allowed to stir under nitrogen for 2 days. Addition of an equivalent volume of ether resulted in the formation of a yellow/brown precipitate, which was separated via vacuum filtration, and the resulting solid was recrystallized from 1:1 acetonitrile and ether and subsequently from 1:1 dichloromethane and ether to obtain the pure product. Yield: 7%. Sample was characterized for use in the subsequent experiments. ESI-MS m/z: 1649, 1695, 1741. Elemental Analysis found *(calculated)* for [Mn(L')Zn(mcb)Ru((CF₃)₂-bpy)₂](ClO₄)₂(PF₆) · 1.5 Et₂O · CH₃CN: %C: 42.19 (42.57), %H: 3.48 (3.52), %N: 8.38 (8.63).

3.2.2 Physical Measurements

3.2.2.1 Electrochemistry

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed in an argon-filled glovebox using a CH Instruments electrochemical analyzer. Compounds were dissolved in dried and degassed CH_2Cl_2 , with the addition of a 0.1 M NBu₄PF₆ as a supporting electrolyte. CH_2Cl_2 offers similar solvent properties to the 3:2 solvent mixture that was used to produce the optical glass for the emission experiments, without the restrictively small solvent window present in the 2-Me-THF. The experimental setup used the standard 3-electrode configuration, with a platinum working electrode, graphite counter electrode, and Ag/AgCl as the reference electrode. Ferrocene was added as an internal standard. Potentials are reported as $E_{1/2}$ values in accordance to the DPV peaks.¹⁶

3.2.2.2 X-Ray Structure Determination

Quality crystals of complexes **1** and **2** were selected and mounted on a 'Bruker APEX-II CCD' diffractometer. The crystals were kept at 173(2) K during data collection. Using Olex2,¹⁷ the structure was solved with the olex2.solve structure solution program¹⁸ using Charge Flipping and refined with the XL refinement package using Least Squares minimization.¹⁹ Structural parameters of the solved structures are reported in table 3-1.

	1	2	
Empirical formula	C₂7H₃2ClMnN₅O8Zn	$C_{27}H_{32}CIN_5O_8Zn_2$	
Formula weight	710.34	720.77	
Temperature/K	173.15	173.15	
Crystal system	monoclinic	triclinic	
Space group	C2/c	P-1	
a/Å	38.075(5)	9.7486(7)	
b/Å	14.8324(16)	11.0696(8)	
c/Å	21.373(2)	14.8787(11)	
α/°	90	70.9210(10)	
β/°	104.833(2)	71.4660(10)	
γ/°	90	77.4810(10)	
Volume/Å ³	11668(2)	1427.25(18)	
Z	16	2	
$\rho_{calc}mg/mm^3$	1.617	1.677	
Goodness-of-fit on F ²	1.029	1.08	
Final R indexes [all data]	R ₁ = 0.0945, wR ₂ = 0.1491	R ₁ = 0.0398, wR ₂ = 0.0854	

 Table 3-1: Crystallographic Data for Complexes 1 and 2.

3.2.2.3 Steady State Spectroscopies

UV/Visible electronic absorption spectroscopy was obtained in lidded quartz cuvettes with samples dissolved in spectro-grade dichloromethane or methanol on a Varian Cary 50 or Perkin Elmer Lambda 1050 spectrometer. Absorption and room temperature emission samples were

prepared in an Ar-filled glovebox by dissolving the sample in dried and distilled CH₂Cl₂ with an absorbance of 0.1 to 0.2 at the excitation wavelength of 475 nm and placed in sealed 1 cm pathlength quartz cuvettes. Room temperature emission spectra were collected on either a Hamamatsu Quantaurus fluorimeter or a Horiba Jobin-Yvon Fluorolog 3 fluorimeter. Emission Spectra on the Fluorolog 3 were corrected for instrumental response by using a NIST standard of spectra irradiance (Optronic Laboratories, Inc., OL220M Tungsten quartz lamp). The Quantaurus-QY instrument is capable of determining absolute quantum yields in addition to LT and RT emission spectra without the need for correction as described by Tobita and coworkers.²⁰

Low temperature steady state emission was obtained on samples prepared in the same Ar-filled drybox by dissolving the samples in a 3:2 mixture of dichloromethane to 2-Me-THF for the purposes of optical glass formation necessary for low temperature emission measurements with an absorbance between 0.1 and 0.2 for samples run on the Fluorolog 3 or an absorbance of 0.4 to 0.6 for the Hamamatsu Quantaurus-QY samples and for were placed in sealed quartz test tubes with a round cross section. Steady state emission spectra were collected on both instruments but while using the liquid nitrogen accessory on the Quantaurus or using the Janis SVT-100 optical cryostat equipped with two LakeShore resistive heaters and temperature controllers in conjunction with the Fluorolog 3 fluorimeter.

3.2.2.4 Time Resolved Spectroscopies

Room temperature time-resolved absorption and emission spectroscopy measurements were obtained using the same sample preparation as room temperature steady state emission, with the exception of the transient absorption samples having an optical absorbance between 0.4 and 0.7 at the excitation wavelength of 475 nm. Time resolved absorption and emission spectroscopy were obtained using an updated Nd:YAG laser system which has been previously described,²¹ upgraded

with the addition of an OPOTEK VIBRANT 355 LD tunable pulsed laser system incorporating both a flashlamp pulsed Nd:YAG laser harmonically producing a 355 nm laser pulse and an optical parametric oscillator (OPO) to allow the production of a visible light laser pulse of nominally 5 ns duration which was used to excite the samples. Excitation energies at the sample were in the range of 0.5 - 2 mJ/pulse, and all data were checked for linearity with regards to the excitation source power. Samples intensity was verified before and after by UV/Vis spectroscopy to verify sample integrity through the course of photophysical measurements. All data manipulations were carried out using the Origin software package.

3.2.2.5 Low Temperature Emission for Complexes 1 and 2

Microcrystalline powder samples of complexes **1** and **2** were loaded into quartz EPR tubes to a height of about 1 cm and placed inside a Janis SCVT-100 optical cryostat, which was cooled to a temperature of 5 K with liquid helium. The samples were excited with a 405 nm laser from PICOQUANT (LDH-D-C-405M, CW-80MHz) operated in CW mode. The resulting emission spectrum was measured on a liquid nitrogen cooled CCD array. The spectra of both compounds were obtained under similar instrumental settings so that comparisons of the two spectra would be possible.

3.2.2.6 Variable Temperature Time Resolved Emission Spectroscopy

Samples were prepared in the same manner as the aforementioned LT steady state emission samples, and placed in round quartz test tubes and sealed with rubber septa before removal from the drybox. Samples were inserted into a Janis SVT-100 optical cryostat charged with liquid helium and equipped with two LakeShore resistive heaters and temperature controllers. The samples were slowly cooled down to 10 K, and allowed to reach a final stable temperature where

the average of the top and bottom temperature readings on the controllers averaged to within 0.5 K of the desired temperature. These temperatures were held for 10 minutes before data was acquired at each temperature point. Time resolved kinetic traces for the compounds excited at 475 nm were obtained on the Nd:YAG laser system with probing the emission at 670 nm and 700 nm. To obtain a full temperature profile, kinetic traces were obtained in 5K increments stepping between 10 K and 100 K and an additional trace at 110 K was obtained. Observations have led us to determine that the glass to fluid transition for the solvent mixture used in these experiments occurs near 120 K, so additional points beyond 110 K will not be considered for modeling the temperature dependent behavior this study, as the nature of the ruthenium emission lifetime changes due to decay processes that are available in fluid solution that are inaccessible in a rigid glass medium, causing discontinuity in the kinetic behavior of these complexes.²²

3.2.2.7 Electronic Structure Calculations

Electronic structure calculations reported in this work were determined using unrestricted density functional theory on the $[Mn(L')Zn(OAc)]^+$ (1) cation. The Becke 3-parameter hybrid density functional based on the correlation functional of Lee, Yang, and Parr $(B3LYP)^{23}$ as implemented in the Gaussian 09 software package²⁴ was employed for these electronic structure calculations. The 6-311G(d,p) Pople-type basis set²⁵ was used as it provided the necessary energetic resolution for the energetic studies performed in this research. Optimized geometries were obtained starting with the previously mentioned X-ray crystallographic structure, which was then optimized for the sextet ground state. The optimized geometry was then further optimized for the quartet state, which was subsequently optimized for the doublet state. Each optimized geometry was checked via frequency calculations for a lack of negative frequencies, signifying that the geometry had reached

a potential energy minimum. Single point energy calculations were used to determine the energies of the relevant spin states at their non-equilibrium geometries.

3.3 Results and Discussion

3.3.1 Syntheses



Figure 3-2: Synthetic scheme of complexes 1 and 3.

Our previous work determined that a Dexter energy transfer mechanism was responsible for the quenching of the $Ru((CF_3)_2-bpy)_2(mcb)$ -based ³MLCT in the $[Mn(L)Mn(mcb)Ru((CF_3)_2-bpy)_2](PF_6)_3$ (4) relative to the rate of decay for the di-zinc model complex.⁴ However, we were unable to determine the exact nature of the energy transfer pathway present in the Mn_2 macrocycle. To elucidate the cause, we attempted to make a mixed-metal equivalent to these two structures that would allow us to gauge the effect of transition metals on the energy transfer mechanism without the complications of the antiferromagnetic spin coupling observed in the Mn_2 -macrocycle studied

previously. However, due to the symmetric nature of the macrocycle, initial attempts at a completely analogous structure were unable to afford pure complexes due to metal scrambling between the coordination sites in the macrocycles, affording a mixture of Zn₂-, Mn₂-, and MnZn-macrocyclic acceptors. To prevent this, an asymmetric version of the macrocycle, which implements a lead(II) template intermediate based on work by Okawa and coworkers¹³ was used to ensure that each macrocycle had a site specific to each metal, so that pure MnZn-macrocycles could be isolated. The synthetic procedure for the synthesis of complexes 1 and 3 is summarized in figure 3-2.

The asymmetric macrocycle starts with the synthesis and isolation of diformyldimethylsalen by the condensation of ethylenediamine and 2,6-diformyl-p-cresol in ethanol, which is deprotonated and metalated by the addition of a stoichiometric amount of zinc acetate in methanol solution to a suspension of diformyldimethylsalen. The completion of the macrocycle is achieved by templating the condensation of the diformyldimethylsalen and N,N-bis(2-aminoethyl)-N-methylamine with lead(II)¹³. After the completed Pn(L')Zn-macrocycle is isolated, the templating lead is extracted via the addition of Mn(SO₄)·4H₂O to precipitate out the lead as PbSO₄ from a methanol solution of Pb(L')Zn. The tetrahydrate is necessary because less hydrated forms of MnSO₄ are insoluable in methanol, rendering the reaction ineffective. After the pure Mn(L')Zn-macrocycle is obtained, a carboxylate bridge can be installed to complete the desired complexes, either from sodium acetate to obtain the [Mn(L')Zn(OAc)]⁺ (1) and [Zn(L')Zn(OAc)]⁺ (2) model complexes, or from [Ru((CF₃)₂-bpy)₂(mcb)](PF₆) to obtain the desired mixed-metal macrocycle appended ruthenium complex.

Single crystals structures of $[Mn(L')Zn(OAc)]^+$ (1) and $[Zn(L')Zn(OAc)]^+$ (2) were obtained as described above. These structures are shown in figure 3-3 and figure 3-4 respectively. Complex 1

crystalizes in the monoclinic space group with a C2/c space group. Each unit cell has two distinct macrocyclic cations arranged with the acetate bridges parallel and the macrocycles facing each other and two perchlorate anions. While each macrocycle is distinct, the structures are very similar for each one. Upon initial inspection, the two cations are observed to be roughly mirror images of each other, with the plane going between the two metal ions and the acetate bridge. The macrocycles consist of an asymmetric Schiff base macrocycle ligand (L') coordinates to a manganese(II) ion in a six coordinate site and a zinc(II) ion in a 5-coordinate site, bridged by both phenolic oxygens from the Schiff base macrocycle and the acetate bridge. The remainder of the Mn(II) six-coordinate site consists of the three triamine nitrogens, two of them imine-based and the third aliphatic central nitrogen, coordinated in a facial manner. The zinc(II) five-coordinate site is rounded out by the ethylenediamine-based imine nitrogens of the macrocycle. The configuration of the macrocycles in these structures is dissimilar to that reported for the Pb(II)Zn precursor,¹³ in which the two macrocycles are bridged by two co-crystallized water molecules and the macrocycle is sort of pleated to make a roughly flat plane instead of an outwardly folding sheet as seen in complex 1. This is likely due to the Pb(II) ion having a poor fit in the 6-coordinate site, causing the folding of the macrocycle.



Figure 3-3: **Drawings of X-ray crystal structure cations of complex** *1* **with atoms drawn as thermal ellipsoids.** The orientation of both structural variants relative to each other is portrayed on the left, with a detailed figure of each variant depicted in the center and right portions. Note the top macrocycle for complex 1 is structure A and the bottom macrocycle is structure B. Anions, solvent molecules, and hydrogens omitted for clarity.



Figure 3-4: Comparison of the different crystal structures obtained for complexes 1 and 2 compared to those previously acquired for the acceptor model complexes of 4 ([Mn₂(L)(mcb)](PF₆)) and 5 ([Zn₂(L)(mcb)](PF₆)). The same atom labeling scheme is observed throughout. The B structural variant is displayed for complex 1 (see figure 3-3). The N5-M1 bonds are not depicted for the analogues of 4 and 5 as they are long enough to not be modeled as a bond by the crystallographic software. Atoms are portrayed as thermal ellipsoids. Anions, solvent molecules, and hydrogens omitted for clarity.

Examination of the 6-coordinate Mn(II) sites in found in the X-ray structure for $[Mn_2(L)(mcb)](PF_6)$ (where (L) is a symmetric Schiff base macrocycle derived from the condensation of 2,6-diformyl-p-cresol and the triamine) as previously reported shows an analogous coordination environment for the Mn(II) ion in the six-coordinate site of complex **1**. It is worth noting that in the complex **1** macrocycle, the aliphatic nitrogen is coordinated, albeit at a longer distance than the imine nitrogens, with the bond distance (average 2.471 Å) being a closer match for the shorter of the two aliphatic nitrogen – manganese bonds in the symmetric Mn₂ analogue (2.438 and 2.613 Å). This is significant as the symmetric Mn₂ analogue was asymmetric with one of the aliphatic nitrogens coordinating at a significantly longer distance. The complex **1** structure suggests that the asymmetry in the aliphatic nitrogen coordination in the Mn₂ macrocycle was caused by the sterics of the symmetric macrocycle, which are less pressing with our asymmetric macrocycle variant.

Complex 2 crystalizes in the triclinic system with a P-1 space group. The unit cell consists of a single $[Zn(L')Zn(OAc)]^+$ macrocyclic cation, and a single perchlorate anion. The cation is very similar to that in complex 1, consisting of the asymmetric Schiff base macrocycle (L'), two Zinc (II) ions, and the bridging acetate. Inspection of the 6-coordinate Zn(II) site in complex 2 reveals that it is very similar to one of the Zn coordination sites in the $[Zn_2(L)(mcb)]^+$ as seen in figure 3-4, with the aliphatic nitrogen from the triamine having a bond distance (2.463 Å) resembling the shorter of the two zinc – aliphatic nitrogen bonds in the symmetric Zn₂ macrocycle (2.317 and 2.813 Å). Figure 3-4 shows that the structure determined for complex 2 is a very close match for the "B" crystal structure determined for complex 1. Comparisons of the Mn(II) ion and Zn(II) ion in the six-coordinate site of complexes 1 and 2, as well as the five-coordinate site in both

complexes show that the complexes are analogous, which makes complex 2 an excellent structural model of complex 1, as seen in the coordination site bond distances summarized in table 3-2.

Bonds	[Mn ₂ (L)(mcb)] ⁺	[Zn ₂ (L)(mcb)]	[Mn(L')Zn(OAc)] ⁺ A	[Mn(L')Zn(OAc)] ⁺ B	[Zn(L')Zn(OAc)]+
M(1)-N(4)	2.186(8)	2.091(2)	2.186(4)	2.180(4)	2.116(2)
M(1)-N(6)	2.183(8)	2.072(2)	2.216(4)	2.205(4)	2.073(2)
M(1)-N(5)	2.618	2.813	2.460(4)	2.478(4)	2.463(2)
M(1)-O(1)	2.212(6)	2.164(2)	2.198(3)	2.195(3)	2.1998(19)
M(1)-O(2)	2.204(6)	2.110(2)	2.225(3)	2.207(3)	2.1497(19)
M(1)-O(4)	2.086(7)	1.993(2)	2.084(3)	2.088(3)	2.020(2)
M(2)-N(1)	2.232(8)	2.131(2)	2.043(4)	2.043(4)	2.047(2)
M(2)-N(2)	2.438(9)	2.317(2)	-	-	-
M(2)-N(3)	2.193(8)	2.086(2)	2.040(4)	2.038(4)	2.033(2)
M(2)-O(1)	2.195(6)	2.102(2)	2.027(3)	2.015(3)	1.9894(19)
M(2)-O(2)	2.178(6)	2.123(2)	2.015(3)	2.004(3)	2.0291(19)
M(2)-O(3)	2.132(7)	2.065(2)	1.977(3)	1.977(3)	1.971(2)
M(1)-M(2)	3.28	3.215	3.0743(9)	3.0534(9)	3.0789(5)

Table 3-2: Comparison of bond distances for X ray structures of complexes 1, 2, and macrocycle core analogues ($[M_2(L)(mcb)]^+$) of complexes 4, and 5 as previously reported.⁴

To synthesize complex **3**, instead of sodium acetate, $[Ru((CF_3)_2-bpy)_2(mcb)](PF_6)$ is substituted as the bridging carboxylate group in an analogous procedure using acetonitrile as the solvent. $[Ru((CF_3)_2-bpy)_2(mcb)](PF_6)$ is synthesized from $Ru((CF_3)_2-bpy)_2Cl_2$ and (mcb)H while refluxing in water and methanol in the dark to drive off the chloride ions without the formation of photoactive side products. The desired product is crashed out of solution with the addition of excess NaPF_6. Purified $[Ru((CF_3)_2-bpy)_2(mcb)](PF_6)$ is then introduced as a bridging ligand to $[Mn(L')Zn]^{2+}$ by stirring the two together for a couple of days, and then precipitating out the product with addition of ether. We have been unable to grow X-ray quality crystals of complex **3**, but since it and complex **1** are derived from the same starting material, one can be confident that complex **1** is a suitable model for the independent behavior of the macrocycle in complex **3**.

3.3.2: Mass Spectrometry

For this project, we relied heavily on Electrospray Injection – Mass Spectrometry (ESI-MS) as a primary characterization technique for our complexes. This was due to the lack of reliable ¹H-NMR data for our complexes containing Mn^{II}, our inability to get crystal structures of complex **3**, as well as the advantages offered by ESI-MS in determining the presence of impurities in our samples consisting of other possible metals in the coordination sites of our mixed metal macrocycles in complexes 1 and 3 which would have been detrimental to our study because they would have had different photophysical behavior than the molecules we wished to study. For example, if there were some residual Pb(L')Zn macrocycle or if some Zn(L')Zn macrocycle was made as a side product in the synthesis of the Mn(L')Zn macrocycle, then there would be impurities in the sample for complex 3 that would not have the same quenching behavior as the intended molecule, which would cause inaccuracies in the kinetic fitting that could affect the outcome of our study. Fortunately, ESI-MS has the ability to pick up on these otherwise undetectable impurities in our systems. So in our characterization of complexes 1 and 3, we checked for the presence of these other compounds to make sure there were no impurities that could affect the outcome of our study.

The ESI-MS results for complexes **1** and **2** were relatively straightforward, with the expected singly charged cationic peaks being observed for the two model systems. Unbridged bi-metallic precursors were often observed to be bridged by residual free acetate or formate ions used as a buffer in the LC injection systems attached to the ESI-MS instruments, which owes to the high affinity of these bimetallic precursors for carboxylate ions.

Measurements for complex **3** on the other hand were much more complicated, as the synthetic procedure for this complex yields the triply charged cation in addition to three anions, in a 2:1 ratio

of ClO₄⁻ to PF₆⁻. When dissolved to make the liquid ESI-MS sample in MeCN, these anions can freely interchange such that when a single anion is removed in the ESI-MS instrument to get a single cation signals, there is the possibility that each ion can have (ClO₄)₂, (ClO₄)(PF₆), or (PF₆)₂ as associated anions in the singly charged cations. If there is a 2:1 ratio of ClO₄⁻ to PF₆⁻ as is expected from the synthetic procedure, then the relative intensity of the [M-2(PF₆)] signal should be roughly half of the intensity of the other two anion combinations for the singly charged cationic signals. This is observed in the ESI-MS results in the appendix figure A3-1 indicating that all three signals can be ascribed to complex **3**.



Figure 3-5: Extinction coefficient plots for complexes 1 (green -- --), 2 (teal ---), 3 (Blue line), 4 (black -- -- -). And 5 (red --- ---).

3.3.3 Electronic Absorption Spectroscopy

The UV/Vis spectra of all five complexes of interest are presented in figure 3-5. Complexes 1 and 2 have an absorption spectra that is fairly representative of other macrocyclic Schiff base ligands

similar in structure, with two absorptions correlating to π to π^* transitions in the p-cresol regions of the macrocycle at ~220 nm (observed in methanol, but not pictured since extinction coefficients were obtained in dichloromethane) and 255 nm. These peaks are observed in previous work on similar Schiff base chromophores^{26,27} and are associated with the phenol-portions of the macrocycle as they are present in all the compounds studied. The third peak of both spectra occurs near 380 nm and correlates to π to π^* transitions in the azomethine portions of the Schiff base macrocycle. This absorption has a fair degree of variability since it is corresponding to an area of the ligand that directly coordinates to the host transition metal ions. The $[Zn(L')Zn(OAc)]^+$ complex has the third absorption at 381 nm while the corresponding absorption occurs at 377nm for $[Mn(L')Zn(OAc)]^+$. This absorbtion feature is slightly higher in energy than the corresponding absorptions in the symmetric macrocycle, which is representative of the lower charge density associated with the azomethine nitrogens having fewer bound carbons in the asymmetric macrocycle than in the symmetric one. The fact that the energy of the N- π to π^* transition is higher in complex 1 than in complex 2 is contrary to the intuition of Zn(II) being a better Lewis acid than Mn(II), which was seen for the symmetric macrocycle where the N- π to π^* in $[Zn_2(L)(mcb)]^+$ was higher in energy. No explanation for this behavior is available at this time.

When appended to the Ru((CF₃)₂-bpy)₂(mcb) moiety, the resulting spectral features due to the asymmetric macrocycle do not appreciably change, with the N- π to π^* transition occurring at 375 nm in the mixed metal ruthenium complex versus 376 nm in the acetate bridged model complex. Compare this to the absorption maximum at 388 nm for complex **4** and 391 nm for complex **5**, which show similar behavior to their mcb bridged analogues as previously reported. The phenolic-based π to π^* transition near 255 nm is also unperturbed with the addition of the ruthenium chromophore. The addition of the Ru((CF₃)₂-bpy)₂(mcb) also brings along the Ruthenium

polypyridyl-based electronic absorption features that are found commonly found in this class of compounds. Specifically, there is a new sharp absorption feature in the UV region at 297 nm that corresponds to the bpy-based π to π^* transitions on the Ru-polypyridyl fragment. These transitions are unperturbed between the mixed metal complex and our previously reported Zn₂ and Mn₂ analogous compounds.⁴ Also present with the addition of the ruthenium polypyridyl fragment are absorption features occurring between 400 and 500 nm that correspond to the electronic transitions from the ruthenium ground state to the ¹MLCT that are a defining characteristic of ruthenium polypyridyl complexes. There is also a sloping shoulder of uniform profile that extends beyond 550 nm present in the three ruthenium appended compounds of interest that is typically ascribed to the ³MLCT spin forbidden optical transition. It is fitting that the MLCT absorption features almost perfectly mirror those of the previously reported Mn₂(L)(mcb) analogue as we were pursuing a model that would behave as electronically similar to the Mn₂ complex with respect to the Ru-chromophore as possible without having two transition metal ions in the macrocycle and by the electronic absorption spectroscopy it appears we have hit the mark.

3.3.4 Electrochemistry

The electrochemical properties of complex **3** were examined using cyclic voltammetry and differential pulse voltammetry, the results of which are plotted in figure 3-6. In complex **3** there is one readily observable irreversible oxidation at 0.69 V that correlates to the Mn^{II} to Mn^{III} oxidation.

Complex	Oxidations		Reductions		
	Mn(II)/Mn(III)	Ru(II)/(III)	E _{red1}	E _{red2}	E _{red3}
[Mn(L')Zn(mcb)Ru((CF ₃) ₂ -bpy) ₂](ClO ₄) ₂ (PF ₆)	0.69	~1.16 ^b	-1.23	-1.47	-1.92
[Mn(L)Mn(mcb)Ru((CF ₃) ₂ -bpy) ₂](PF ₆) ₃	0.28 & 0.63°	1.12	-1.17	-1.40	-1.85
$[Ru((CF_3)_2-bpy)_2(mcbEt)](PF_6)_2$		1.14	-1.15	-1.38	-1.83

^a Potentials reported verses the ferrocene/ferroceneium couple as described in the experimental section. ^b Value obtained from a separate experiment performed analogously as to the description in the experimental section with the substitution of a glassy carbon working electrode. Mn(II)/(III) redox was not observable for this experiment. ^c The Mn₂ system has two Mn(II)/(Mn(III) oxidations.

Table 3-3: Electrochemical data for complexes 3, 4, and $[Ru((CF_3)_2-bpy)_2(mcbEt)](PF_6)_2$ in CH₂Cl₂ solution.^a $[Ru((CF_3)_2-bpy)_2(mcbEt)](PF_6)_2$ data are presented as electrochemical data were unobtainable for complex 5.



Figure 3-6: Electrochemical data for complex 3, with potentials plotted relative to the ferrocene/ferrocenium redox couple.

This feature is in a similar range as that reported for the second Mn oxidation in a Mn₂ macrocycle as seen in complex **4**, as well as other similar Mn₂ macrocycles reported previously.^{4,26} A Ru^{II}/Ru^{III} oxidation feature was not observable using our setup with platinum working electrode as described, however an analogous experiment utilizing a glassy carbon working electrode indicated a pseudo-reversible oxidation feature near 1.16 V,²⁸ which is assigned as a Ru^{II}/Ru^{III} oxidation feature by

merit of its reasonable match with the Ruthenium oxidation potential in complex **4** as was previously reported.

Two reversible reductions and one pseudo-reversible reduction were also observed for complex **3**, at potentials of -1.23 V, -1.47 V and -1.92 V, corresponding to the three incremental bpy reductions in this system. While these are in the neighborhood of what was previously reported for complex **4**, as summarized in table 3-3, they are not exactly the same. These differences could be attributed to the difference in counter ions between complex **4**, which has only PF₆ anions, and complex **3** which has two perchlorate anions and a single PF₆ anion, but we are not certain at this time.

3.3.5 Photophysical Characterization of [Mn(L')Zn(mcb)Ru((CF3)2-bpy)2](ClO4)2(PF6).

The presence of the ruthenium polypyridyl chromophore on the main complexes of interest (**3** and **5**) allows us to tap into several decades of experience when interpreting their photophysical properties.^{5,29} The centerpiece of this work is the variable temperature kinetic profile of complex **3**, especially when compared to the variable temperature kinetic profile of the structural analog, complex **5**. To adequately gauge which wavelengths to probe, the steady state emission spectra of both complexes were obtained at 10K while exciting the sample at 475 nm which for most ruthenium polypyridyl complexes is on the red edge of the ¹MLCT absorption. However, due to the electronic withdrawing effects of the trifluoromethyl groups on the (CF₃)₂-bpy ligands, the charge transfer bands are lower in energy, placing our excitation wavelength right in the middle of the ¹MLCT absorption band for both complexes. However, exciting the sample at the edge of the MLCT absorption at 500 nm had no effect on the emission profile, so 475 nm was chosen for consistency with previous results.



Figure 3-7: 10 K corrected emission spectra for complexes 3 (blue) and 5 (red). Sample was excited at 475 nm.

Figure 3-7 shows the LT emission spectra for complexes **3** and **5**, which show a strong vibronic progression as can be expected for emission spectra obtained in rigid media. Noteworthy is the shift in emission maximum from 604nm for complex **5**, to 608 nm for complex **3**. Since the emissive state for this feature is localized on the $(CF_3)_2$ -bpy ligands, this implies that the ground state of the ruthenium is slightly higher in energy in this complex than for the di-zinc, which is consistent with the apparent ¹MLCT absorption features being slightly higher in energy for complex **5** than for complex **3**. This points to the slight differences between the emission spectra of these two complexes being related to the differences in the Lewis basicity of the two different macrocycles, which effects the ruthenium center via the aromatic linkage provided by the (mcb) bridging ligand. A single-mode spectral fitting analysis of Claude and Meyer³⁰ was used to determine the value of E_{00} of the low temperature emission spectra. The E_{00} value of the ³MLCT

was determined to be 16,550 cm⁻¹ for complex **5**, which will be used in the proceeding analysis of the photophysics of complex **3**.

It is based on these spectra that the probe wavelengths for our time resolved emission studies were selected. On first inspection one would believe that the optimal probe wavelength would be near 610 nm for both these complexes. However, at low temperatures residual emission from both macrocyclic impurities and stabilizers from the 2-Me-THF make probing at these shorter wavelengths impractical. We therefore picked two wavelengths that were well red of these features in 670 and 700 nm. These wavelengths are not near the emission maximum at low temperatures, but they are guaranteed to have stable emission throughout the temperature range studied as 670 nm corresponds roughly to the room temperature emission maximum of these compounds, in agreement with the room temperature emission spectra previously reported.⁴

3.3.6 Variable Temperature Emission

Initially, we wished to probe the effects of having available ligand field excitations as a potential energy acceptor on the ground state recovery of an emissive energy donor. It was suspected that the transition metal could quench the energy donor, since this was found to be true for complex **4**, which contains a pair of spin coupled transition metal ions. However, we needed to test this hypothesis on a donor-acceptor complex analogous to complex **4**, but containing a transition metal ion without any of the complicating factors that could be folded into the Heisenberg spin-exchanged system present in complex **4**. It was for this purpose that complex **3** was created. As was the case in our previous studies, to discern the effects on the dynamics of the ruthenium polypyridyl donor, baseline studies containing no transition metal based dynamics on the complex

5 structural model were also necessary. We therefore proceeded to collect variable temperature time resolved emission spectra on both complexes **3** and **5** to better understand the dynamics in these model systems before attempting to determine the cause of the dynamics in complex **4**.

Kinetic Traces for each individual emission experiment, as well as background traces where the laser beam was blocked in front of the sample in an attempt to correct for scatter were obtained from the digital oscilloscope and saved as ASCII text files. These text files were then imported into the Origin data analysis software and plots of the corrected signal versus time were generated. The kinetic lifetime of the emissive state is determined by fitting the corrected kinetic data to an exponential decay function of the form:

$$y = y_0 + Ae^{\frac{-x}{\tau}} \tag{1}$$

Since the time resolved emission features are presumed to be due to the ³MLCT emissive state of the Ru chromophore present in complexes **3** and **5**, it makes sense that there should only be one kinetic process occurring and the data should follow a mono-exponential decay model. In the case of the kinetic traces from complex **5**, a single exponential decay model was adequate for the kinetic traces at all temperatures studied. The rates of decay were determined while probing at 670 and 700 nm, and the average of those two is reported as the observed rate of decay, with the range of values serving as the uncertainty.

For complex **3**, kinetic traces were collected while probing at 670 and 700 nm, but at the lowest temperatures studied the data could not be properly fit to a monoexponential decay. These deviations from the mono-exponential model are consistent with the presence of a second short time component to the decay signal. To account for this fact, the kinetic traces for complex **3** were fit with a bi-exponential model, of the form:

$$y = y_0 + A_1 e^{\frac{-x}{\tau_1}} + A_2 e^{\frac{-x}{\tau_2}}$$
(2)

These bi-exponential fits revealed that an unexpected shorter lifetime kinetic process was present in addition to the longer lifetime component, assigned to the ruthenium emission lifetime due to the similarity in observed lifetime compared to the Zn_2 analogue. These two distinct decay processes were significant at low temperatures only, necessitating a bi-exponential fit of the decay traces for temperatures up through 35 K. Starting at 40 K, the magnitude of the second component to the decay was small enough to not make a significant difference between the long time component from a bi-exponential fit, or a mono-exponential fit of the decay trace. A monoexponential model was used to fit the data starting at 40 K for the rest of the experimental temperature profile.

The presence of the second exponential decay component of the observed decay traces is most likely due to an emissive impurity of additional unbound mixed metal macrocycle which results from the excess of macrocycle used in the preparation of complex **3**. While the impurity amount is too small to detect via elemental analysis, it could be present in high enough amounts that at the lowest temperatures the organic based emission would have an extremely high quantum yield and a long enough lifetime to be detected in our experiment, while at higher temperatures, the decay of the macrocycle impurity would be too fast to be detected on a nanosecond timescale. The emission of this impurity is expected to peak near between 500 and 520 nm and is visible in the low temperature steady state emission spectra seen in figure 3-7, where the emission peak is much larger at 10 K for complex **3** than it is for complex **5**, explaining why it affected the data for complex **3** but not **5**. It is also much higher in intensity at 10 K than it is at 77 K, which is consistent with our hypothesis of a trace organic impurity affecting the kinetics of complex **3**.



Figure 3-8: Variable temperature time resolved emission data of complexes 3 and 5. Red points correspond to the observed rate of decay for complex 5. Blue points correspond to the observed rate of the decay (for the longer lived decay process when kinetic traces were fitted with a bi-exponential decay) of complex 3. It is possible to fit the data to an Arrhenius (complex 5) and a double Arrhenius (complex 3) equation, which are shown in black.

The rates of emission decay determined from exponential fits were plotted as a function of temperature for both complex **3** and **5**, as is shown in figure 3-8. When observing figure 3-8, one can make a few general observations of how the plotted rates of decay change with temperature. Most easily observed is the fact that both the mixed metal complex and the di-zinc model both have temperature dependent behavior. The rate decay of the mixed metal complex **3** seems to increase faster than that for the Zn_2 bearing complex **5**. For the latter, this behavior can be easily explained as a thermal population of an addition electronic state in the multiplex of states commonly described as the ³MLCT as described in previously reported works by Crosby and

coworkers.³¹ The energy barrier (E_a) for this thermally activated decay pathway can be determined by fitting the kinetic trace to an Arrhenius model of the form:

$$k = y_0 + A e^{\frac{-E_a}{k_b T}} \tag{3}$$

This activation barrier is determined to be 60 ± 5 cm⁻¹ higher in energy than the populated states in the ³MLCT at 10 K. This barrier is consistent with previously reported in heteroleptic ruthenium polypyridyl complexes.³¹ The pre-exponential factor (A) for this Arrhenius fit also provides useful information, as it can be thought of as the intrinsic rate of decay for the thermally activated state at the limit of no thermal barrier. For complex **5**, the pre-exponential factor from the Arrhenius fit is $4.8 \pm 3 \times 10^5$ s⁻¹, which gives an indication of the innate rate of decay for the additional pathway in the ³MLCT that is thermally accessible.

When a simple Arrhenius model was used to fit the temperature rate profile of complex **3**, a similar result for the activation barrier is obtained, along with a larger pre-exponential factor determined by the fit. This indicates that at least one additional process is occurring in complex **3** and being folded into the kinetics of the ruthenium ³MLCT seen in complex **5**. This is the case because the intrinsic rate of decay afforded by accessing an additional level of the ³MLCT (the pre-exponential term) should be the same for both complex **3** and complex **5** since they both have the same ruthenium polypyridyl fragment.

The difference in pre-exponential factors indicates that there is an additional thermally activated process occurring in the mixed metal complex. However, since they exhibit the same decay rates at the lowest temperatures, this process must also be thermally activated. To capture the dynamics of a second thermally activated pathway, a double Arrhenius fit was required with the following form:

$$k = y_0 + A_1 e^{\frac{-E_1}{k_b T}} + A_2 e^{\frac{-E_2}{k_b T}}$$
(4)

Initial attempts to allow the fitting software determine the parameters was fruitless. However, since we had a very good idea of the similarity of any ruthenium related thermal rate dependence between the two complexes, double Arrhenius fits were obtained where the first temperature dependent component had fixed values determined by the single Arrhenius fit of the di-zinc rate versus temperature data. Using this approach, we were able to determine that there is a second thermally activated decay pathway in the mixed metal complex. The activation barrier determined by this fit had errors on the order of 50% of the energy barrier value, so another way to determine the thermal barrier was needed.

An alternative way to obtain the value of this thermally activated decay process is to subtract the observed rates for complex **5** from the observed rates for complex **3**. Figure 3-9 shows the results of this treatment, which shows a clearly thermally activated process that only grows in at higher temperatures. A fit of this data to the single Arrhenius equation yields a value of 84 ± 5 cm⁻¹ for the activation barrier. Considering the values and variance in the thermal barriers obtained for the double Arrhenius fits described earlier, an activation barrier of 80 ± 20 cm⁻¹ higher than the populated states at 10 K is what we can confidently report from this fitting analysis.

Furthermore, inspection of the pre-exponential factor for the quenching rate ($A = 1.4 \pm 2 \times 10^5 \text{ s}^{-1}$) yields that the intrinsic rate of this decay pathway is slower than the rate of decay afforded by the additional pathway in the ³MLCT, which explains why a single Arrhenius fit yielded an activation barrier that was very close to the ruthenium temperature dependent behavior.



Figure 3-9: Observed quenching rate (difference between observed rate of complex 3 and observed rate of complex 5) plotted as a function of temperature. A fit to the Arrhenius equation is shown in black corresponding to an activation energy of 84 ± 5 cm⁻¹.



3.3.7 Transient Absorption Spectroscopy

Figure 3-10: (left) Transient absorption kinetic trace for complex *1* excited at 475 nm and probed at 370 nm. (right) Transient absorption decay trace of complex *1* excited at 475 nm and probed at 490 nm. The red lines are plotted fits to a single exponential decay, which had the same kinetic lifetime within the error of the experiment. See text for details.

The transient absorption spectra were obtained for both complex 3 and complex 5 to assign the observed quenching in complex 3 as being caused by either electron transfer or energy transfer. Room temperature time resolved emission studies showed complex **3** having an emission lifetime of 440 \pm 30 ns in the solvent mixture used for the variable temperature measurements while exciting at 475 nm. Therefore, the lifetimes of different spectral features observed via transient absorption spectroscopy should have a similar lifetime if there are no electron transfer photoproducts. The electrochemical measurements indicate that at room temperature the reductive quenching of the ³MLCT of the Ru chromophore is thermodynamically viable. The transient absorption spectra of complex 5 were previously reported⁴ and the emissive excited state has two main transient features that were assigned with the aid of spectroelectrochemistry.³² There is an absorption feature centered near 350 nm associated with the reduced bipyridine radical, and there is a bleach centered near 470 nm that corresponds to the loss of the MLCT absorption in the complex. For reductive quenching, the MLCT bleach should disappear with the same lifetime as the emission but the absorption from bpy⁻ will persist as the negative charge will be stranded on the ligand as the Ru^{III} will have already been reduced by the Mn^{II}. This means the transient absorption lifetime for the bpy⁻ radical should be longer than the observed emission lifetime. Transient absorption lifetimes were measured at 370 nm and 490 nm with the resulting kinetic traces shown in figure 3-7. The observed lifetimes of these transient absorption features were 390 \pm 40 ns at 370 nm and 360 \pm 40 ns at 490 nm. The transient absorption data were noisy as the experimental setup had weak probe white light intensity at the time of these experiments. This in turn gives a larger than desired uncertainty on the fits of the transient absorption data. These lifetimes are not statistically different from the observed emission lifetime of complex 3, which indicates that there is no sustained intramolecular electron transfer processes occurring at room
temperature in complex **3**. Time resolved transient absorption measurements were also performed on complex **5** as a standard for the experiment. At the same probe wavelengths, the transient absorptions had lifetimes of 660 ± 70 ns at 370 nm and 650 ± 70 ns at 490 nm. These are not statistically different from the observed room temperature lifetime of 730 ± 30 ns.

3.3.8 Identification of the quenching pathway in Complex 3

If one inspects the body of data on complex **3** and its various models up to this point one can deduce the following: There is the standard temperature dependent excited state decay for both complexes **3** and **5** and there is an additional thermally activated quenching mechanism present with an energy of 80 ± 20 cm⁻¹ above the ground state at 10 K. Low temperature emission studies on complex **1** show there is a low energy emissive state whose presence is attributable to the Mn^{II} ion since the state is not seen in complex **2**, as will be discussed below. Since the only substantial difference between the Zn^{II} and Mn^{II} ions is the presence of excited ligand field states, one can conclude that the emissive state seen in the LT emission is the lowest energy excited ligand field state for the Mn^{II} ion. If these ligand field states of the Mn^{II} ion are lower in energy than the emission maximum observed for the ruthenium chromophores, which is suggested by the LT emission spectra for complex **1** as seen in figure 3-8, then any sort of quenching could be thermodynamically allowed. The fact that there is a thermal activation to the process implies that there is a mechanism that makes the quenching energetically uphill (by 80 cm⁻¹).

Based on the room temperature transient absorption measurements, we know there is no sustained electron transfer quenching processes. The Rehm-Weller equation³³ applied to the electrochemical data suggests that reductive quenching of the ³MLCT emission is thermodynamically viable, with

a $\Delta G = -0.96$ eV. However, in optical glasses the large outer sphere reorganization energy associated with the solvent has to be added to the driving force for the electron transfer.³⁴ Most electron transfer processes have outer sphere reorganization energies in the range of 1-2 eV.³⁵ A large reorganization energy that is suddenly added to the driving force for electron transfer means that the formation of an optical glass should result in a discontinuity in the rate of emission decay of complex **3** that is drastically different from that observed for complex **5**, which is not what we observe in this case. This suggests that any electron transfer process, which includes rapid sequential reductive electron transfer from the MnL'Zn macrocycle to the Ru chromophore with a subsequent back electron transfer to the Mn center, is very unlikely to occur as the outer sphere reorganization energy is more than enough to cancel out the driving force for electron transfer in rigid media.

Since there is not any significant absorption of the ligand field states of Mn^{II} in the macrocycle of complex **1**, we can assume the same is true for complex **3**, which rules out the possibility of a Forster electron transfer mechanism as there is no donor-acceptor spectral overlap.⁵ This leaves us with Dexter energy transfer as the only viable mechanism by which the ³MLCT can be quenched in complex **3**. However, it is not enough to know that the presence of Mn^{II} is causing a thermally activated energy transfer quenching pathway. We carried out LT steady state emission studies on complex **1** in the hopes of learning more about the identity of the ligand field states that could be quenching the emission from the ³MLCT in complex **3**.

3.3.9 LT Emission of Mn(L')Zn(OAc):

Emission at 5 K was collected for complex **1** and is shown in figure 3-8. The primary feature observed in this compound is a broad emission band centered near 500 nm that is due to the ligand-based emission of the macrocycle. This macrocycle-based emission is observed in the $[Zn(L')Zn(OAc)]CIO_4$ (**2**) complex as well, which confirms the assignment of this feature, as there can be no metal-involved charge transfer states deriving from the d¹⁰ Zn^{II} ion. Of more interest however are the two shoulders present in the complex **1** sample that are absent from the complex **2** sample as seen in figure 3-11.



Figure 3-11: Low temperature emission spectra of complex 1 (blue) and complex 2 (red).

These shoulders derive from the Mn^{II} ions, which is possible as emission from Mn^{II} has been reported in the past for crystalline systems.³⁶ Ligand field emission for Mn^{II} is typically reported

from the ${}^{4}A_{1}$ state. However, the observed emission is too low in energy, with values well below the 20,000 to 25,000 cm⁻¹ range that is usually reported. The first shoulder is relatively sharp and has a maximum at 683 nm, while the second shoulder peak is slightly broader and less intense, centered at 725 nm. Since these emission features have to come from lower energy ligand field transitions than those reported for ${}^{4}A_{1}$ emission, our emission shoulders can be assigned as being derived from quartet ligand field states; either a symmetry split ${}^{4}T$ ligand field state, or an extreme case of vibronic progression for the emission of a single ${}^{4}T$ ligand field state.

The coordination environment of the Mn^{II} center is low in symmetry, owing to both the *fac*-N₃O₃ coordination environment and the identities of the ligands to which the coordinating atoms are attached. The structure obtained via X-ray crystal diffraction confirms this coordination asymmetry, resulting in the Mn^{II} center possessing at most C_S symmetry. This low symmetry coordination environment cannot support the three-fold degeneracy of the ⁴T₁ ligand field state, resulting in it splitting into theoretically three states, of which only two are readily observed in the emission shoulders reported herein. The shoulders are only derived from the equivalent of a single octahedral ⁴T₁ ligand field state since there is no evidence of additional peaks observed outside the window reported. Splitting of the emissive ⁴T₁ states has been reported in the past for low symmetry Mn^{II} systems,³⁷ although the published splitting is of a higher magnitude. Since the 683 nm feature is sharper and more intense, the potential energy surfaces between this feature and the ground state are better nested, so the total energy difference between the emissive states is better estimated by the higher-energy emission shoulder.

There is another case in which the lower energy shoulder is an observed emission from a separate frozen geometric configuration that is in the microcrystalline compound, in addition to the sharper emission line described above. If one presumes that in the microcrystalline lattice there were two configurations present, which is entirely feasible given the two morphologies observed in the Xray crystal structure of complex **1**, and imagines that one of these is at the absolute equilibrium geometry for the ${}^{6}A_{1}$ ground state while the other is distorted slightly towards the ${}^{4}T$ equilibrium geometry on the reaction coordinate of the complex. In this case any emission from the exactly frozen ${}^{4}T$ would be sharp as it does not need to change geometry during the relaxation back to the ground state, while any emission from the slightly distorted geometry would be lower in energy as the ${}^{4}T$ state would be lower and the ${}^{6}A_{1}$ state would be higher in energy at this distorted geometry and therefore the energy difference between the two states would be lower. Also, the slight geometric difference between the two states would broaden out the emission peak as is observed in the LT emission spectra.

Therefore the actual energy of the emitting ligand field excited state is significantly lower in energy than the ³MLCT excited state energy as determined by the single mode spectral fitting analysis because the high-energy emission line from the 5 K emission on complex **1** represents an upper limit to the energy of the quartet ligand field state. As a result, the observed thermal barrier to quenching of the ³MLCT seen in the VT Time resolved emission studies must be due to a reorganization of the Mn^{II} ion which in the frozen medium that the sample is dissolved in manifests itself as a driving force barrier as there are no geometric degrees of freedom that can serve to reorganize the acceptor geometry in a rigid medium.

Based on this assignment of the quenching state to the ${}^{4}T_{1}$ ligand field excited state of the Mn^{II} ions, we can then use the information from the Arrhenius fits to determine the reorganization energy associated with this excitation since all kinetics associated with the ruthenium reorganization are tied into the Zn₂ molecule, which is already accounted for when we subtract the Zn₂ kinetics from the mixed metal kinetics. To estimate the reorganization energy, we will depend

on the standard Marcus equation for electron transfer rates,³⁸ under the assumption that rates for energy transfer processes are proportional to the same variables as a Dexter energy transfer is the same as two simultaneous electron transfer events:³⁹

$$k_{ET} = \frac{2\pi}{\hbar} |H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} e^{-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T}}$$
(5)

This equation has similarities to the Arrhenius equation and if one assumes the components of the equation are interchangeable, one can solve for an expression that gives the activation barrier in terms of Marcus equation variables as seen below:

$$E_a = \frac{(\Delta G_{EnT} + \lambda)^2}{4\lambda} \tag{6}$$

Some rearrangement of equation 2 and solving the resulting quadratic equation gives two possible values for the reorganization energy as shown in equations 7 and 8, which are determined by whether or not the magnitude of the thermodynamic driving force of the reaction is larger or smaller than the reorganization energy:

$$\lambda = -2\left(\sqrt{E_a} \cdot \sqrt{E_a - \Delta G_{EnT}} - E_a + \frac{1}{2}\Delta G_{EnT}\right)$$
(7)
$$\lambda = 2\left(\sqrt{E_a} \cdot \sqrt{E_a - \Delta G_{EnT}} + E_a - \frac{1}{2}\Delta G_{EnT}\right)$$
(8)

In this case, the thermodynamic driving force for this energy transfer reaction is essentially fixed since the entropic effects are negligible for this system, resulting in two possible values for the reorganization energy. In determining which of the two values is correct, we must rely on previously reported reorganization energies for transition metal ligand field excitations. Our fitting of the variable temperature kinetic data is used in addition to the energy values from the low temperature emission results on both complex **1** and complex **5** to determine the reorganization

energy of the mixed metal core for the promotion of the Mn^{II} into an excited ligand field state. Depending on which value is used from the low temperature emission of complex 1, one obtains a reorganization energy of either 0.16 \pm 0.02 eV or 0.36 \pm 0.02 eV when an emission energy of 14,640 cm⁻¹ is used or 0.24 ± 0.02 eV or 0.48 ± 0.05 eV when an emission energy of 13,790 cm⁻¹ is used. Recent work in our group has found a value for the reorganization energy associated with Fe^{II} spin-crossover of ~1.0 eV.⁴⁰ Since that transition requires the removal of two e_g^* electrons and the pairing of a two sets of electrons, while our suspected ${}^{6}A_{1g}$ to ${}^{4}T_{1}$ transition only requires the removal of a single $e_g{}^{\ast}$ electron and a single electron pairing in the t_{2g} orbital set, one can assume that the reorganization energy of the Mn^{II} ligand field in our complex should be close in energy to ~0.5 eV. Based on this reasoning, of the two values determined from the parameters from the Arrhenius fit, it makes sense to assume the reorganization energy is near the average of the two values, or in the range of 0.43 ± 0.10 eV. However, the sharp peaks of the LT emission of complex 1 indicate relatively similar geometries between the quartet and the sextet as measured. This should result in smaller reorganization energy value unless there are other factors involved. To give ourselves a better idea of what is happening in this system, electronic structure calculations were performed on the ligand field states of interest and their results are discussed below.

3.3.10 Computational Results

For the theoretical determination of reorganization energies, Optimized geometries for the lowest energy sextet, quartet, and doublet electronic state were obtained starting from the X-ray crystal structure using unrestricted B3LYP density functional theory. The resulting optimized geometries reveal geometric distortions in both the quartet and doublet state relative to the sextet ground state of the complex, which are evident when viewing the geometries in figure 3-9.





Figure 3-12: Drawing of the three UB3LYP optimized geometries of complex 1. The top view is from the side and the bottom view is from the top looking down. The indicated non-bonding distance in the ${}^{4}T_{1}$ geometry is highlighted as this correlates to a bond in the other two structures. The dashed lines are shown to emphasize the geometric changes as a function of the multiplicity.

M-L Bond	Sextet Distance (Å)	Quartet Distance (Å)	Doublet Distance (Å)
Mn-01	2.243	2.055	2.163
Mn-O2	2.230	2.203	2.007
Mn-O4	2.096	2.055	2.069
Mn-N6	2.205	2.046	2.059
Mn-N4	2.240	2.073	1.963
Mn-N5	2.465	2.507	2.204

Table 3-4: Select bond distances for the UB3LYP optimized geometries of complex 1.

These distortions take the form of a pinching together of the two cresol ring moieties of the macrocycle and a slight canting of the ring planes relative to each other, both of which are more pronounced in the doublet relative to the quartet. The Mn-ligand bond distances on average also shorten as the multiplicity drops, as would be expected from ligand field theory. These bond distances are summarized in table 3-4. This is consistent with what would be expected from ligand field theory, as lower multiplicities have less antibonding character in the metal ligand bonds. The energies of the lowest lying quartet and doublet state were evaluated at their optimized equilibrium geometries, and at the optimized ground state (sextet) geometry, in addition to the evaluation of the sextet energy at all three optimized geometries. The results from these calculations are summarized in table 3-5. From these results, a qualitative picture of the relative ordering of the potential energies of these states can be assembled, and it is pictured in figure 3-13.

The first noteworthy result from these calculations is that for all geometries studied, the sextet electronic state is the lowest in energy. This means that the magnitude of the reorganization energy is smaller than that of the free-energy difference between the sextet ground state and the quartet and doublet excited states. The second result of note in these calculations is the determination of the reorganization energy values by evaluating the energy of the sextet electronic state at the equilibrium geometry of the quartet and the doublet and subtracting the energy of the ground state sextet at its equilibrium geometry. These values are noteworthy because the reorganization energy for the doublet is more than twice that for the quartet, agreeing with our assessment of greater geometric distortions in the doublet.

Since the reorganization energy is smaller than the free energy difference any emission from the quartet states should have a λ_{max} at wavelengths correlating with an energy lower than that of the

Excited	Energy Difference:	Reorganization Energy:	Destabilization Energy:	Franck-Condon Energy:
State	ΔE	λ	DE	FC
Quartet	1.38 eV	0.49 eV	0.43 eV	1.81 eV
	11,100 cm ⁻¹	3,950 cm⁻¹	3,470 cm ⁻¹	14,600 cm ⁻¹
Doublet	1.80 eV	1.12 eV	1.09 eV	2.89 eV
	14,500 cm ⁻¹	9,030 cm ⁻¹	8,790 cm ⁻¹	23,300 cm ⁻¹

Table 3-5: Table of UB3LYP energy calculation results. Thermodynamic values are correlated to labels in figure 3-13.



Figure 3-13: A simple energy diagram of the B3LYP thermochemistry results. Energy difference labels match values listed in table 3-5. Each color and corresponding italic term state corresponds to the electronic state calculated for a particular geometry designated by the column in which the state is placed.

free energy difference assuming the emission is from a thermalized quartet state into a nonthermalized ground state.

However, emission into a non-equilibrium ground state would result in a relatively broad emission feature, which is not what is observed in this case. In order to have the relatively sharp emission features that are observed, the geometry must not change much between the emissive and ground states. Since the low temperature emission is occurring in the rigid medium of a micro-crystalline lattice, one could make the assumption that the emissive state is frozen at the ground state geometry. If this is the case, then the emission energy would include the additional energy of the destabilized quartet state in addition to the free-energy difference, as has been reported previously for emissive compounds in rigid media.³⁴ Since the conformation of the molecule would be stationary in this case, the observed emission peaks would be relatively sharp in appearance. Based on the agreement of the observed emission peak sharpness to that expected for a frozen geometry, it is more likely that the observed emission peaks in complex 1 include both the free energy change and the destabilization energy of the quartet relative to the sextet. Indeed the match between the energy of the higher energy LT emission peak for complex 1 and the calculated energy difference between the sextet and quartet states with the geometries frozen at the ground state sextet geometry is uncanny.

This means that if we use the emission values for the free-energy difference when fitting the VT data, as was previously discussed, there is the potential for this energy value to already include the destabilization energy associated with the Mn(L')Zn core being unable to reorganize, which then leads to the issue of what is causing the observed thermal barrier. The variable temperature emission measurements are taken in a rigid glass, so ostensibly the core is in a similar locked ground state geometry. Since the low temperature Mn(L')Zn emission is in a microcrystalline

lattice, there could be a different outer-sphere reorganization energy for the two experiments or the differences in the reorganization of the carboxylate bridges that could make up the observed difference in reorganization energy. If that is the case however, then the additional reorganization energy is likely the smaller of the two possible values that were determined earlier. If one uses the LT emission energy as a value for free-energy, one could take the smaller solved value of the reorganization energy ($0.16 \pm 0.02 \text{ eV}$) as an additional reorganization process not accounted for in the destabilized LT emission. If one then adds the destabilization energy to the additional solved reorganization energy, this result of 0.59 eV is still plausible as a value for the reorganization energy for this process in a locked ground state geometry.

There is of course the alternate scenario to be considered in the case of a rigid geometry. While the sharp emission peaks for the LT emission of complex **1** indicate that the geometry is frozen at 5 K in a microcrystalline lattice, there is no guarantee that this is the case in the optical glass medium that the VT time resolved emission measurements are collected in. Especially since the excited states involved require a net qualitative shrinking of the molecule, it is possible that the excited states could be accessible in their relaxed states. If that is the case, if we use the non-frozen free energy difference derived from calculations in our equations to determine the reorganization energy, one obtains 0.53 ± 0.02 eV and 0.84 ± 0.05 eV as the possible values of the reorganization energy. The smallest of these two values is the reasonable estimate of the reorganization energy as was discussed earlier, and is close to the value for the 0.49 eV reorganization energy value as was determined by the calculations.

While the two scenarios discussed above operate on different assumptions and there is an inherent question as to the accuracy of using the Marcus equation to solve for additional reorganization processes, it is comforting that the two different assumptions on how the macrocyclic core could

behave in the VT emission spectroscopy of complex **3** still give similar values for the reorganization energy as the origin of the observed thermal barrier to quenching by the quartet state of the manganese in the mixed metal macrocycle found in complex **3**. As it is the case that the energetics of all the involved electronic states that observed experimentally are such that energy transfer should be spontaneous, as is depicted in the summary diagram seen in figure 3-14, this reorganization energy barrier seems a most logical explanation for the kinetics seen in complex **3**.



Figure 3-14: Simple energetic diagram showing relative energies of the Ru ³MLCT states as determined experimentally and the experimentally derived energies of the emissive $[Mn(L')Zn(OAc)]^+$ ligand field states. The computationally derived value of the quartet and typical literature value for the ⁴A₁ listed for reference.

It is tempting to think that perhaps the doublet could also quench the emission in a similar fashion as that which was determined for the quartet. If one plugs in the calculated reorganization energy from the lowest energy doublet state as was determined with DFT and uses the energy determined from DFT when calculating the energetic difference for the energy transfer process, one can plug the values and determine a hypothetical thermal barrier for quenching by the doublet state. When all the values are substituted and the math evaluated, the doublet state would have a thermal barrier to quenching of approx. 1340 cm⁻¹, which would have virtually no influence in the variable temperature quenching rate in the optical glass temperature range studied in this report. This means that while it is not spin allowed for the doublet to quench the ³MLCT of the energy donor, it would also not be thermodynamically allowed. This study initially set out to show a spin dependence on the quenching of the ³MLCT. However, since the high reorganization energy of the doublet state would not allow for it to participate in quenching, such a conclusion cannot be made based on this study.

3.4 Conclusions

We have observed the temperature dependent quenching behavior of a ruthenium polypyridyl ³MLCT excited state by a manganese (II) containing Schiff-base macrocycle in covalently linked intramolecular donor-acceptor assemblies. This quenching process was compared to an equivalent structural model and determined to have a thermal barrier of 80 ± 20 cm⁻¹. It was determined that this quenching process is due to a Dexter energy transfer from the Ru-based ³MLCT into the ⁴T₁ ligand field state of the Mn^{II} in the macrocycle. Since the energy of the acceptor states in the Mn^{II} is lower than the ³MLCT, this thermal barrier is found to be due to a reorganization process in the mixed-metal macrocycle as both theory and experiment show that the energy difference between

the lowest sextet and quartet states is below the energy of the ³MLCT in the ruthenium donor. For a variety of scenarios considered, this reorganization process was determined using a simplification of the Marcus equation into the Arrhenius equation and solving for reorganization energy. In all the cases considered above, the reorganization energy for this quenching process is determined to be on the order of 0.5 - 0.6 eV.

While we were unable to find conclusive evidence of a spin conservation requirement in Dexter energy transfer, this study has enabled us to gain a great deal of knowledge concerning the quenching of a Ru³MLCT by the ligand field excited states of a transition metal center, which will prove invaluable when considering the variable temperature quenching behavior of complex 4. Furthermore, this is to our knowledge the first instance of simple ligand field transitions acting as energy transfer acceptors exclusively via a Dexter energy transfer mechanism, even though it has been observed for Forster energy transfer processes.^{2b-e} We hope to utilize the detailed understanding of how the Mn^{II} ion quenches the Ru chromophore in the $[Mn(L')Zn(mcb)Ru((CF_3)_2-bpy)_2]^{3+}$ complex to better interpret future studies on the $[Mn_2(L)(mcb)Ru((CF_3)_2-bpy)_2]^{3+}$ complex.

APPENDIX

Appendix: Supplemental Figures



102913 MS5093-2P-2 50uM CH3CN_01 #1-100 RT: 0.00-3.05 AV: 100 SM: 5G NL: 4.21E4 T: ITMS + p ESIZ ms [150.00-2000.00]

Figure A3-1: ESI-MS results of complex 3 in dichloromethane.

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Chapter 4: Electronic Structure Calculations of the [Mn₂(L)(mcb)]⁺ Exchange Coupled Dimer

4.1 Introduction

4.1.1 Background Information

Previous research in our group has explored how to differentiate between electron transfer and different types of energy transfer in a well characterized series of covalently linked donor-acceptor complexes such that the mechanism of the electron and/or energy transfer can be easily determined.^{1,2} Of particular interest were studies on a series of donor-acceptor systems consisting of a ruthenium polypyridyl complex covalently appended to a di-manganese Schiff-base macrocycle,¹ which includes the $[Mn_2(L)(mcb)Ru((CF_3)_2-bpy)_2]^{3+}$ (1) complex as seen in figure 4-1, where (L) is a Schiff base macrocycle, (mcb) is 4-carboxy,-4'-methyl-2,2'-bipyridine, and (CF₃)₂-bpy is 4,4'-bistrifluoromethyl-2,2'-bipyridine. The ruthenium polypyridyl moiety is used as an extremely well characterized chromophore which exhibits emission from a triplet metal-toligand charge transfer state (³MLCT).³ This emission allows the ruthenium polypyridyl to function as a kinetic handle by which the rates of energy or electron transfer can be measured.⁴ The energetics of the ligands also allow for the directed localization of the ³MLCT either closer or in the case of complex **4** farther from the binuclear macrocycle.^{1,4} The Mn^{II} macrocycle was chosen for its extremely small ligand field absorptions to prevent the possibility of Forster energy transfer⁶ while still allowing for the study of possible Dexter energy transfer or electron transfer reactivity with a transition metal dimer complex. In our previous work, we observed the quenching of the ³MLCT in these previously studied systems and it was determined that this quenching was caused by a Dexter energy transfer mechanism.³

In the previous chapter, the Schiff base macrocycle from complex **1** was replaced by an analogue with a single manganese ion to make a mixed metal complex $[Mn(L')Zn(mcb)Ru((CF_3)_2-bpy)_2](ClO_4)_2(PF_6)$ (**3**) and it was found that the ³MLCT was quenched via a similar Dexter energy transfer mechanism by a excited ligand field state of the Mn^{II} ion. The rate of this quenching was relatively small for the range of temperatures studied. However, in the case of the complex **1**, preliminary results indicate the rate of quenching of the ³MLCT by the macrocycle is much larger.⁴



Figure 4-1: Drawings of the systems either referred to or studied in the course of this chapter. Complexes 1-3 and 5 were studied previously, the results of which are referred to in this work. Complex 4 was the primary molecule studied via computation in this work.

4.1.2 Unanswered Questions from the MnZn Complex

From our studies on complex **3** which were supplemented with studies on complex **5**, when the Mn^{II} ion in its ground ${}^{6}A_{1}$ state participates in quenching, it is excited to its lowest energy excited state, which is the ${}^{4}T_{1}$ state. If one now considers this occurring for a single Mn^{II} ion in the Mn_{2} macrocycle, the ${}^{4}T_{1}$ state on the excited metal center can still interact with the five unpaired spins on the other Mn^{II} center in the binuclear cluster. It was not known initially what the nature of this spin coupling would be, as it was possible for it to be ferromagnetic or anti-ferromagnetic, large

or small in magnitude. Depending on the magnitude and nature of the spin coupling in the excited state, it was possible that the energetics of the quenching ligand field transition could have been substantially changed. It was therefore necessary to study both the ground state ${}^{6}A_{1} + {}^{6}A_{1}$ spin exchange, as well as the so called 'quartet excited spin manifold' where there is spin exchange between the ${}^{4}T_{1}$ and the ${}^{6}A_{1}$ states in the Mn₂ dimer.

While our previous results were able to ascertain the mechanism of the quenching in Mn_2 dimer, there remained many questions on this system that needed to be answered. We have obtained preliminary data on the LT emission lifetime of the complex **1** at low temperatures and have determined that the emission lifetime at 10 K is less than 30 ns and on the order of tens of nanoseconds. This is similar to the observed room temperature emission lifetime of 1.5 ns which was also previously reported. While our data are extremely limited, and there is a lack of data on the intermediate temperature points such that we cannot tell if there is a discontinuity in the quenching rate as a function of temperature at the glass-to-fluid transition of the optical glass solvent mixture, it appears that the temperature is not having much of an effect on the emission lifetime of the complex. It is hoped that by developing a more detailed understanding of the electronic structure of the Mn_2 acceptor, we will be able to determine the cause of the faster quenching from the Ru polypyridyl moiety where the Heisenberg spin exchange coupled macrocyclic core opens up a host of spin allowed electronic excited states responsible for the observed quenching of the Ru complex.

4.1.3 Objectives for Computational Study

One of the key assumptions we are forced to make when relying exclusively on experimental data is that all of the energetics associated with the ligand field transition that was determined to be causing the quenching in MnZn are unchanged in the Mn₂ system. While the macrocycles are similar, there are structural differences that could cause this assumption to be incorrect. Specifically, the analysis of these systems depends on having a good estimate of the energy difference between the excited and ground ligand field states and the reorganization energy associated with populating the excited state. We were able to obtain experimental estimates of these values on the MnZn system, with the help of electronic structure theory. We wish to corroborate the strength of the MnZn model at estimating the ligand field state energy differences and reorganization energy values for the Mn₂ system. If it is found from theory that these estimations are not accurate, we then wish to use the theoretically determined values to better understand the thermodynamics of this system, while referring to the similar calculations in the MnZn structure to ensure the determined values are reasonable.

The energy difference between the ${}^{6}A_{1}$ and ${}^{4}T_{1}$ ligand field states and the reorganization energy were computationally determined in Chapter 3. The resulting reorganization energy had good agreement with the experimental determination of the reorganization energy for the ligand field excitation of the mixed metal dimer. The experimental value for the ligand field energy difference (derived from LT emission) was also able to be explained using values derived from theory. These results provided confidence in the ability of computational studies to estimate the reorganization energy in the Mn₂ system. It was also desirable to obtain an estimate for the energetics of the analogous transitions in the Mn₂ complex and ensure they are not significantly altered compared to the transition for the mixed metal dimer as was previously mentioned. We also want to understand the electronic structure of the Mn_2 acceptor as hopefully by understanding how the spin states are altered between the ground and excited state of the energy acceptor, we can gain insight as to why the reaction proceeds so much faster in the Mn_2 than it does in the MnZn molecule.



Figure 4-2: The reported X-ray structure of complex 4, with the hydrogen atoms omitted for clarity and the atoms displayed as thermal ellipsoids. The atom labels from this structure were used consistently in reporting the results of our computational studies.

4.2 Experimental

All computational work reported herein was performed using the Gaussian 09^7 electronic structure package. Geometry optimizations were started from the previously reported X-ray crystal structure¹ for the $[Mn_2(L)(mcb)]^+$ (4), which is depicted in figure 4-2 and whose Cartesian coordinates were imported in a manner similar to that described in Chapter 2.

Geometries of the so called ground state spin coupled manifold (where each Mn^{II} ion has S=5/2) of complex **4** were optimized using the B3LYP⁸ and BPW91⁹ density functionals along with a 6-311G(d,p) basis set.¹⁰ These functionals were again chosen as they were in Chapter 2 for the verification of functional independent behavior in these systems. The 6-311G(d,p) basis set was exclusively used as this is the required level of theory for energetic accuracy and so the optimizations were performed at the same level to assure the molecules were optimized to the proper potential energy surfaces.

Also studied was an excited state spin coupling of the Mn_2 system where one of the two Mn^{II} centers has been excited to the lowest energy quartet state. The high spin (S=4) and low spin (S=1) geometries were optimized in B3LYP for this quartet excited spin coupled system as well. It was procedurally efficient to first optimize the high spin state for B3LYP since it was expected this would be the closest match for the X-ray structure. Then the low spin optimization for B3LYP was performed starting at the high spin optimized geometry. Finally, the BPW91 geometries were optimized using the corresponding B3LYP optimized geometry as a starting point. A similar approach was taken for the quartet excited state spin manifold optimizations, where the quartet excited high spin state (S=4) optimization was performed first starting from the B3LYP high spin optimized geometry for the ground state spin manifold (S=5). After this geometry was obtained, the quartet excited low spin state (S=1) was optimized from its corresponding high spin optimized geometry.

The electronic structure of low spin states (S=0 and S=1) and where appropriate high spin states (S=4) was modeled with broken symmetry wavefunctions,¹¹ which were generated with the fragment based guess methodology as described in the appendix of Chapter 1. Guesses for these broken symmetry electronic states were generated before optimizations were performed, and as

recommended form Chapter 1, the spin density on the metal centers was tracked for all broken symmetry wavefunctions to ensure a proper low spin state was obtained.

For each optimized geometry, a high spin and low spin energy calculation was performed as is necessary for the determination of the electronic coupling constants via the Broken Symmetry method as implemented by Yamaguchi and coworkers.¹² To investigate the possibility of a functional dependence on the calculation of the coupling constants, these energy calculations were performed in both BPW91 and B3LYP for the low spin and high spin optimized [Mn₂(L)(mcb)]⁺ molecules optimized in B3LYP and BPW91. This means that a total of four optimized geometries resulted in the need for sixteen energy calculations. All optimized geometries were checked for convergence to a global minimum by performing a frequency calculation on the resulting geometry and confirming a lack of negative frequencies.

In addition to the geometry optimizations on the full $[Mn_2(L)(mcb)]^+$ complex, a geometry optimization on the high spin state using B3LYP/6-311G(d,p) was performed on a simplified version of the complex based on the full optimized geometry where the mcb was replaced with a carboxypyridine bridge to see if the mcb was imparting asymmetry to the macrocyclic core.

The optimized simple geometry and the optimized excited state coupling manifolds were studied only with B3LYP/6-311G(d,p) as this was determined to be the best energetic match to experiment for the sake of modeling the spin exchange mechanism before these other calculations were attempted. Again, these optimized geometries required two energy calculations to be performed to determine the spin coupling constants.

For the determination of the ligand field energy differences between the sextet and the quartet spin manifolds, the difference in calculated B3LYP/6-311G(d,p) energies from the already available

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optimized S=4 ground state of the excited manifold and the optimized singlet ground state of the basal spin manifold was determined. This was subsequently corrected by using information available from the calculations mentioned above and described in subsequent sections to yield the energy difference between the lowest energy excited state of the quartet excited state spin manifold and the ground state of the molecule. The calculation of the reorganization energy associated with this process was determined by performing an additional electronic structure calculation of the ground S=0 state of the Mn₂ system had its energy evaluated at the optimized quartet excited S=4 geometry. This was done with B3LYP since again it had the best energetic accuracy of the functionals used in this study.

4.3 Results and Discussion

4.3.1 Geometry Optimization Results

The optimized geometries of the X-ray crystal structures were obtained for both the S=0 and S=5 states of the ground state spin coupling manifold with both BPW91 and B3LYP density functionals, the results of which are summarized for select bond distances and compared to the X-ray structure values in table 4-1. As was found previously in Chapters 2 and 3, the theoretically determined bond distances were in all cases longer than those found in the X-ray crystal structure, with the exception of the Mn1-N5 and Mn2-O3 bond distances.

These longer bonds are a common occurrence when comparing geometries determined via X-ray diffraction with geometries obtained via electronic structure calculations. It is not directly known why the Mn1-N5 bond and Mn2-O3 distances are longer in the X-ray structures, but since in all the optimizations so far mentioned these bond distances are shortened, it is presumed that these

bonds are lengthened in the crystal structure due to intermolecular forces present in the crystal lattice that are not present and accounted for in our computational modeling of the system. It is possible that these forces are related to a pressing or torqueing down of the bipyridine ligand which is pivoting around O4 and sterically interacting with the methyl group on N5, causing the observed lengthening of the two bond distances.

Opt. Parameter	Xray	B3LYP LS Opt	B3LYP HS Opt	BPW91 LS Opt	BPW91 HS Opt	Excited LS Opt	Excited HS Opt	Simple HS Opt
M(1)-N(4)	2 186/8)	0.003	2 223	2 100	2 100	2 218	2 217	0 000
M(1)-N(6)	2 183(8)	2 199	2 198	2.150	2.190	2 212	2.217	2 200
M(1) N(5)	2.618	2.580	2.586	2.566	2.560	2.538	2.538	2.587
M(1) - N(3) M(1) - O(1)	2.010	2.305	2.300	2.000	2.000	2.330	2.550	2.307
M(1)-O(1)	2.212(0)	2.203	2.207	2.213	2.210	2.139	2.141	2.202
M(1)-O(2)	2.204(6)	2.200	2.212	2.200	2.211	2.320	2.323	2.200
M(1)-O(4)	2.086(7)	2.090	2.090	2.084	2.084	2.080	2.080	2.103
M(2)-N(1)	2.232(8)	2.223	2.223	2.190	2.190	2.022	2.024	2.222
M(2)-N(2)	2.438(9)	2.598	2.595	2.583	2.576	2.782	2.783	2.596
M(2)-N(3)	2.193(8)	2.205	2.204	2.166	2.167	2.038	2.038	2.198
M(2)-O(1)	2.195(6)	2.202	2.207	2.197	2.207	2.185	2.186	2.209
M(2)-O(2)	2.178(6)	2.199	2.200	2.209	2.211	2.006	2.006	2.202
M(2)-O(3)	2.132(7)	2.105	2.105	2.095	2.097	2.021	2.021	2.102
Mn1…Mn2	3.28	3.29	3.30	3.33	3.35	3.28	3.28	3.30
0102	2.68	2.63	2.64	2.61	2.62	2.61	2.61	
Mn1-O1-Mn2	96.2(2)	96.8	96.9	98.1	98.3	98.5	98.5	96.9
Mn1-O2-Mn2	96.9(2)	96.8	96.9	98.2	98.4	97.9	98.1	97.0
01-Mn1-02	74.7(2)	73.5	73.5	72.4	72.4	71.4	71.4	73.7
01-Mn1-04	90.9(2)	90.0	89.8	88.4	88.1	92.1	91.9	89.8
02-Mn1-04	100.7(2)	97.1	96.8	97.1	96.6	91.5	91.5	98.2
02-Mn2-01	75.5(2)	73.7	73.7	72.5	72.6	76.9	76.9	73.6
02-Mn2-03	93.4(2)	91.2	91.0	89.2	89.0	91.5	91.6	90.1
01-Mn2-03	92.4(3)	99.7	99.4	99.7	99.3	96.7	96.5	98.3

Table 4-1: Selected bond distances and angles for the optimized geometries of complex 4 compared to the X-ray crystal structure.

When comparing the high and low spin geometries obtained with B3LYP, it is generally observable that the metal oxygen bond distances associated with bridging the two metal centers together are slightly shorter in the low spin geometries than they are in the high spin geometries. It is also the case that the metal nitrogen bonds associated with the diethylenetriamine portion of the macrocycle are either slightly longer or unchanged between the high spin and low spin optimized geometries. While the trends in the Mn-O bond distances were consistent between B3LYP and BPW91, the behavior of the Mn-N bond distances was not consistent with the B3LYP

optimized geometries. Since all of these geometries were confirmed to converge to global minima via a lack of negative frequencies, these geometries should be rather accurate. Therefore, it is unclear why the behavior of these bonds is less uniform when transitioning between high and low spin states.

When generally comparing the performance of the different functionals in matching the X-ray crystal structure, it was surprising to observe that for a majority of the bonds investigated, the both functionals obtained bond distances within the experimental error of the X-ray structure. Furthermore, it appears that there is no systematic outperformance of one functional over the other, with B3LYP being closer to experiment for some values, and BPW91 being closer to experiment for other values. It is significant that when low spin and high spin bond distances are averaged, there were more B3LYP calculated Mn-O bond distances that were closer to the X-ray structure values than there were BPW91 calculated Mn-O bond distances closer to the X-ray structure values. Since it is the Mn-O bonds that are responsible for the spin coupling interaction between the two metal centers, it can be said that B3LYP is ever so slightly better than BPW91 for the purposes of modeling the geometries of these systems.

Angles involving the bridging oxygens and the Mn atoms were also tracked for changes across the geometries studied. In general the Mn1-O-Mn2 bond angles were larger in the optimized geometries than they were in the X-ray structure, and the O1-Mn-O2 bond angles were smaller in the optimized geometries than in the X-ray structures. As for the differences between functionals, BPW91 usually had the larger deviations from X-ray structure angles, with the B3LYP values being intermediate to the X-ray structures and the BPW91 bond angles. The optimized geometries showed bond angles near 90 degrees for O1-Mn1-O4 and O2-Mn2-O3, which are smaller than the bond angles for O1-Mn2-O3 and O2-Mn1-O4, which had values near 99 and 97 degrees

respectively. These sets of bond angles show similarity via a rotation of the molecule around a pseudo- C_2 rotation axis centered between the oxygens of the bridging phenoxy groups and bisecting the carboxylate bridge. The differences in the values of the O1-Mn2-O3 and O2-Mn1-O4 angles are likely due to the asymmetry imposed by the bipyridine bridge as has been discussed earlier. These values contrast with the X-ray structure where Mn1 shows large variance between the 90 degree O1-Mn1-O4 and 100 degree O2-Mn1-O4 angles, but the corresponding O2-Mn2-O3 and O1-Mn2-O3 angles are the same within the error of experiment with a value near 93 degrees. It appears that the optimized geometries prioritize the interaction of O1 with Mn1 and O2 with Mn2, which is reflected by the more square angles even though the bond distances are not that different from the Mn1-O2 and Mn2-O1 bond distances.

When comparing bond angles from the low spin and high spin optimized geometries, for both B3LYP and BPW91 the Mn1-O-Mn2 bond angles were larger for the high spin state, and the O1-Mn1-O4, O2-Mn1-O4, O1-Mn2-O3, and O2-Mn2-O3 bond angles were smaller in the high spin state. The O1-Mn-O2 bond angles did not really change much between high and low spin states. It is assumed that these bond angle changes between low and high spin state must destabilize the spin interaction between the Mn²⁺ ions as the low spin state is the ground state of these molecules.

Besides bond angles, other useful structural parameters were able to help determine morphological changes in the molecules. The easy to identify parameters were the Mn1…Mn2 intermetallic distance and the O1…O2 interatomic distances in the optimized geometries. The intermetallic bond distance is helpful because it gives an easy way to track the overall change in the shape of the Mn1-O1-Mn2-O2 core, while the O1…O2 interatomic distance gives a superb handle for how folded the macrocycle is since the only way the distance between the two oxygens can change is by folding the phenoxide portions of the macrocycle closer together.

In the optimized ground state spin coupling manifold geometries, we can see the intermetallic bond distances are longer in B3LYP than for the X-ray structures, and even longer in BPW91. This is consistent with the closing of the O1-Mn-O2 bond angles that causes the core to elongate along the Mn1…Mn2 axis. The O1…O2 interatomic distance shows the opposite trend, with the macrocycle getting more folded as one goes from the X-ray structure to B3LYP to BPW91 optimized geometries. Since there seems to be a correlation between the two interatomic distances changing, it may be the case that the folding together of the macrocycle portions forces the other angles to change as has been discussed, but it is not certain since both distances increase slightly when comparing low spin and high spin optimized geometries.

The optimized geometries of the quartet excited spin manifold had several key differences when compared to the X-ray structures and the optimized ground state spin manifold optimized geometries. When these structures were optimized, it is important to note that Mn2 was the Mn center which was designated to be in the lowest quartet excited state, so we would expect to see larger distortions in the bond distances associated with Mn2 when compared to those for Mn1. This notion is certainly consistent with what we observe for the Mn-N bonds in these optimized geometries. As for the deviations in the Mn-O bond distances, when averaged the deviations for Mn-O bond distances were larger for Mn2 than for Mn1. However, it is noteworthy that the Mn1-O2 bond distance is much longer than the X-ray structure while the Mn2-O2 is shorter than the X-ray structure. This may have been due to the contraction of the Mn2-O bond distances as all of the Mn2-O bond distances were shorter than the X-ray structure and optimized ground state spin manifold geometries.

In fact, with the exception of the Mn2-N2 bond distance, all of the bond distances associated with the Mn2 ion were shortened compared to the X-ray structure and optimized geometries of the

ground state spin manifold. This behavior is consistent with what one would expect from ligand field theory as the lowest energy quartet state involves a pairing of an electron from the e_g^* orbital into a t_{2g} orbital, which results in less occupation of the antibonding e_g orbital set and a subsequent shortening of bond distances. As for why the Mn2-N2 bond distance is lengthened, the best hypothesis available at this time is that is a steric consequence of the other bond distances being shortened.

The differences between high and low spin optimized geometries in the quartet exited spin manifold were extremely small, with no bond distances changing more than 0.002 Å. These changes were not really consistent between high and low spin states either, so there is really not much that can be inferred by comparing the bond distances of these high and low spin optimized geometries.

Inspection of the bond angles in the quartet excited spin coupling manifold revealed some interesting changes relative to the ground state spin coupled manifold geometries optimized with B3LYP. For one, the Mn1-O-Mn2 bond angles were more obtuse than their equivalents in the ground state manifold, which could be due to the shifting of the Mn-O(phenoxy) bond distances discussed above. As for the O1-Mn-O2 bonds, there is a decrease in the value of the O1-Mn1-O2 bond angle and an increase in the O1-Mn2-O2 bond angle relative to the ground state spin manifold optimized B3LYP geometries. These changes can be interpreted as an increase in the interaction of the bridging oxygens as a consequence of the shortening bond distances, which opens up the O1-Mn2-O2 bond. The average bond angles for O(phenoxy)-M-O(carboxy) also decrease towards 90 degrees in the quartet excited spin coupling manifold geometry relative to their values in the ground state spin manifold B3LYP optimized geometries. Again, this is likely due to the Mn-

O(carboxy) bond distances getting shorter for both Mn atoms and thus the angles getting more square due to this increased interaction.

There were few significant changes in the bond angles that were tracked when comparing the low and high spin optimized geometries in the quartet excited spin manifold, with no change being larger than 0.2 degrees. The Mn1-O2-Mn2 bond angle was larger for the spin optimized geometry but the Mn1-O1-Mn2 bond angle was unchanged between the low spin and high spin geometries. The only other angle variations are slight changes with the O(phenoxy)-Mn-O(carboxy) oxygen angles, but they do not appear to be systematic, with O1-Mn1-O4 and O1-Mn2-O3 appearing to decrease and O2-Mn2-O3 increasing between low spin and high spin optimized geometries. Indeed, the overall shape of the complex appears to be conserved between the low spin and high spin optimized quartet excited spin manifold geometries as the Mn1…Mn2 and O1…O2 interatomic distances are seemingly unchanged between the high spin and low spin forms.

When comparing the interatomic distances for O1····O2 and Mn1····Mn2 between the quartet excited spin coupled manifold geometries and the ground state spin coupled manifold optimized geometries for B3LYP, one can see that there are significant deviations between the two sets of geometries. Specifically, the Mn1-O1-Mn2-O2 core is actually less elongated than in the ground state spin coupled manifold, while the macrocycle is more folded as seen in the reduced O1···O2 interatomic distance in the quartet excited spin manifold optimized geometries. The reason for this likely resides in the shorter Mn-O bond distances which have the overall effect of contracting the core relative to the ground state spin manifold geometries.
4.3.2 Coupling Constant Determination

Coupling constants were determined using the Yamaguchi method¹² which utilized the electronic energy and spin expectation values derived from the low spin and high spin calculated wavefunction at each geometry studied. In this way, the coupling constants for the ground state spin coupled manifold at the X-ray crystal structure geometry and all of the optimized geometries were obtained using both B3LYP and BPW91 wavefunctions, with the relevant computationally derived parameters and the resulting coupling constants recorded in table 4-2.

	BPW91 Coupling Data			B3LYP Coupling Data				
Geometry	BS S ²	HS S ²	E _{HS} - E _{BS}	BPW91 J (cm ⁻¹)	BS S ²	HS S ²	E _{HS} - E _{BS}	B3LYP J (cm ⁻¹)
B3LYP BS	4.994	30.012	199.26	15.93	5.002	30.008	87.35	6.99
B3LYP HS	4.994	30.012	191.95	15.35	5.002	30.008	83.12	6.65
BPW91 BS	4.994	30.014	197.97	15.82	5.003	30.009	85.24	6.82
BPW91 HS	4.995	30.014	185.15	14.80	5.003	30.009	78.37	6.27
X-ray Structure	4.993	30.014	219.56	17.55	5.002	30.008	90.16	7.21

Table 4-2: Relevant data and the coupling constants determined with the data for the optimized geometries of the ground state spin manifold. This data was obtained from low and high spin wavefunctions studied with UBPW91 and UB3LYP functionals in conjunction with a 6-311G(d,p) basis set.

For both functionals at all geometries, the Yamaguchi method in concert with the appropriate high spin and broken symmetry low spin wavefunctions correctly predicted the weakly antiferromagnetic coupling present in the di-manganese macrocyclic core, as was previously determined via VT magnetic susceptibility measurements to be approximately 6 cm⁻¹.^{1,13} Furthermore, this method of calculating coupling constants was extremely accurate even though the energy differences between high and low spin states have extremely small values. This also resulted in excellent consistency, as the coupling constants were within 2 cm⁻¹ for B3LYP at all

geometries and within 3 cm⁻¹ for the BPW91 determined values. When comparing the B3LYP and BPW91 coupling constants, the BPW91 values are substantially larger than the B3LYP values as was observed in Chapter 2 for the Fe₂ complexes. This propensity to overestimate antiferromagnetic coupling constants again is likely due to the qualities of the pure GGA functional to over-stabilize singlet states¹⁴ and the increased metallic character of the orbitals responsible for spin coupling. Theoretically determined coupling constants on Mn₂ systems have been reported in the past, and it been observed that hybrid functionals such as B3LYP give adequate estimates of the coupling constant.^{15,22} This was the case in our B3LYP calculated coupling constants as the calculated constants were extremely close to the experimental value at all geometries; even the simplified Mn₂ optimized geometry. As the simplified molecule showed no discernable difference in coupling value, it was determined that further analysis for this system was unnecessary.

When comparing the low spin and high spin optimized geometries for both functionals studied, we again see the trend of the low spin optimized geometries having slightly larger coupling constants when evaluated with the same functional. This is again hypothesized to be due to the shorter bond distances between the Mn^{II} and bridging oxygen atoms in the macrocyclic core in the low spin optimized geometries. The deviation between high and low spin optimized geometry values was higher for coupling constants evaluated with the BPW91 functional, but this was exaggerated for geometries optimized in BPW91 in coupling constants calculated in both functionals suggesting that this is due to the larger variance in the bond distances for the BPW91 functional optimized geometries.

Quartet excited spin manifold calculated coupling constants were evaluated on the appropriate B3LYP optimized high and low spin states with values derived from the B3LYP energy calculations and are reported in table 4-3.

	B3LYP Coupling Data					
Geometry	BS S ²	HS S ²	E _{HS} - E _{BS}	B3LYP J (cm ⁻¹)		
B3LYP BS	5.077	20.083	-11.87	-1.58		
B3LYP HS	5.077	20.083	-14.62	-1.95		
X-ray Structure	5.476	20.476	-29.8	-3.97		

Table 4-3: Relevant data and the coupling constants determined for the optimized geometries of the ${}^{6}A_{1} - {}^{4}T_{1}$ excited state spin manifold. These data were obtained from low and high spin UB3LYP/6-311G(d,p) wavefunctions.

The resulting coupling constants were about half as large and ferromagnetic, with the high energy state being lower in energy than the low spin state. The calculated coupling constant was smaller for the low spin optimized geometry, which is consistent with the notion of this state being ferromagnetic, as the appropriately coupled ground state should be lowest in energy.

The explanation for why the coupling is ferromagnetic in nature is has much to do with the changed nature of the spin unpaired electrons in the transition metal centers. Specifically, now that there is an entirely empty d-orbital in one of the Mn^{II} centers which is in its lowest energy quartet state (⁴T₁ state) there is an enhanced spin coupling pathway where electrons can freely go from one metal to the other without flipping spin. This results in an enhanced ferromagnetic coupling between the metal centers, yielding an overall ferromagnetic interaction.^{15,16} There is literature precedence for this type of excited quartet manifold ferromagnetic coupling which was reported by Gamelin and coworkers.¹⁵ They too did broken symmetry calculations to determine the coupling of a Mn^{II} Mn^{II} spin coupled excited state. Their results were similar to ours, with the excited state being weakly ferromagnetically coupled. This is encouraging as it validated our methodology used to obtain information on these excited states.

4.3.3 Coupling Pathway Analysis

As was previously done for the Fe₂(OH) systems discussed in Chapter 2, it was thought to be beneficial to look at the molecular orbital mechanisms of spin exchange¹⁷ as they could provide possible insight both into the electronic structure of the Mn_2 acceptor complex in its ground and excited state, as well as possibly provide insight as to which coupling mechanisms could interact via the mcb bridge with the ruthenium portion of the donor-acceptor complex. However, there were some unique challenges in the interpretation of the coupling pathways in these systems that were not present in the Fe₂(OH) dimers previously analyzed with these techniques.

The first challenge was the identification of a suitable Cartesian axis system that could be used to identify the type of d-orbitals on each of the metal centers. Remarkably, this was difficult since the coordination sites of the Mn^{II} ions were only vaguely similar by a pseudo- C_2 rotation, as the presence of the mcb bridge makes the molecule asymmetric overall. Since the strongest interaction between the Mn centers is mediated by the presence of the phenoxide bridging units of the macrocycle, it is not illogical for the axes to be aligned with them, as was the case of the axes of



Figure 4-3: The Cartesian axis system used for the assignment of d-orbital nature of the NMOs used to study the coupling pathways of the system. The y-axis on each Mn^{2+} ion is oriented perpendicular to the plane of the paper along the metal-carboxylate oxygen bonds.

the Fe centers lining up with the hydroxo bridge in the systems discussed in Chapter 2.¹⁸ With this idea in mind, the axes were established as shown in figure 4-3.

The problems with this axis systems were encountered because the morphologies of the d-orbitals were not extremely clear cut when using this system to assign d-orbital labels. While the axis system we have portrayed here is acceptable for the B3LYP NMO morphologies, it has deficiencies in that the d-orbitals appeared in certain cases distorted such that there was not a rigid adherence to the axes. This is most notable for the d_{xy} and d_{x2-y2} orbitals, which look nearly superimposable, even though ideally they would be more easily differentiated. This means that the establishment of the axes is much more open to interpretation, with the axes ultimately being decided by the idea that they should be oriented toward the phenoxide bridges and the identification of a few easily distinguishable orbitals such as the d_{z2} orbital.

However, this axis system did not match well to the symmetric Hay-Hoffman^{17,18} type orbitals that we were also interested in studying in Chapter 2. Since it was suspected that the axes would not be symmetric between the two metal centers based on the asymmetry in the molecule, the Hay-Hoffman method was not likely to provide easily interpretable results in any case, so it was decided that the NMO analysis^{17a,19} would be the focus when studying this system. Since we saw better and more consistent results in optimized geometries for the Fe₂(OH) system from Chapter 2 when compared to results from the X-ray structures, it was these that we focused on for this study. The established axis system was then used to make Natural Magnetic Orbital assignments for the broken symmetry orbitals that were obtained with B3LYP on the B3LYP low and high spin optimized geometries. These NMOs are plotted in figure 4-4.

It was fortunate that we were able to obtain good looking NMOs with a high degree of metal character using B3LYP broken symmetry orbitals on these optimized geometries containing the

full mcb ligand, as it made the determination of the orbitals easier than it otherwise would have been. What was noteworthy about these NMOs was that most of the orbitals had little interaction with the mcb bridging ligand apart from the coordinating carboxylate oxygen that was coordinating to the metal of interest. The only NMOs with significant mcb character were those for the d_{yz} orbitals, which had electron density on most of the mcb bridge. The implications of this are that any coupling pathways that depend on the d_{yz} NMOs could be directly influenced by a ³MLCT located on the mcb ligand in the full donor-acceptor complex.

The alpha-beta overlap values were calculated with the MultiWfn program²⁰ for the low and high spin optimized geometries of the quartet excited spin manifold using the NMOs generated with the B3LYP density functional. The resulting overlap values are presented in table 4-4. These overlaps were analyzed to determine the greatest contributing pathways to the coupling the Mn₂ macrocycle. As would be expected, there were many significant contributions to the spin coupling from the so called local symmetry asymmetric orbital pathways, where a d-orbital on one Mn^{II} center interacted with a different type of d-orbital on the other Mn^{II} center, since the coordinate axis system was not symmetric between the two metal centers.

However, what was unexpected was the quantity of large overlaps compared to those found in the Fe₂OH system in Chapter 2. In this system there are many more significantly overlapping pathways for spin coupling, which is likely due to the unsquare nature of the angles in the Mn1- O1-Mn2-O2 macrocyclic core. Even the so called symmetric coupling pathways were large as a result of this distorted nature of the core.



Figure 4-4: Plots of the NMOs of complex 4 as determined from the low spin B3LYP/6-311G(d,p) wavefunction for the geometry optimized under the same conditions. These surfaces are plotted with a 0.04 isovalue from a top down perspective with the majority of the bridging mcb ligand and associated surfaces clipped for clarity. The assigned d-character of each NMO is provided in the top row of the table.

	High Spin Opt	. Geometry	Low Spin Opt. Geometry		
d Orbitals	Orbital Numbers	Overlap Value	Orbital Numbers	Overlap Value	
xy/xy	208/208	0.381	208/208	0.381	
xz/xz	210/210	0.345	210/210	0.329	
z2/z2	207/207	0.341	207/207	0.346	
x2-y2/x2-y2	211/211	0.298	211/211	0.289	
yz/yz	205/205	0.219	205/205	0.206	
z2/xy	207/208	0.422	207/208	0.425	
xy/xz	208/210	0.421	208/210	0.426	
xy/z2	208/207	0.393	208/207	0.396	
xz/xy	210/208	0.383	210/208	0.387	
xy/x2-y2	208/211	0.383	208/211	0.377	
x2-y2/xy	211/208	0.364	211/208	0.358	
z2/xz	207/210	0.298	207/210	0.294	
x2-y2/xz	211/210	0.282	211/210	0.288	
xz/z2	210/207	0.279	210/207	0.275	
xz/x2-y2	210/211	0.273	210/211	0.279	
yz/xz	205/210	0.169	205/210	0.171	
z2/x2-y2	207/211	0.160	207/211	0.164	
xz/yz	210/205	0.140	210/205	0.142	
x2-y2/z2	211/207	0.129	211/207	0.132	
xy/yz	208/205	0.077	208/205	0.079	
yz/xy	205/208	0.062	205/208	0.064	
yz/z2	205/207	0.042	205/207	0.046	
yz/x2-y2	205/211	0.033	205/211	0.036	
z2/yz	207/205	0.012	207/205	0.015	
x2-y2/yz	211/205	0.008	211/205	0.006	

Table 4-4: Calculated alpha-beta overlap integral absolute values for the NMOs of complex 4, as seen in figure 4-4. All 25 possible overlaps between NMOs are enumerated, with the resulting overlap values ranked in descending order for the symmetric and asymmetric coupling pathways.

When comparing the overlap values between the high and low spin optimized geometries, there are not any drastic differences observed between the high and low spin states, which is consistent with the small deviation we observed for the bond distances between these optimized geometries. There are many pathways that increase when the geometry goes from the low to high spin state,

and there are just as many pathways with significant overlaps that decrease over the same change in geometry. It is possible to think of the former pathways as ferromagnetically coupled because they are enhanced as the geometry goes from low to high spin and the latter pathways are antiferromagnetic because their overlaps decrease between the low and high spin states. This could mean that there is a virtual tug-o-war between ferromagnetic and antiferromagnetic coupling pathways in the macrocyclic core. It is significant that the overlaps of the antiferromagnetic pathways have higher average values than the ferromagnetic pathways, which suggests that the molecule is overall antiferromagnetic in the ground state because these interactions slightly win out over the ferromagnetic pathways.

It was of interest in this study to look for coupling pathways that involved electron density on the mcb bridging ligand, as this ligand is thought to be excitable in the donor-acceptor complex. The only NMOs that had significant mcb ligand character were those associated with the d_{yz} metal based orbitals, as can be seen in from figure 4-4 and also seen in figure 4-5. It was thus found that only in the symmetric coupling pathway of d_{yz} - d_{yz} was the mcb ligand able to possibly influence the spin coupling of the system.

This makes sense, as the overlap depends on similar ligand character between the NMOs, so only the d_{yz} symmetric pathway had the same ligand character for both metals, as was seen in figures 4-4 and 4-5. This means that while an MLCT state located on the bridging mcb ligand could have considerable influence, it would not necessarily greatly interfere in the ground state coupling pathways of the macrocycle acceptor, especially since the electron density responsible for the large overlap value of the d_{yz} - d_{yz} spin coupling pathway is located mostly on the mcb, and it is possible that it does not actually participate in the spin coupling of the metal centers to the degree suggested by the orbital overlap value. The fact that spin coupling value on our simplified geometry was identical to that obtained for the equivalent optimized geometry of complex **4** suggests that any transient electronic changes to the mcb would have a minimal effect since the calculated coupling constant does not change despite the modification of the bridging carboxylate ligand.



Figure 4-5: A side by side comparison of the NMO surfaces corresponding to the d_{yz} (205 α) and $d_{x^2-y^2}$ (211 α) Mn centered orbitals for complex 4. The d_{yz} orbitals possess the only significant electron density on the mcb ligand, with the NMOs containing the next highest amount corresponding to $d_{x^2-y^2}$. These two surfaces are plotted to show that only the d_{yz} NMOs would have significant overlap mediated through the mcb ligand. Surfaces are plotted with an isovalue of 0.04.

An analysis of the coupling pathways in the quartet excited spin manifold was attempted to understand what changes caused a ferromagnetic excited state. However, the broken symmetry orbitals for triplet state that corresponds to the low spin state of this excited spin system did not yield satisfactory NMOs that could be used for the orbital overlap analysis of the coupling pathways. It was noteworthy however, that the unpaired alpha orbitals that did not have equivalent occupied beta orbitals corresponded to d_{xy} located on Mn2 and $d_{x^2-y^2}$ on Mn1. The overlap of this pathway would by definition be zero since they are both alpha orbitals, and while this is a significant coupling pathway in the ground state, since it has a lower overlap at the low spin geometry, it seems that it may be a ferromagnetic pathway for the NMO analysis. It may be the case that since these electrons no longer have anti-symmetric spins, that they can still interact in a spin coupling interaction in the absence of orbital overlap and in that case, it makes sense that this would be a ferromagnetic interaction. However, as there were no appropriate metal rich orbitals with the exception of the two aforementioned orbitals, any additional analysis of coupling pathways in the quartet excited spin manifold is not available at this time.

4.3.4 Energetics of the Mn₂ Acceptor System

As was previously mentioned in Chapter 3, DFT can be used to understand the energetics of the ligand field excitation of the Mn^{II} to the ${}^{4}T_{1}$ state that is responsible of the Ru ${}^{3}MLCT$ in complex **3**. It seems logical that any excited state in the Mn_{2} complex that is analogous to the ${}^{6}A_{1}$ to ${}^{4}T_{1}$ transition in the MnZn should also be responsible for the quenching observed in complex **1**, as there are states that are derived from ${}^{6}A_{1}$ to ${}^{4}T_{1}$ transitions present in the spin coupled dimer. Therefore, the first step was to determine equivalent ligand field excitation energy in complex **4** and compare to the value calculated for complex **5**.

The first challenge was to determine what comprised the analogous ligand field excitation in the Mn_2 spin coupled system. At the onset it is assumed that quenching will only provide energy to excite on of the Mn^{II} centers, but not both, as there is insufficient energy in the ³MLCT for a double excitation event, allowing us to focus on a single excitation. When a single Mn^{II} ion is promoted to its lowest energy ligand field excited state, the resulting ⁴T₁ state on one metal center can still

interact with the five unpaired spins on the other Mn^{II} ion in the binuclear cluster. It was not known initially what the nature of this spin coupling would be, as it was possible for it to be ferromagnetic or anti-ferromagnetic but determining this allows the identification of the lowest energy excited state derived from the excitation to a quartet ligand field state. Based on the previously discussed results on the X-ray structure and the optimized geometries, it was determined that this lowest energy excited state corresponds to the high spin S=4 state of the excited spin manifold. If we take the difference between the calculated electronic energy of that S=4 state at its equilibrium geometry and the calculated S=0 optimized low spin state that is the ground state of the molecule we can determine the equivalent ligand field energy differences for the sextet to quartet transition in the Mn₂ system. This value was determined to be 1.23 eV.

It should be noted that at this level of significance, the difference in energy between the broken symmetry singlet and the actual singlet energy seems insignificant at this scale (it's approximately 0.002eV), but this difference is 19 cm⁻¹, which is significant as the ground state spin coupling constant for this system is on average 6.8 cm⁻¹. This correction is necessary because the spin contamination of the calculated low spin states inadvertently increases the energy of the low spin state by mixing in higher multiplicity spin state character into the low spin state, which increases the calculated energy in anti-ferromagnetic coupled systems. This spin contamination is accounted for in the Yamaguchi method¹² used to determine the calculated coupling constants. The calculated high spin states on the other hand have almost no spin contamination, as at least in the ground state spin manifold the high spin state can be described as a single determinant wave function with all the spins parallel. So, to adjust the calculated low spin energy to be closer to the true value, the energy of the high spin state at its optimized geometry was used as a set point, and 15 *J* was subtracted from that energy as it is the case that the total energy between low and high spin states

for two S=5/2 centers is 15 *J*. The *J* value used for this determination was the average of that obtained at the low and high spin optimized geometries. The resulting energy was 19 cm⁻¹ lower than the energy of the optimized broken symmetry state. Using the energy expression for spin coupled states described in Chapter 1 (equation 1.2) and the average ground and excited state B3LYP coupling constants from optimized geometries, one can then use the previously determined values to plot out the all of the energetic states for these spin manifolds. The resulting plot is portrayed in figure 4-6.

Using similar concepts one can also determine what the energy difference between the spin barycenters in the absence of the spin coupling interaction would be. By using the equation for the energy of spin coupled states and the calculated ground state and excited state *J* values that were discussed in the previous section, one can determine that the energy difference between the barycenters would be 9850 cm^{-1} . This means that the energy difference between the lowest energy states of the ground and excited state spin manifolds is actually larger by ~55 cm⁻¹ than the ligand field transition would be in the absence of spin coupling as the large stabilization of the ground state by the spin exchange interaction (59.7 cm⁻¹) and the smaller stabilization of the S=4 state of the quartet excited spin manifold (6.6 cm⁻¹) have the net effect of making the ligand field state higher in energy for the spin coupled complexes that the transition would be for their hypothetical spin barycenters.

This means that the lowest energy state associated with the sextet to quartet transition in one of the Mn^{II} ions in the Mn_2 (~9900 cm⁻¹) is significantly lower in energy than the ${}^{4}T_1$ state relative to the ${}^{6}A_1$ ground state of the MnZn macrocycle (~11,100 cm⁻¹). To be specific, this makes energy difference between the excited ligand field state and the ground state about 1,200 cm⁻¹ lower in



Figure 4-6: An energetic diagram depicting the relative energetic positioning of the ground and excited state spin manifolds relative to the S=0 ground state in complex 4. The solid double ended arrow indicates the calculated energy difference between the optimized ground states of the ${}^{6}A_{1} - {}^{6}A_{1}$ and ${}^{6}A_{1} - {}^{4}T_{1}$ spin manifolds. The dashed single ended arrows depict the eight spin allowed energetic transitions between the ${}^{6}A_{1} - {}^{6}A_{1}$ and ${}^{6}A_{1} - {}^{4}T_{1}$ spin manifolds that are presumed to be responsible of the quenching of the ${}^{3}MLCT$ in complex 1. See text for details.

energy than the analogous quantity in the MnZn. Given that we have an approximately 80 cm⁻¹ thermal barrier to quenching in the mixed metal system, this lowering of the ligand field excited state should potentially remove the thermal barrier to this quenching pathway in the Mn_2 donor acceptor assembly.

However, as was discussed in Chapter 3, the thermalized ligand field excited states of the MnZn were already lower in energy than the emissive ³MLCT of the Ru polypyridyl chromophore. The cause of the thermal barrier was determined to be due to a reorganization energy associated with the quenching process,²¹ composed of the reorganization energy theoretically determined for the sextet to quartet ligand field transition and an additional reorganization term that was found from fitting the quenching rate as a function of temperature. It is reasonable to assume that this additional reorganization is constant between the MnZn and Mn₂ systems, as the two systems are geometrically similar and the nature of the excited states is involved in energy transfer are analogous. Therefore, by comparing the sums of the reorganization energy and thermalized energy differences between the analogous sextet to quartet ligand field transitions, we should be able to see if the thermal barrier to quenching is in fact removed in the Mn₂ donor- acceptor assembly.

The reorganization energy of the Mn_2 acceptor for the transition to the quartet ligand field excited state was calculated by obtaining the energy of the antiferromagnetic ground state at its optimized geometry using broken symmetry DFT wavefunctions and obtaining the energy of the same electronic state at the optimized geometry of the quartet excited spin manifold high spin state. The difference between these energies corresponds to the reorganization energy, which was found to be on the order of 0.60 eV. This value was of a similar magnitude to the reorganization energy of the sextet to quartet ligand field transition in the mixed metal macrocycle of 0.49 eV. It is however larger than that calculated for the equivalent transition in the mixed metal dimer. These and the proceeding results compared to the analogous results for complex 5 are plotted in figure 4-7.



Figure 4-7: A depiction of the calculated thermodynamic quantities for complex 4 (left) and complex 5 (right). The two positions on the x axis depict the optimized geometries of the indicated states (ground on left, ligand field excited on right) while green states show relative energies of the ground state (S=0) wavefunctions at the indicated geometry and red states are the excited state wavefunction (S=4) evaluated at the indicated geometry. FC indicates the Franck-Condon excitation energy and DE indicates the energy difference between the FC energy and the thermalized energy of the excited state.

While the spin contamination of the broken symmetry states causes the exact energy of the low spin states to be offset from the actual singlet state, these broken symmetry states still represent the best approximation of the singlet wavefunction we have available without resorting to multi-reference methods.¹¹ This means that for our purposes, the optimized geometries obtained with the

broken symmetry wavefunctions were assumed to be equal to the actual singlet geometries for the sake of evaluating reorganization energies. It should also be noted that the systems used to determine the reorganization energies in the Mn₂ and MnZn systems were not perfectly analogous; in that the Mn₂ system was modeled with complex **4** which has a mcb ligand while the mixed metal system was modeled using complex **5**, with only an acetate bridging ligand. However, it does not seem likely that these differences would contribute greatly to the changes in the reorganization energy of the Mn^{II} centers upon ligand field excitation, so for the sake of simplicity, we will assume the difference is negligible.

The calculated sum of the energy difference and reorganization energy associated with a single ${}^{6}A_{1}$ to ${}^{4}T_{1}$ transition in the Mn₂ macrocycle was determined to be 1.83 eV. This value is less than the analogous value of 1.87 eV for the MnZn system by approximately 300 cm⁻¹. This puts the overall energy of the quenching state lower in energy than ${}^{3}MLCT$ in the Mn₂ complex even after accounting for the reorganization energy requirements, which contrasts with the quenching being thermally activated with an 80 ± 20 cm⁻¹ barrier for the mixed metal. This means that the quenching of the ${}^{3}MLCT$ is spontaneous at all temperatures. While it cannot be said that these calculations represent what is actually happening in this donor-acceptor system without further experimental results with which to compare, it seems likely given the insensitivity of the quenching rate to temperature that was observed in our preliminary results that there is no thermal barrier to quenching and that there are insufficient data at this time to suggest otherwise.

This lowered energy difference associated with a single ${}^{6}A_{1}$ to ${}^{4}T_{1}$ transition in the Mn₂ macrocycle is likely caused by an effective increase in the ligand field strength of the Mn₂ macrocycle compared to that for the MnZn macrocycle. This ligand field increase can either be caused by the presence of spin exchange in the Mn₂ increasing the ligand field felt by the Mn^{II} ions contained within compared to that felt by the Mn^{II} center in the MnZn acceptor complex, or it can be caused by other structural differences between the two systems affecting the ligand field strength felt by the contained Mn^{II} ions. The only way the presence of spin exchange can conclusively be determined to be the sole cause of the ligand field increase is to rule out the aforementioned latter possibility.

Unfortunately, there is a large number of structural differences between complexes **4** and **5**, some of which were necessary for the synthetic implementation of a MnZn acceptor complex as was discussed in Chapter 3.The ligand field strength of the two different macrocycles is suspected to be different as the Schiff base absorption peak in the symmetric macrocycle bearing systems is visibly lower in energy than the equivalent absorption present in the systems with the asymmetric macrocycle. Additionally, the bridging carboxylate bridge is different between complex **4** and **5** such that it is possible this too is contributing to differences in the ligand field strength between the two macrocycles. This means that additional studies will be necessary to determine if the structural differences in the macrocycles are causing differences in the ligand field experienced by the Mn^{II} ions before we can conclude if the spin exchange interaction itself is responsible for the reduced ${}^{6}A_{1}$ to ${}^{4}T_{1}$ energy difference.

4.3.5 Implications for the Conservation of Spin Angular Momentum

At the onset of this work, we wished to use the information gained in Chapter 3 on the quenching dynamics of the ³MLCT by the ⁴T₁ excited ligand field state in the MnZn macrocycle in concert with new information on the Mn_2 macrocycle obtained via theory to determine a plausible reason for the vastly increased ³MLCT quenching in the Mn_2 appended donor-acceptor complex. Based

on the results here described, we cannot say that a new type of quenching is now accessible, since the computational results suggest the quenching is still related to the ${}^{6}A_{1}$ to ${}^{4}T_{1}$ ligand field transition in the Mn^{II} centers.

The fact that there is no longer a thermal barrier cannot alone account for the increased rate of quenching. Based on the pre-exponential term from the Arrhenius fit for the rate of quenching from the MnZn compared to the Zn_2 donor-acceptor complexes, if there was only one quenching pathway that facilitated the decay of the ³MLCT, it would conceivably only have a rate of $1.4 \pm 2 \times 10^5 \text{ s}^{-1}$ since the pre-exponential term is a good approximation of the rate of quenching if there was no thermal barrier. What has changed when the Mn^{II} is exchange-coupled is the quantity of spin allowed quenching pathways. This is because the ground and excited state spin manifolds together allow for a total of eight spin allowed pathways as depicted in figure 4-6. Furthermore, since the excited state is ferromagnetic and the ground state is antiferromagnetic, this means that as one increases the temperature and thermally accesses more pathways, the energy difference associated with these pathways decreases, which means these pathways are always thermodynamically favorable. Since at 10 K half of the ground state spin manifold is already accessible, there are already many spin allowed pathways at the lowest temperature studied.

Another point worth considering is whether or not thermal population of all the states is even necessary for all of them to contribute to the quenching of the ³MLCT. The fact that the rate of quenching appears insensitive to temperature suggests that the opposite is true, and that the quenching pathways are accessible at all temperatures via coupling to the rest of the spin allowed pathways. This means that there are at least eight spin allowed pathways via which quenching can occur at all temperatures for the Mn_2 system as opposed to a single spin allowed pathway that is thermally activated in the MnZn system. It is this change in the number of spin allowed states and

the removal of the thermal barrier that makes the quenching of the Mn_2 system able to be described as still deriving from an excitation of a manganese ion to the ${}^{4}T_1$ from its ground state.

4.4 Conclusions

We wanted to investigate how spin affects chemical reactivity using these covalently bound donoracceptor complexes. The interaction of the different spins in the Heisenberg spin coupled dimer creates many spin allowed pathways where there was only one in the absence of the Heisenberg spin exchange. By performing electronic structure calculations, we have confirmed the antiferromagnetic nature of the ground state spin manifold and have determined that the lowest ligand field excited state spin manifold is ferromagnetic. We have also been able to use the results of these electronic structure calculations to deduce the absence of a thermal barrier to the quenching of the Ru ³MLCT excited state in the Mn₂ donor-acceptor complex which is in contrast to what was encountered in the MnZn system. It is the interaction of spins that opened up the multiple pathways and may have lowered the energy of the analogous ligand field excited state, so we can conclude spin has an effect on the reactivity of these systems. REFERENCES

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Chapter 5: Conclusions and Future Directions

5.1 Project Goals

The goal of this project was to demonstrate cases where the effects of populating different available spin states in molecules were manifested by changes in the reactivity of those molecules. In the course of the research presented in this dissertation, this was tested in two main ways.

The first portion of this dissertation investigated whether thermal population of higher spin states in a spin-coupled cluster resulted in changes to the crystal structure that were independent of other effects associated with the temperature change. These results in conjunction with already performed studies would have provided information on the reactivity of this system since there already exists a large body of prior work on magneto-structural correlations such that if there were measurable structural changes in a spin coupled molecule, it has already been established that this would result in the potential to change the reactivity of the system.^{1,2}

After these temperature dependent changes due to different spin states were identified, a detailed analysis using density functional theory was performed to identify changes in the calculated spin coupling constant and the molecular orbital contributions to the spin exchange associated with these structural changes.³⁻⁷ This study was then concluded with an investigation to determine whether these conformational changes were correlated to changes in the spin state population.

The second part of this research focused on whether there was a spin angular momentum conservation requirement in a Dexter energy transfer donor-acceptor complex.^{8,9} It was thought that by examining the rates of energy transfer to both a spin coupled bimetallic acceptor and its

single transition metal analogue, one could show a requirement of spin conservation by determining the energetics of spin allowed and spin forbidden energy transfer pathways.

5.2 Dissertation Results

In the first section of the dissertation, we were able to show significant changes in the crystal structures of $[Fe_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2](CIO_4)$ with an increase in temperature that were independent of temperature induced changes in the non-coupled $[Ga_2(\mu-OH)(\mu-O_2CCH_3)_2(HBpz_3)_2](CIO_4)$ structural analogue. These changes unique to the spin coupled complex involved two main distortions in the bond distances: a slight shortening in one of the Fe- μ OH bond distances and a substantial shortening of the O-H bond distance on the μ OH. These changes were found to cause substantial changes in the calculated coupling constant and the mechanisms of spin coupling. This allows a correlation between the changes caused by population of higher spin states and the energetics of the various spin states in this system. However a direct relationship between the populations of the higher spin states in the spin coupled dimer and these geometric changes was unable to be established.

In the second section of this dissertation, we were able to observe the temperature dependent quenching behavior of a ruthenium polypyridyl ³MLCT excited state¹⁰ by a manganese (II) containing Schiff-base macrocycle in covalently linked intramolecular donor-acceptor assemblies. This quenching process was found to be due to a Dexter energy transfer⁹ from the Ru-based ³MLCT into the ⁴T₁ ligand field state of the Mn^{II} in the macrocycle and was found to have a thermal barrier of 80 ± 20 cm⁻¹ based on comparisons to an equivalent structural model. Since the energy of the acceptor states in the Mn^{II} as measured by experiment and theoretical calculations on a model

of the energy acceptor was found to be lower than the ³MLCT energy donor. By using theory it was determined that while the energy of the doublet state was in the same range as the donor ³MLCT state, the reorganization energy was too great to allow participation of the doublet state in the quenching at for temperatures studied, leading to the conclusion that the only confirmed effect the different possible spin states were having on quenching activity was due to their different reorganization energies. ¹¹

In the final section of the dissertation, we were able to use density functional theory and the analytical methods used in the study of the previous systems to thoroughly analyze the thermodynamics of the Mn₂ acceptor. This included gaining detailed knowledge of the energetics of the different spin states present in the ${}^{6}A_{1} + {}^{6}A_{1}$ ground state spin manifold, the energetics of the spin manifold that correlates to a single ligand field excitation that was found to quench the energy donor in the mixed metal system (the ${}^{6}A_{1} + {}^{4}T_{1}$ excited spin manifold), and most importantly, the energies of the spin levels of both spin manifolds relative to each other. The major conclusion of these studies is that ${}^{6}A_{1} + {}^{4}T_{1}$ excited spin manifold is substantially lower in energy that the ${}^{4}T_{1}$ state in the mixed metal system. The energy difference is reduced such that there is no thermal barrier to the quenching of the Ru donor by this excited spin manifold. This, coupled to the fact that there are eight spin allowed quenching pathways in the Mn_2 system compared to the single spin allowed pathway in the mixed metal system is what is proposed to result in the observed increase in the quenching rate in the few preliminary experimental results on this system. In this manner, evidence was found of more spin affecting reactivity in energy transfer by Heisenberg spin coupling allowing for more spin allowed pathways and potentially lowering the energy of the excited ligand field states.

5.3 Future Work

5.3.1 Current Di-manganese Systems

As we were unable to get a full variable temperature time resolved emission profile for the Mn₂ donor-acceptor system, the most pressing future work to be done on this system should be the acquisition of the VT time resolved emission profile analogous to those obtained for the di-zinc model and mixed metal donor acceptor complex. Our estimates on the quenching rate in the di-manganese are based on only a couple of low temperature emission lifetime measurements in the optical glass solvent mixture and the room temperature lifetime measured in dichloromethane. While these values show low variability (room temperature lifetime is only about an order of magnitude higher than the low temperature values), it is important to get the full temperature profile before concluding that there is no significant temperature dependence on the quenching rate of this system.

As was previously mentioned, the energetics of the doublet excited state spin manifold were not considered in this work due to the difficulty of these studies and time constraints. As the entire manifolds consists of an S=2 and S=3 state, there is the potential to obtain optimized geometries of the entire spin manifold. If one were to estimate the nature of the coupling in this spin manifold, one should be inclined to think that any changes between the ground state and quartet excited spin manifolds would be roughly repeated between the quartet and doublet excited spin manifolds. This leads us to predict a larger ferromagnetic coupling in this doublet spin manifold. Based on this "doubling of effects" idea for the di-manganese ligand field excited spin manifold and based on comparisons to the mixed-metal acceptor, where the energetics of the doublet exited spin manifold states. One would expect the energy difference of the ground state of the doublet excited spin manifold

manifold and the S=0 ground state of the di-manganese to be in a range of 1.5 eV to 1.7 eV as well as a reorganization energy in the range of 1.2 to 1.4 eV. While these predicted values would result in a thermal barrier that could not be crossed in the low temperature studies, one cannot be certain until the DFT calculations are actually performed. Therefore, it would be beneficial if a similar energetic study for the doublet excited spin manifold were performed in the future for the dimanganese acceptor.

5.3.2 Aliphatic Bridged Mn₂/MnZn Systems

It was determined in our previous work that the activation barrier to accessing the ³MLCT located on the mcb bridge of the di-manganese system is sufficiently high such that the quenching pathway of the ³MLCT of the Ru donor is only mediated by the bonding interaction between the donor and acceptor portions of the donor-acceptor assembly. This is in contrast to the possibility that the observed quenching is a multi-step energy transfer process between the ³MLCT located on the ((CF₃)₂-bpy) ligands, followed by an inter-ligand energy or electron transfer to the mcb, and followed by a subsequent energy transfer into the di-manganese acceptor.

However, when these molecules were initially designed, it was with a mind to study the rate of the different thermal population of the spin states on electron transfer, as electron transfer processes involving spin-coupled systems are much more prevalent in biological systems. It is thought that the reorganization energy for electron transfer is such that the Dexter energy transfer process outcompetes the electron transfer for all of the solution and glass phase temperatures studied previously.

To perhaps coax the system into performing a desired electron transfer quenching of the ruthenium donor, it is postulated that extending the mcb linker by the addition of a methylene group between the carboxylate and the bipyridine ring, as pictured in figure 5-1, could promote electron transfer compared to the previous sytem with the mcb linker which is known to not undergo electron transfer. The addition of an aliphatic linker to the mcb ligand would lessen the bonding interaction between the donor and acceptor states as the carboxylate would no longer be coupled into the aromatic π cloud of the bpy rings. Not only that, but the increased distance of the added methylene group in addition to the weakening the bonding interaction between the donor and acceptor states in such a donor-acceptor system. This would be beneficial for two reasons; in the first place, if this promoted electron transfer quenching in the donor acceptor system, and second, if there was still no electron transfer quenching, it is likely that the Dexter energy transfer rate would be reduced such that it would be much easier to study on the nanosecond timescale, perhaps providing us with more detail on the rate of energy transfer quenching as a function of temperature.



Figure 5-1: Drawings of the previously studied $[Mn_2(L)(mcb)Ru((CF_3)_2-bpy)_2]^{3+}$ (A) complex and the proposed extended linker analogue (B).

This extended mcb linked system would also provide the advantage that the thermal population of the spin states in the di-manganese spin coupled dimer would remain unchanged. This was concluded by performing preliminary calculations on the high spin optimized di-manganese cluster with the mcb replaced with an acetate to approximate the aliphatic linker for the determination of the coupling constant as was previously done in Chapter 4. The resulting coupling constant derived from B3LYP is almost identical to that found for the analogous mcb bridged structure, with the acetate bridged dimer having a calculated coupling constant of 6.7 cm⁻¹ compared to 6.6 cm⁻¹ for the mcb bridged complex. The significance of this result is that one would know that the temperature controlled changes in spin would be consistent between the already studied system and the analogous systems with the extended mcb linker. This fact may allow for interesting comparisons between the two systems especially if it is found that the extended linker still quenches via a Dexter energy transfer mechanism.

The synthesis of this modified bridging ligand has already been worked out by another esteemed group member,¹² such that it would be a trivial matter to adapt this ligand for use in our already established synthetic procedures to making all of these complexes. It is likely that the di-zinc analogue would not be necessary to synthesize as the difference in ground state recovery between the existent di-zinc complex and one with the methylene extended bridge is likely to be negligible. The existing procedures for the mixed metal and di-manganese donor-acceptor complexes could be followed with the substitution of this new extended bridge for the mcb with minimal modification, as the solubility of the starting materials and intermediates incorporating this modification should be similar to our preexisting versions. Therefore the synthesis and variable temperature emission studies of these two modified donor-acceptor complexes would seem to be

a facile extension of this work to elucidate the effects of varying population of spin states on the reactivity of donor-acceptor complexes.

5.3.3 Studying the Energetics of the Fe₂OH system.

Previous and ongoing work in our group is dedicated to the determination of spin effects on the electron and energy transfer dynamics in covalently linked donor acceptor complexes where our extensively studied Fe₂ μ -OH and the analogous Fe₂ μ -O spin coupled dimers are integrated as energy and electron acceptors in a similar manner to the di-manganese acceptor from the donor-acceptor complexes reported in this dissertation.^{1,13} To correctly interpret the results of these studies it would be beneficial to know the energetics of both the reduced di-iron core as if it had played the role of an electron acceptor and the quartet excited di-iron core as if it had acted as an energy acceptor in a donor-acceptor complex.

Preliminary investigations of these states employed the optimized high spin X-ray structures for the Fe₂OH molecule reported in Chapter 2 and used methods similar to those in Chapter 4 to optimize the high spin excited quartet state (S=4) and the high spin reduced versions of the Fe₂OH complex. (S=9/2) From these optimized geometries one is able to obtain an estimate for the energy difference between the ground and excited state spin manifolds of 0.30 eV, which is substantially less than the equivalent energy difference in the di-manganese system. An inner sphere reorganization energy of 0.38 eV was calculated for the reduction of the di-iron hydroxo complex, which is a useful quantity to have available when interpreting results from electron transfer donoracceptor systems. Coupling constants were also obtained employing the standard broken symmetry wavefunctions for the low spin states. These were determined to be -3 cm⁻¹ for the excited quartet spin manifold, and -189 cm⁻¹ for the reduced spin exchange manifold. The small ferromagnetic coupling value obtained for the quartet excited spin manifold remarkably mirrors the results obtained for the analogous di-manganese state. The calculated coupling constant for the reduced spin manifold of the di-iron is ferromagnetic and much larger than for its native unreduced value. It is not surprising that the magnitude of the coupling should increase as the mixed valent nature of the reduced core opens up a double exchange mechanism resulting in large coupling constants. It is noteworthy too that the coupling is ferromagnetic in the reduced state, as this would have the effect of causing the relative population of high spin states to substantially increase upon photo-induced electron transfer into this system, especially if the electron transfer photoproducts are long lived. One can therefore imagine an intriguing experiment to test for electron transfer in a donor-acceptor system the system by comparing the magnetic moment of the sample in the dark and under illumination.

5.4 Concluding Comments

The methods described herein and some of their derivations have broad applicability to any system where estimates of thermodynamic quantities of spin coupled or other transition metal complexes are desired. Therefore it would be trivial to extend these kinds of electronic structure investigations and obtain other similarly useful results pertinent for donor-acceptor complexes with other spin-coupled acceptors. Indeed the author hopes that this dissertation will provide a strong foundation on which to build the use of these electronic structure methods in our research group.

Using experiment and theory, we have been able to answer questions that neither technique could confidently answer in isolation, which has furthered our understanding on the subtle ways spin effects chemical reactivity. In effect, what we have accomplished over the course of this dissertation is to reaffirm the validity of using density functional theory to provide insight into actual experimental results, which is in the author's opinion the best way in which theory can be used to advance the knowledge of the chemical sciences.

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