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3rd Year Seminar
25 September, 2003

Semiquinone-Containing Biradical Systems: Towards Molecular Magnets

INTRODUCTION

Biradicals are molecules which possess two weakly interacting unpaired electrons that are individually associated with different atomic centers within a molecule.¹ Biradicals are observed as intermediates in organic reactions, play roles in biological processes and serve as energy-transfer intermediates in photosynthetic processes. Biradicals can also possess magnetic properties, creating the possibility of assembling organic compounds with bulk magnetic properties, i.e. a “molecular magnet.”

There are many different types of magnetism that can be associated with molecules or atoms.² Diamagnetism results from electrons in *closed* shells that cause a material to be repelled by an external magnetic field. All other types of magnetism involve unpaired spins, or moments. How these spins interact determine the type of magnetism in this open shell case. Paramagnetism results from randomly oriented and rapidly reorienting spins with no permanent or spontaneous magnetic moment. Ferromagnetism results from a tendency of moments to align parallel and this can result in a permanent magnetic moment. Antiferromagnetism results from spins which tend to align antiparallel, resulting in no permanent moment. Finally, among the major types of magnetism, there remains ferrimagnetism. Ferrimagnetism requires two chemically distinct species with different moments which couple antiferromagnetically. Magnetite is a well known example of a ferrimagnet.

In order to design a material which has bulk ferromagnetic properties, several design considerations must be taken into account.¹ Electron spin is contained in a spin containing unit

(SCU) and these spins may be coupled, either ferromagnetically or antiferromagnetically.³ In order to obtain ferromagnetic coupling, the linker between the SCUs must not allow for spins to be combined into pi bonds, in the most basic of considerations. For biradical systems, ferromagnetic coupling of spins results in an $S=1$, or triplet ground state. The $S=0$, or singlet ground state, is the result of antiferromagnetic coupling of spins. The preference of a compound to have a triplet or singlet ground state is governed by the singlet-triplet gap, ΔE_{ST} (**Figure 1**). The singlet-triplet gap is also related to the exchange parameter J ($\Delta E_{ST} = 2J$). The magnitude of ΔE_{ST} is ultimately determined through experiments which quantify J , which will be discussed briefly in the following section.

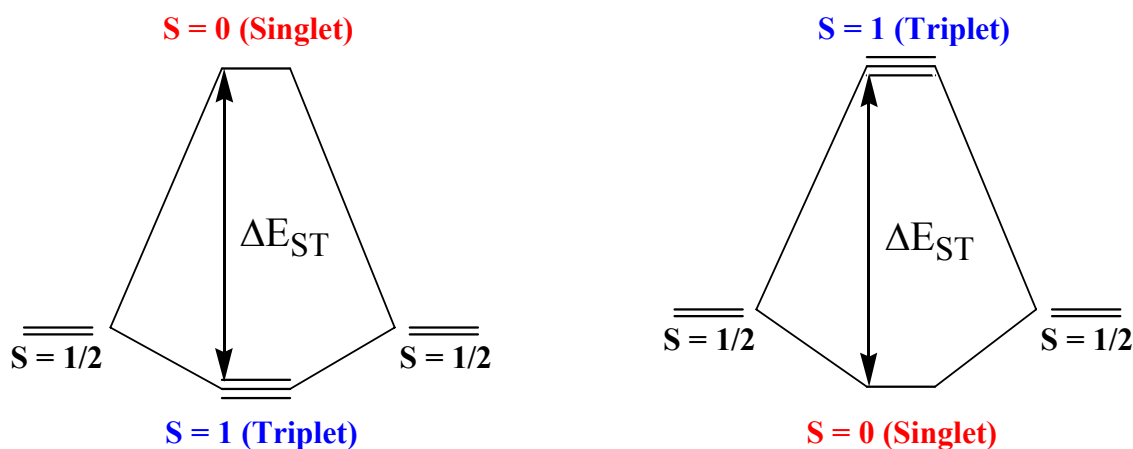


Figure 1: Illustration of ΔE_{ST} resulting from both ferromagnetic and antiferromagnetic interaction of spins.

The manner in which spins couple (ferromagnetic versus antiferromagnetic) can be ascertained in a number of ways, with two of the more common being variable temperature ESR experiments and magnetic susceptibility experiments. Both methods make utility of the temperature dependence of ΔE_{ST} . In the variable temperature ESR experiment, a plot of ESR intensity is made versus $1/T$ where the temperature is in K (**Figure 2**) and this is referred to as a Curie plot. Linear plots are consistent with ferromagnetic coupling ($J > 0$) or non interaction of

the spins, whereas a curved plot signifies antiferromagnetic ($J < 0$) coupling. In utilizing magnetic susceptibility data, one plots magnetic susceptibility versus temperature. In this instance, one looks for magnetic susceptibility to increase asymptotically as the temperature is lowered (**Figure 3**), and when this occurs it signifies ferromagnetic coupling.

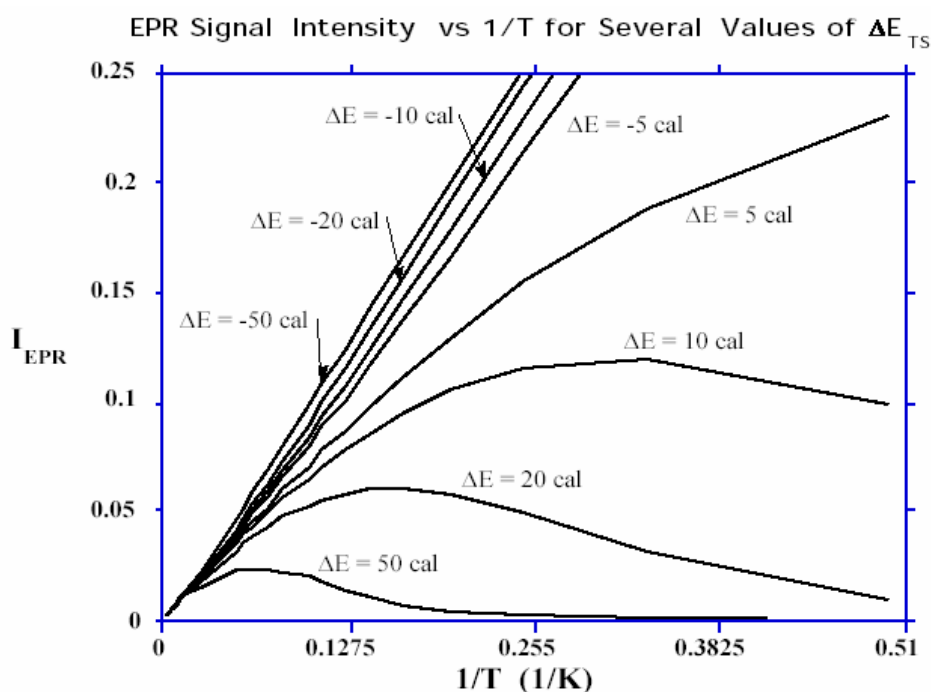


Figure 2: Curie plots for several values of J .⁴ Linear plots indicate ferromagnetic coupling.

The manner in which electron spins couple is directly affected by the topology of the linker, or coupling unit. Two very common linkers which typically enforce ferromagnetic coupling (triplet ground states) are trimethylenemethane and *meta*-xylylene (**Figure 4**). Spins connected by these types of coupling units typically will be coupled in a ferromagnetic manner; however this is not always the case due to other factors which must be considered, including bond torsions, the possibility of different conformers for a given biradical, and the potential for dimerization of molecules.

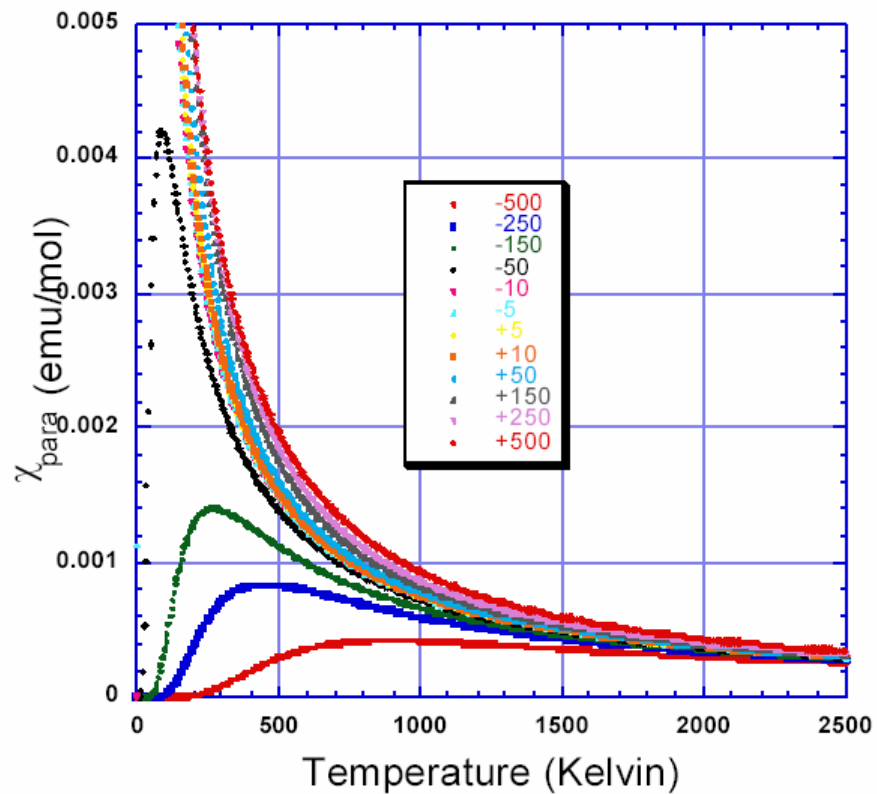


Figure 3: Plots of magnetic susceptibility versus several values of J .

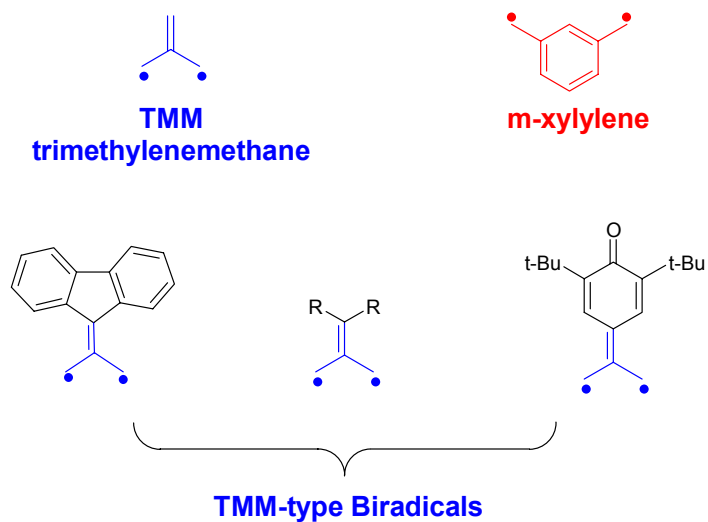


Figure 4: Trimethylenemethane (TMM) and *m*-xylylene: example ferromagnetic coupling units.

BIS(SEMIQUINONE) BIRADICALS

Semiquinones are the one-electron reduced forms of quinones and can further be reduced by one electron to catechols (**Figure 5**).⁵ These molecules are common in biological pathways,^{6,7} play roles in photosynthetic reaction centers,⁸ have been known for quite some time to behave paramagnetically,^{9,10} and are further attractive as SCUs for high-spin systems for several reasons. First, the unpaired spin is typically localized on the heteroatoms and not extensively delocalized.⁵ Secondly, in the case of *ortho*-quinones, they can bind to metal centers as a bidentate ligand, opening up the possibility of magnetic exchange between the organic radical and unpaired spin on a transition metal center. Finally, these types of compounds are fairly easy to synthesize, which makes them quite attractive to researchers.

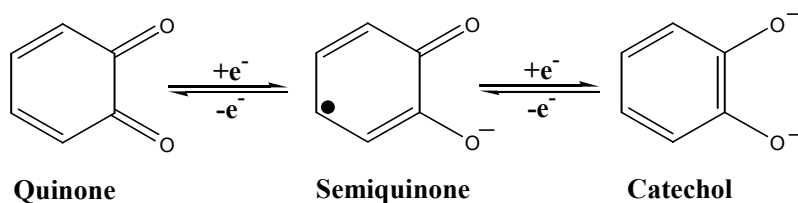
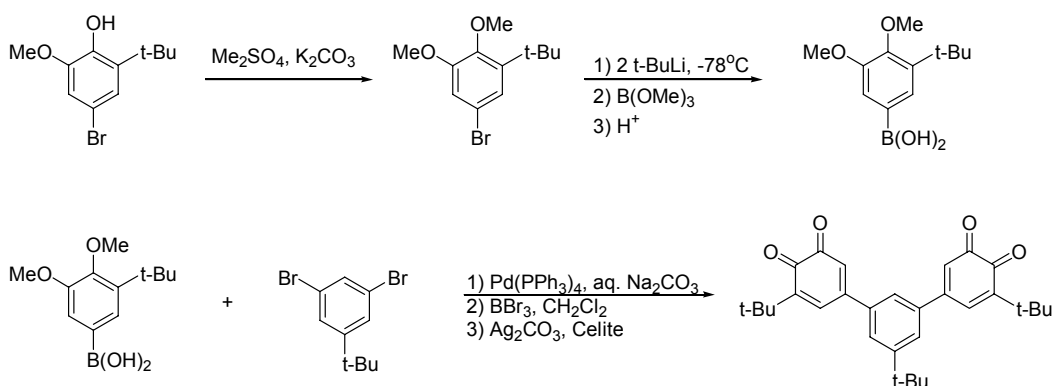


Figure 5: The Quinone/Semiquinone/Orthoquinone Redox Series.

Shultz and coworkers synthesized a *m*-phenylene linked bis(semiquinone) (**Scheme 1**) in order to determine the magnetic properties of the system.¹¹ Indeed, this system was found to behave as a ground state triplet, with a small amount of a doublet impurity visible in the ESR spectrum. The Curie plot for this compound was shown to be linear, which is consistent with ferromagnetic coupling ($J>0$) or non-interaction of the spins.¹²

Shultz and coworkers have also synthesized a series of TMM-based bis(semiquinones) and, for comparative purposes, a fluorenyl linked system (**Figure 6**).¹² As expected, the TMM bridged compounds coupled in a ferromagnetic manner ($J>0$) with the fluorenyl bridged system coupled antiferromagnetically based on the respective Curie plots. As was observed in the

previously discussed case, small amounts of doublet impurities were observed in the ESR spectra, but the signals were predominantly triplets.



Scheme 1: Synthesis of a *m*-phenylene linked bis(orthoquinone). Two electron reduction yields the bis(semiquinone).

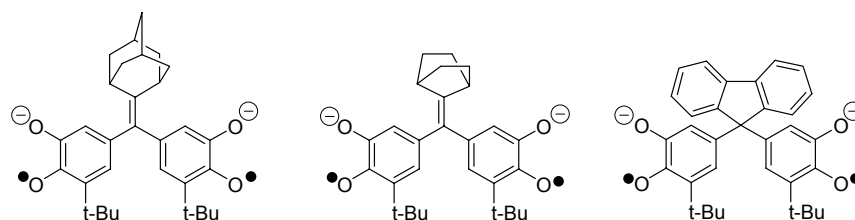


Figure 6: TMM-based bis(semiquinones) and a fluorenyl-bridged bis(semiquinone)

Additionally, Shultz and coworkers have begun to probe the effect of substituents on the magnitude of J in a series of *m*-phenylene bridged bis(semiquinones).¹³ It was found that both electron withdrawing and releasing groups tend to lower the value of J relative to a comparatively inactive *t*-butyl group. Electron withdrawing groups were observed to attenuate J slightly more than electron donating groups. X-ray crystal structures of the compounds studied indicate quite similar torsions and other geometric parameters, suggesting that twists are not responsible for the modulation of J .

SEMIQUINONE-METAL COMPLEXES

There are numerous examples of semiquinone-metal complexes that exhibit magnetic properties.¹⁴⁻²⁰ Systems of this nature can result in triplet state radicals and may also be utilized

in the construction of higher-spin coordination polymers.¹⁴ Important considerations in these types of complexes include the coordination geometry about the metal center, the coordination sphere, and the nature of the coupling between the metal center and semiquinone ligand. In tetrameric Fe^{III} semiquinone complexes, the coupling between metal and ligand is antiferromagnetic.¹⁶ Problematic so far in the construction of higher spin coordination polymers are competing interactions present in these systems. Specifically, in the case of a Cu-SQ coordination polymer, the Cu-SQ electronic coupling is ferromagnetic but the SQ-SQ interactions are antiferromagnetic, which makes magnetic characterization of these systems problematic. It is unfortunate that many metal-semiquinone systems either couple antiferromagnetically, or are incredibly difficult to characterize magnetically, as some of these complexes have the benefit of being air-stable radical systems.¹⁹ Efforts are still underway to characterize such systems. Bis(semiquinones) have been used as ligands, such as *m*-phenylene bridged bis(semiquinones) and in Ni complexes a septet (S=3) ground state is enforced.²¹ In this complex, however, the ground-spin state is not completely populated due to the very close proximity of other singlet and triplet states. Finally, Zn metal centers have been coordinated to a TMM-based bis(semiquinone) and the coupling observed was ferromagnetic between the semiquinone spins (triplet ground state).²² Other complexes have been studied which incorporate similar iminoquinone ligands, where one oxygen is replaced by NH.^{23-24,25} Upon reduction, the spin resides mainly on the oxygen atom, as is the case with semiquinones. These systems, so far, have been demonstrated to couple antiferromagnetically.

CONCLUSION

High-spin semiquinone-based biradicals can be achieved in several ways. The spin containing centers may be coupled to one another through an organic bridge that enforces ferromagnetic coupling, such as trimethylenemethane or *m*-phenylene. Metal centers can be utilized to form high spin coordination complexes of semiquinones. While the latter has been successfully accomplished, it is generally the case that ferromagnetic coupling is mainly observed when the organic spins are simultaneously bridged by a ferromagnetic coupling unit. Other complexes have proven to be quite difficult to characterize due to competing ferromagnetic and antiferromagnetic coupling interactions between the spins.

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