Semiquinone-Containing Biradical Systems: Towards Molecular Magnets

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Organic 3rd Year Seminar

University of Wisconsin-Madison

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Outline

- Magnetism
- Inducing High Spin in Diradicals
- ESR Experiments/Magnetic Susceptibility
- Bis(Semiquinone) Diradicals
- Semiquinone-Metal Complexes
- Biradicals Incorporating Additional Spin Sources or Modified Semiquinone Structures

General Introduction to Magnetism

Diamagnetism

- closed shell electrons cause a material to be repelled by H

Paramagnetism

- unpaired spins randomly oriented and rapidly reorienting

Ferromagnetism

- moments tend to align parallel in a material (can have permanent M)

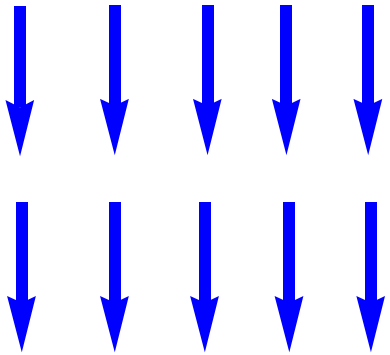
Antiferromagnetism

- spins tend to align anti-parallel (no permanent M)

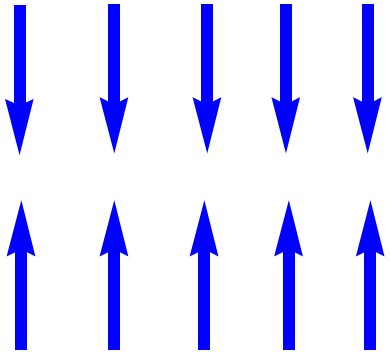
Ferrimagnetism

- two chemically distinct species
- coupled antiferromagnetically
- bulk behavior similar to ferromagnetism

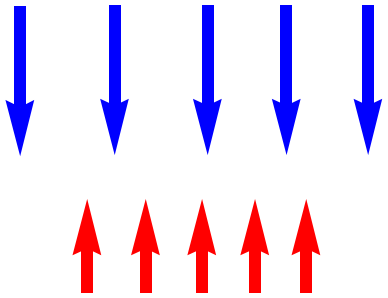
Intermolecular Magnetic Interactions



Ferromagnetism

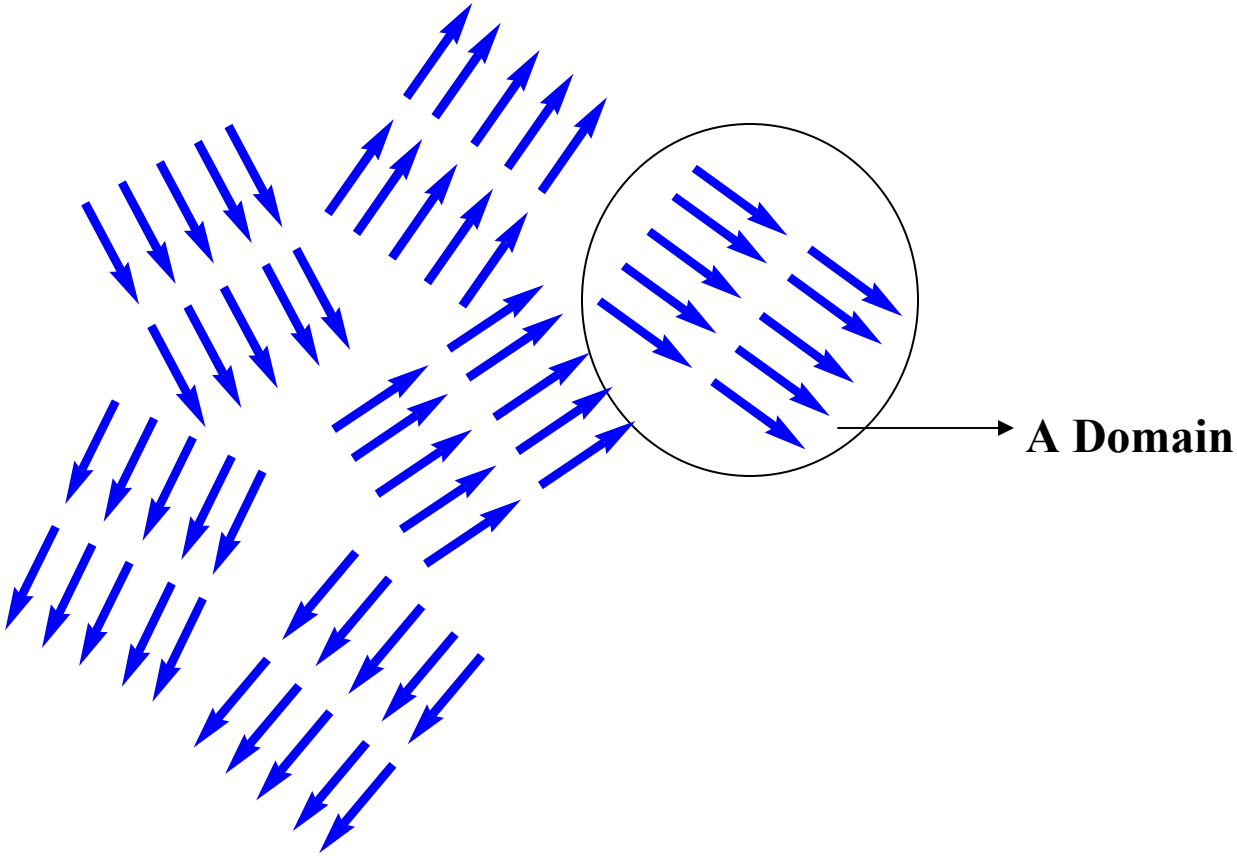


Antiferromagnetism



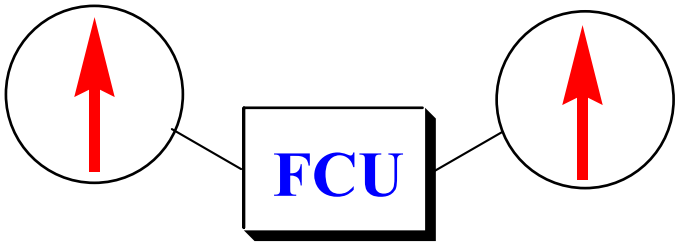
Ferrimagnetism

Ferromagnetism: A Better Illustration

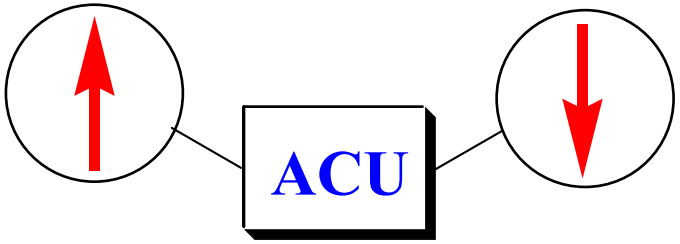


- Each “grouping” of spins is a domain
- Domains may or may not be aligned with one another
- Application of external H causes domains to align
- Alignment persists after removal of external H

Design of Biradicals: The Basics



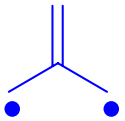
- **FCU** is a Ferromagnetic (**FM**), or high-spin, coupling unit
- A triplet ground state is enforced in biradicals



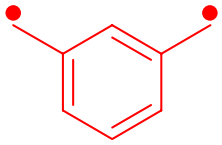
- **ACU** is an Anti-ferromagnetic (**AFM**), or low-spin, coupling unit
- A singlet ground state is enforced in biradicals

Rajca, A. *Chem. Rev.* **1994**, *94*, 871

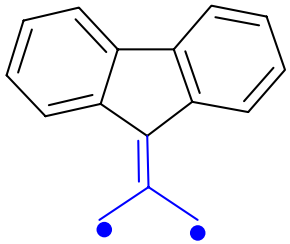
Ferromagnetic Coupling Units (FCUs)

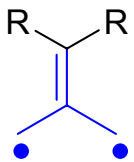


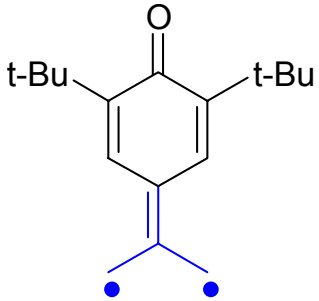
TMM
trimethylenemethane



m-xylylene



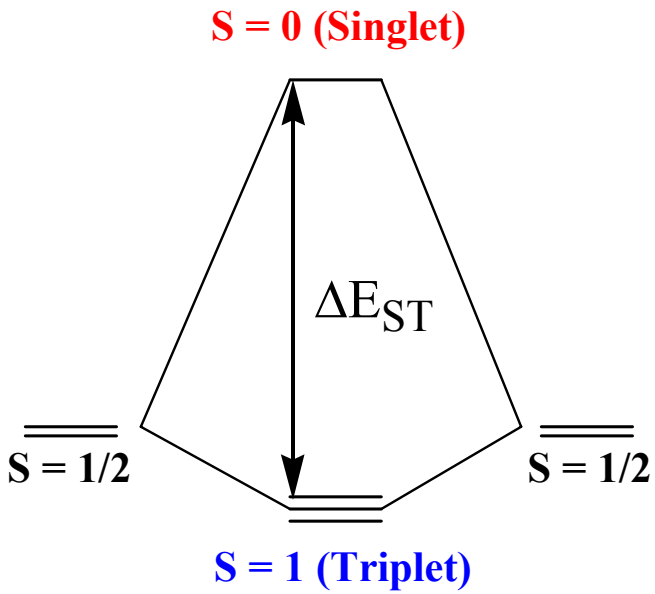


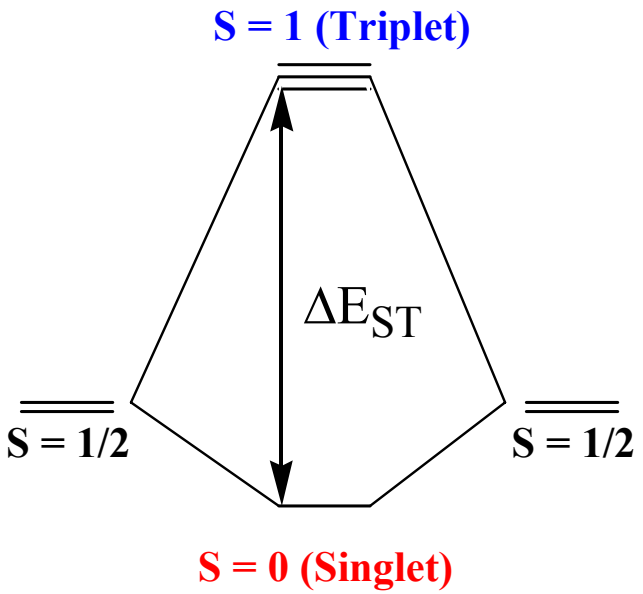


TMM-type Biradicals

Rajca, A. *Chem. Rev.* **1994**, *94*, 871

The Singlet-Triplet Gap (ΔE_{ST})





$$\Delta E_{ST} = E_S - E_T$$

By this definition:

$\Delta E_{ST} > 0 \quad \Rightarrow \quad$ Triplet

$\Delta E_{ST} < 0 \quad \Rightarrow \quad$ Singlet

Electronic Interactions within Biradicals

- Exchange coupled unpaired electrons
- HDVV Hamiltonian models electron interaction

$$\hat{H}_{ij} = -2\boldsymbol{J}_{ij}\hat{S}_i\hat{S}_j$$

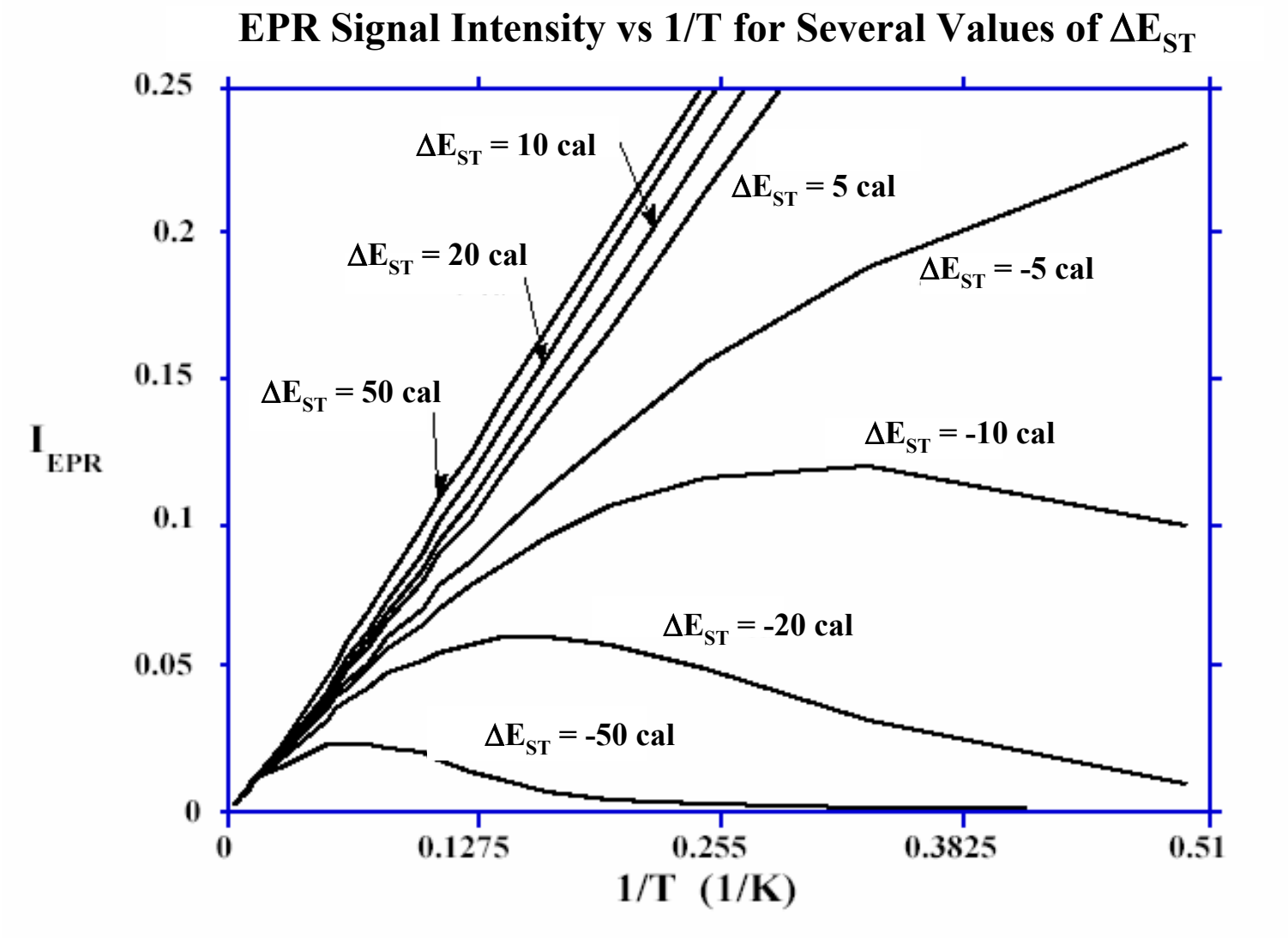
$\boldsymbol{J}_{ij}$ is the exchange parameter representing the magnitude of the interaction

- $\boldsymbol{J}_{ij}$ governs the singlet (AFM) /triplet (FM) ground-state preference
- $2\boldsymbol{J}_{ij} = \Delta E_{ST}$

The ESR Experiment

- Method for detection of unpaired spin in molecules
- "Half field" ($\Delta m_s=2$) transition characteristic of triplet biradicals
- Plot of I_{epr} vs 1/T (Curie Plot) is linear for ferromagnetically coupled ($\boldsymbol{J}>0$) or non-interacting spins
- $2\boldsymbol{J}$ is attainable from Curie Plot

Curie Plot


EPR Signal Intensity vs 1/T for Several Values of ΔE_ST
I_EPR
0.25
0.2
0.15
0.1
0.05
0
0
0.1275
0.255
0.3825
0.51
1/T (1/K)
ΔE_ST = 10 cal
ΔE_ST = 5 cal
ΔE_ST = 20 cal
ΔE_ST = -5 cal
ΔE_ST = 50 cal
ΔE_ST = -10 cal
ΔE_ST = -20 cal
ΔE_ST = -50 cal

Measuring 2*J*: Magnetic Susceptibility

Magnetic Susceptibility = $\chi_{dia} + \chi_{para}$

Diamagnetic susceptibility

- $\chi_{dia} < 0$ via ***paired*** electrons

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Paramagnetic susceptibility

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- for ***exchange-coupled*** species, χ_{para} is ***temperature-dependent…***

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Heisenberg-Dirac-van Vleck susceptibility expression

$$\chi_{para} T = \frac{Ng^2\beta^2}{3k} \frac{\sum_S S(S+1)(2S+1)\exp\left(-2J/kT\right)}{\sum_S (2S+1)\exp\left(-2J/kT\right)}$$

Measuring 2*J*: Magnetic Susceptibility

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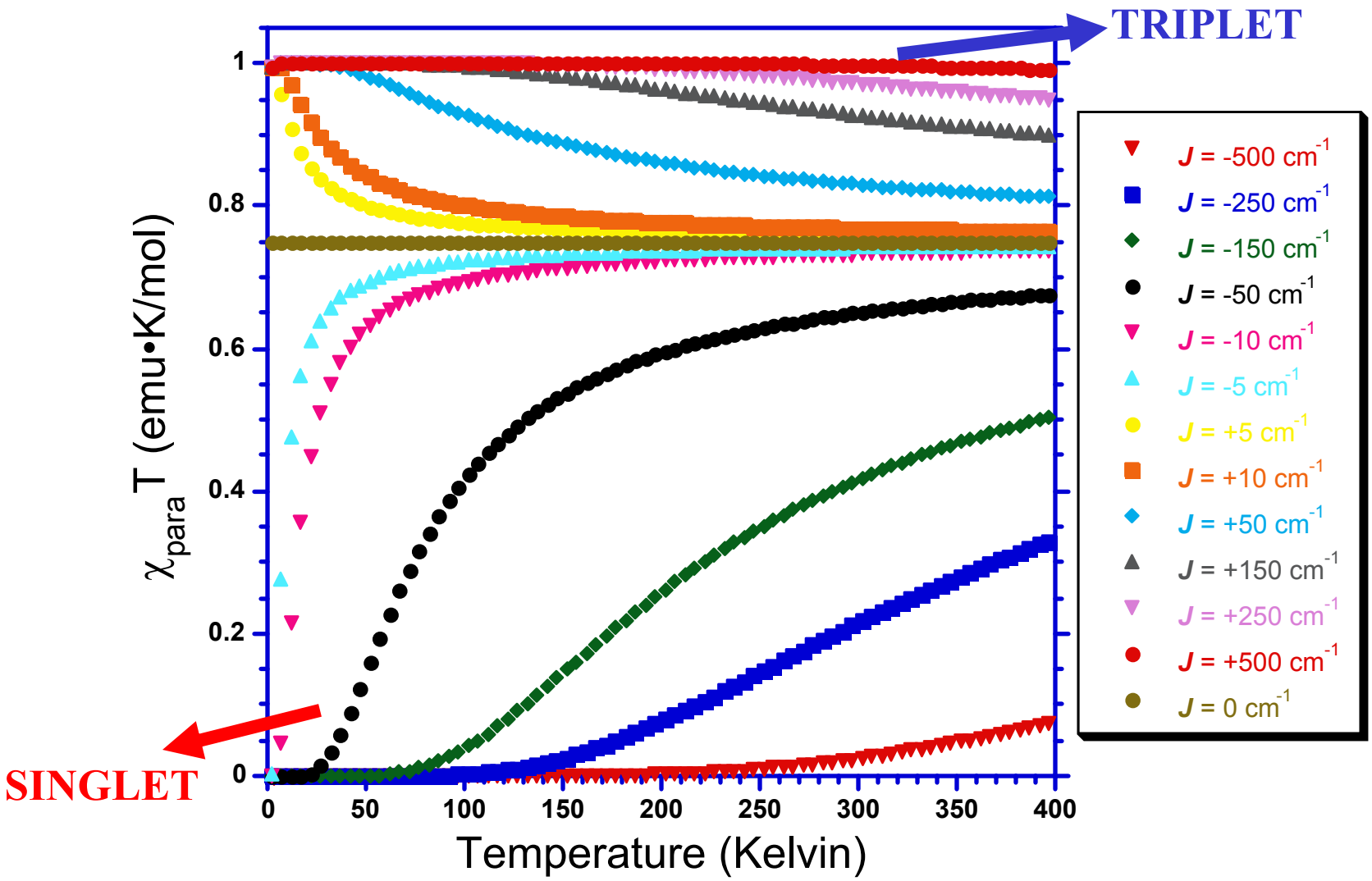
χ_{para}T (S = 1) = **1** emu K/mol; χ_{para}T (S = 0) = **0** emu K/mol

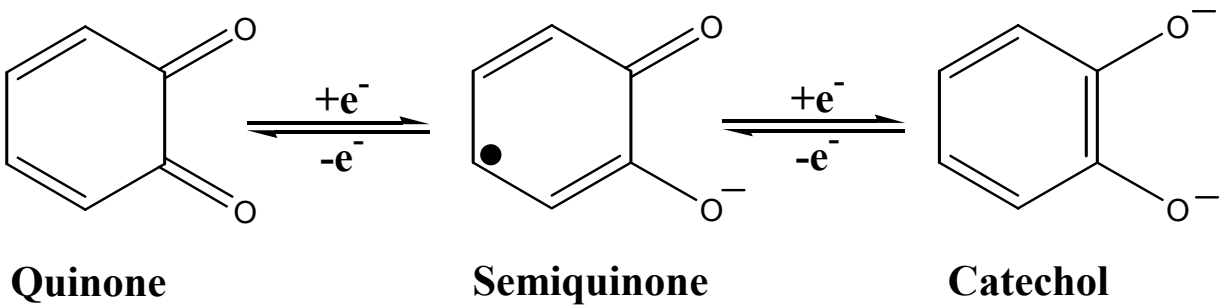
$\chi_{para}T$ as a function of T and J looks like this…



Private Communication with D. A. Shultz

Semiquinones and Bis(Semiquinone) Biradicals

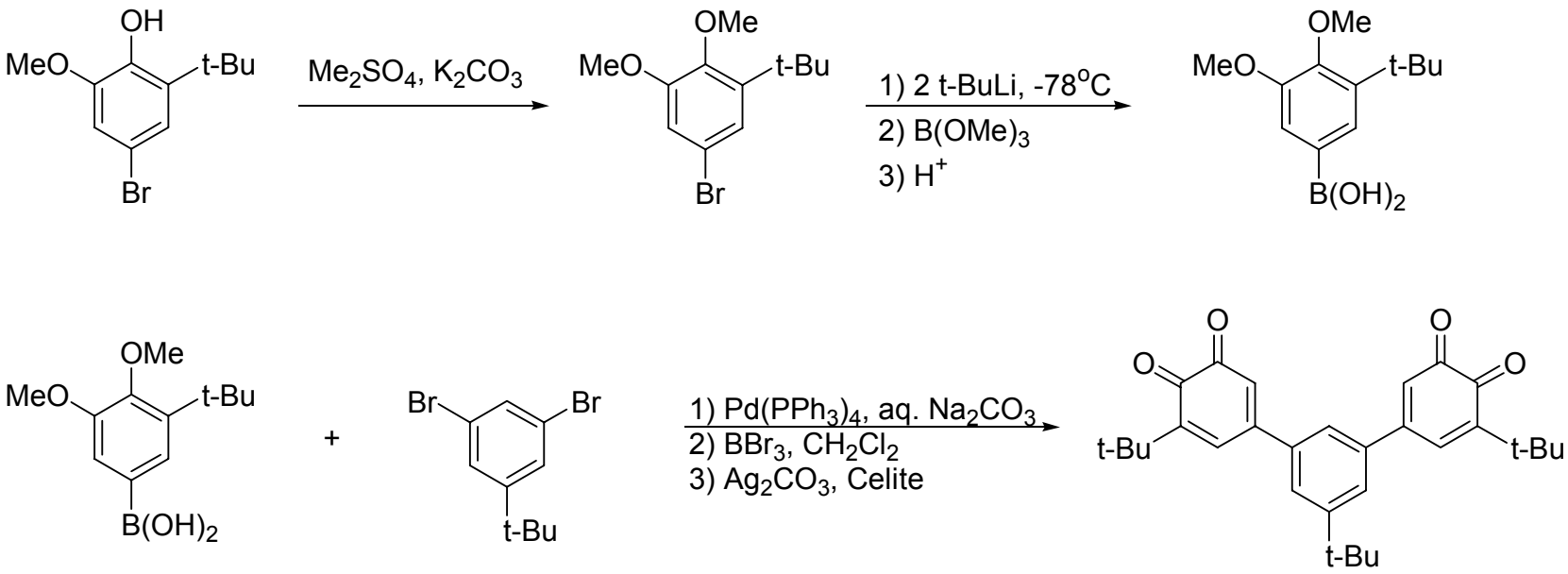
The Semiquinone Spin Containing Unit (SCU)



- Semiquinone form has 1 unpaired electron
- Semiquinone and catechol forms can bind to transition metals
- Magnetic Exchange possible between open-shell metal centers and semiquinones

Wheeler, D. E.; Rodriquez, J. H.; McCusker, J. K. *J. Phys. Chem. A.* **1999**, *103*, 4101-4112

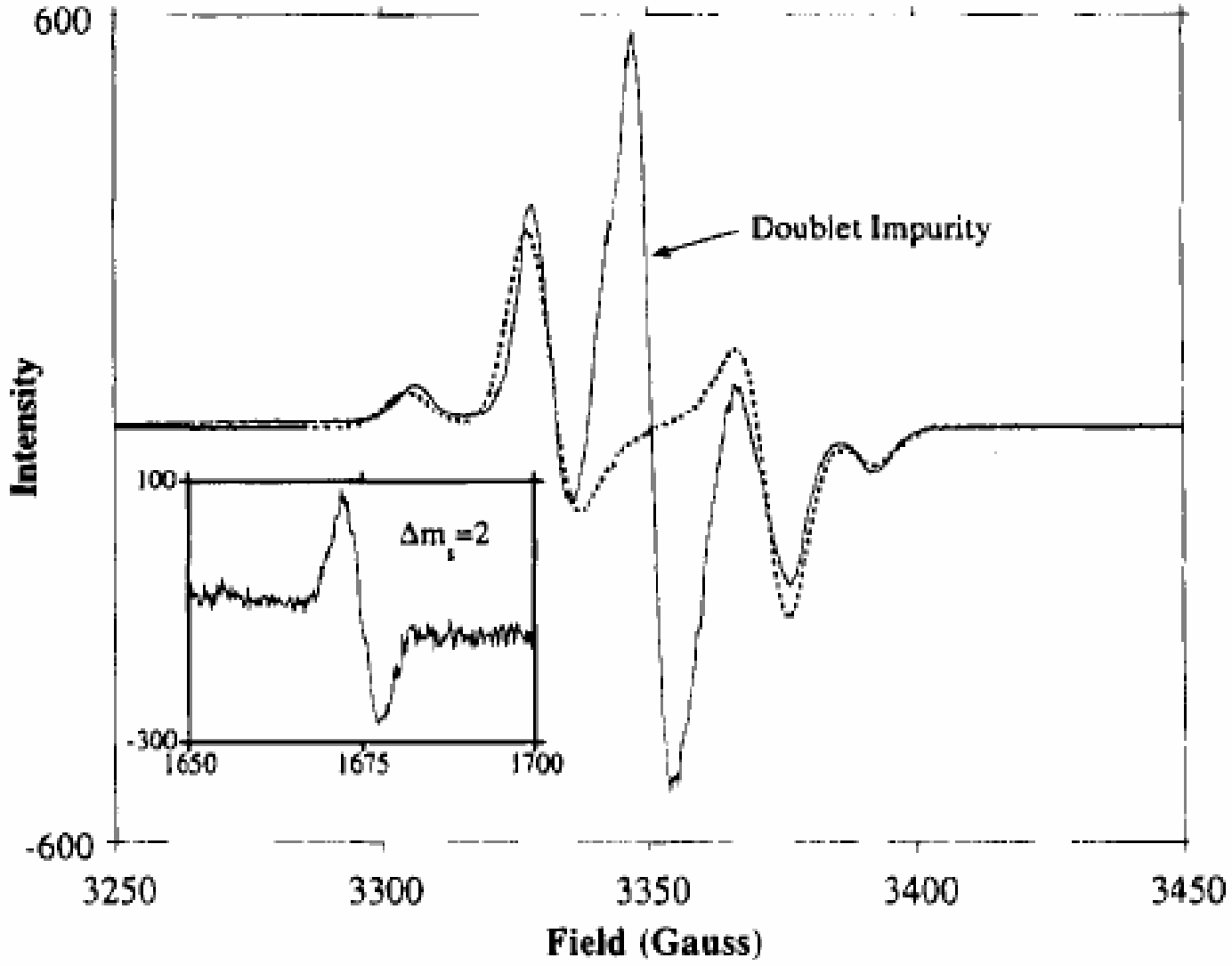
m-Phenylene Bis-Semiquinone Synthesis



Most other organic Bis(semiquinones) prepared similarly

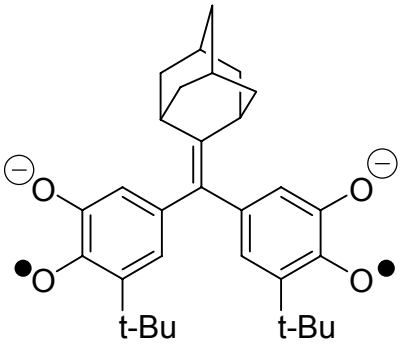
Shultz, D. A. et al., *J. Org. Chem.* **1995**, *60*, 3578-3579

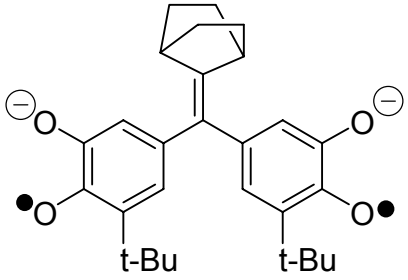
ESR Results and Interpretation

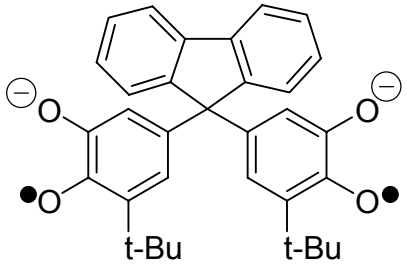


Shultz, D. A. et al., *J. Org. Chem.* **1995**, *60*, 3578-3579

TMM-Based Bis(Semiquinones)





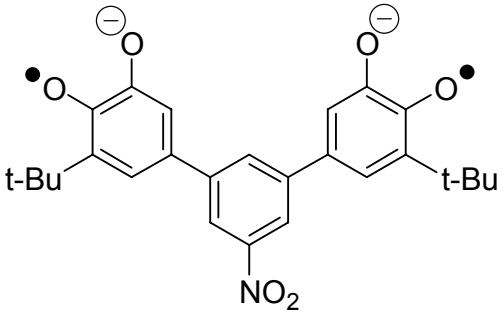


$E_{1/2}(1)$	-0.73	-0.72	-0.73
$E_{1/2}(2)$	-0.94	-0.94	-0.93
$\lvert D/hc\rvert/10^{-4}$	94.7	91.0	130.9 (102.6)
Curie Plot	linear	linear	curved

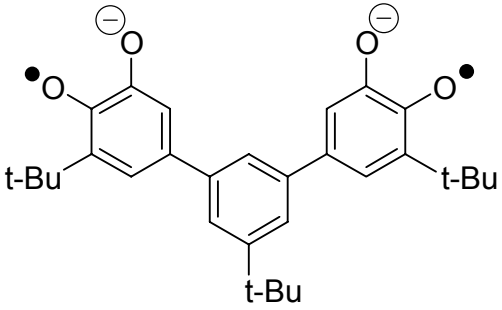
TMM-Based Bis(Semiquinones) Above Have Linear Curie Plots Consistent With J>0 (Ferromagnetic Coupling)

Shultz, D. A.; Boal, A. K.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 9462-9469

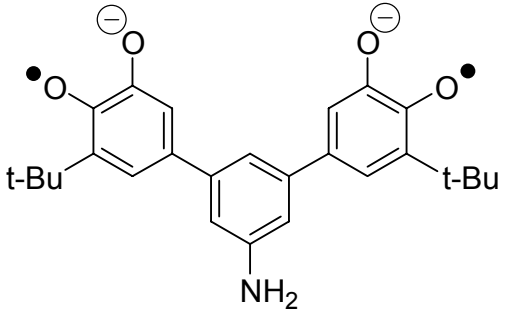
Substituent Effects on S-T Gap for Semiquinone Biradicals



J=31.0cm^{-1}



J=59.3cm^{-1}

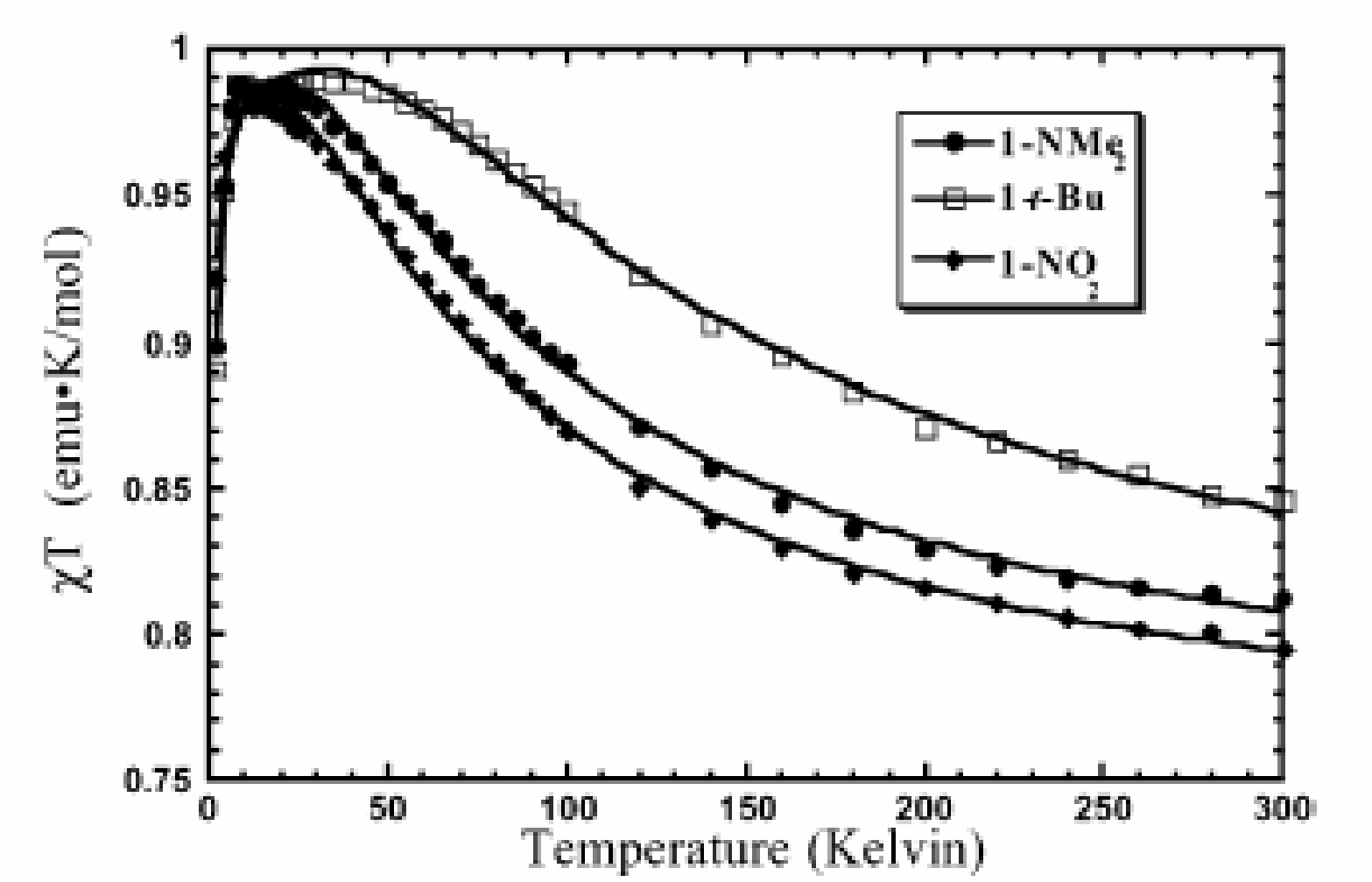


J=34.9cm^{-1}

EWG attenuate J slightly more than **EDG**
J modulation **NOT** likely associated with changes in torsions

Shultz, D. A. et al. *J. Am. Chem. Soc.* **2002**, *124*, 10054-10061

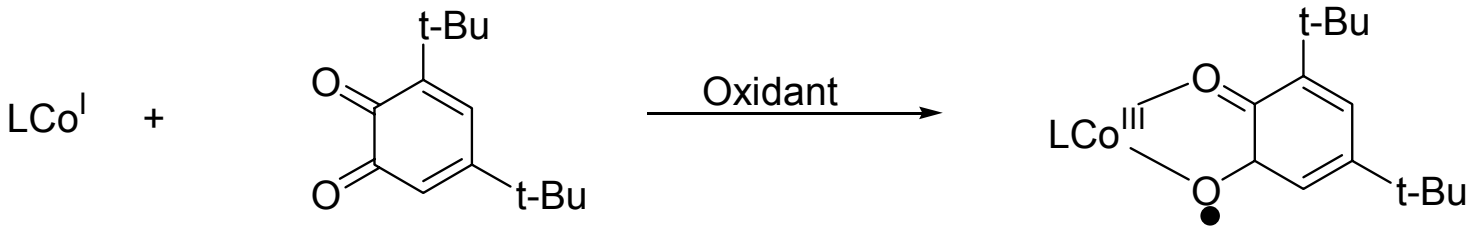
Magnetic Susceptibility Studies



Shultz, D. A. et al. *J. Am. Chem. Soc.* **2002**, *124*, 10054-10061

Semiquinone-Transition Metal Complexes

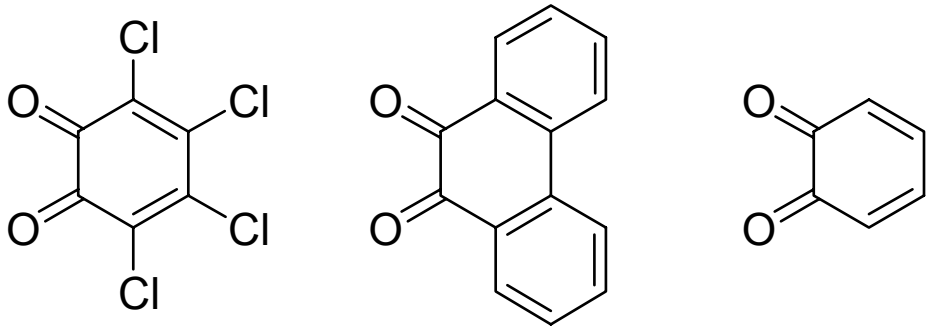
Semiquinone Complexes of Co^{III}



- Co^{III}-Semiquinone Complexes Shown to be Neutral Species
- Similar Hyperfine Coupling Constants for free Ligand and Complex
- Unpaired SQ spin largely localized on the oxygen atoms

Brown, D. G.; Hemphill, W. D. *Inorg. Chem.* **1979**, *18*, 2039-2040

Semiquinone Complexes of Co^{II} and Ni^{II}

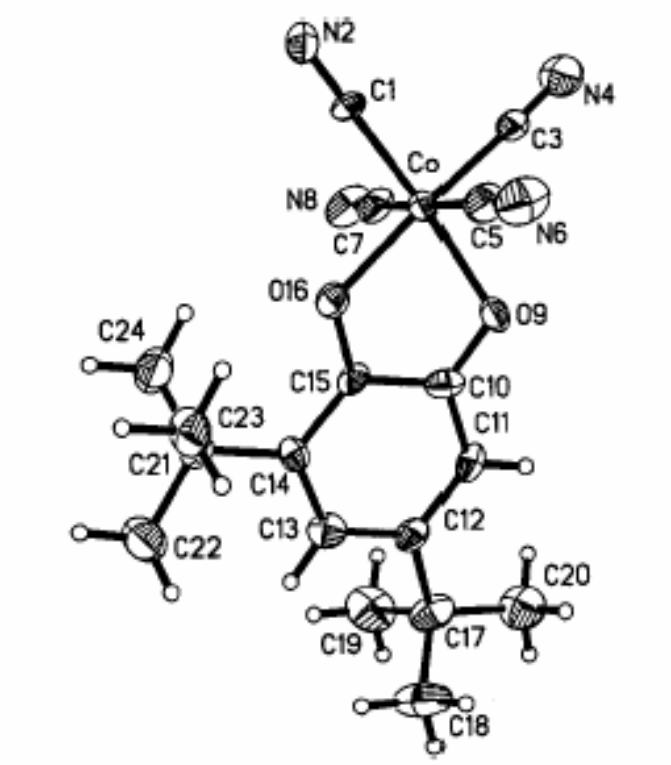


- **Bis(Semiquinone)-Metal complexes with oligomeric structures**
- **Magnetic Susceptibilities Similar for respective metal series**
- **Spin-Spin Coupling suggested by Susceptibilities**

Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439-3443

Air-Stable Semiquinone/Co^{III} Complexes

$Co(3,5\text{-}DBSQ)CN_4$

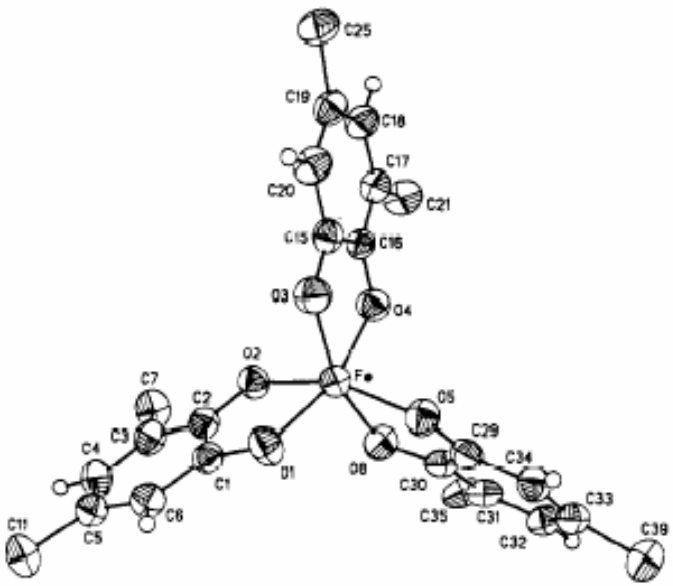


- **Air-Stable as solid and solution**
- **Eight line ESR spectrum**
- **Spectrum consistent w/ S=1/2 GS**
- **Low spin Co^{III} precludes higher spin states**

Arzberger, S. et al. *Inorg. Chem.* **1999**, *38*, 757-761

Semiquinone Complexes of Fe^{III}

$Fe(DBSQ)_3$

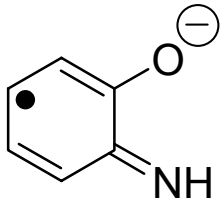


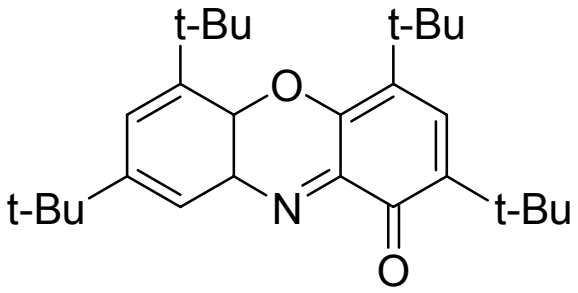
- **C3 symmetric structure**
- **S=1 ground state**
- **AFM Coupling between Fe/SQ**
- **Bridged tetramers formed ($Fe_4SQ_4Cat_4$)**
- **FM M-M Coupling, weaker than M-SQ**

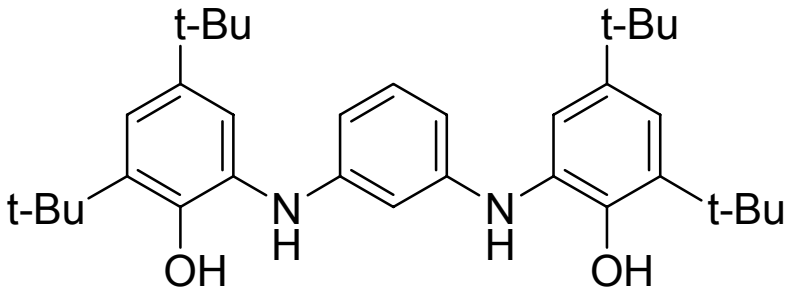
Boone, S. R. et al. *J. Am. Chem. Soc.* **1989**, *111*, 2292-2299

Biradicals Incorporating Additional SCUs or Modified Semiquinone Structures

Iminosemiquinones



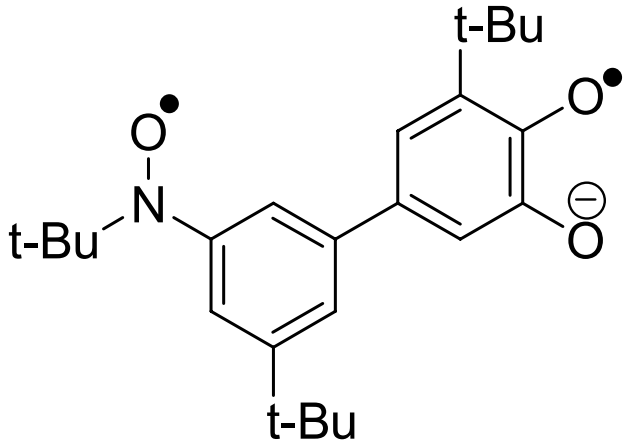




- **Antiferromagnetic coupling in complexes with metals**
- **Bis(Iminoquinone) complexes exhibit both AFM and FM coupling**
- **Bidentate ligand antiferromagnetically coupled (torsions)**

Whalen, et al. *Inorg. Chem.* **1994**, *33*, 347
Dei, et al. *Inorg. Chem.* **2003**, *42*, 1701

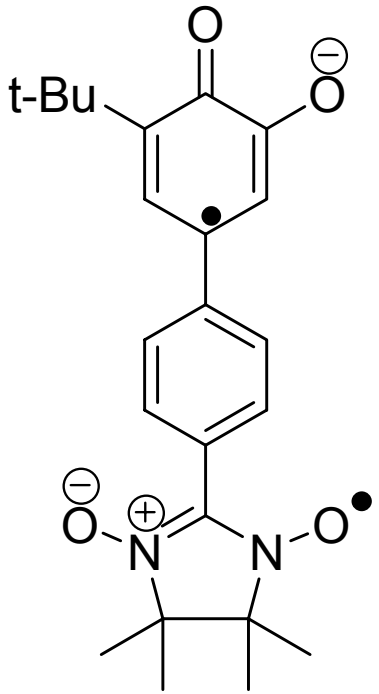
Nitroxide-Semiquinone Biradicals



- **Ligand possesses two coordination modes**
- **Curie plot is linear indicating Ferromagnetic coupling**
- **Limited possibility of largely different in-solution conformers**

Shultz, D. A.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 6254

Nitronyl Nitroxide-Semiquinone Complexes



- **Mn, Co, Ni, Cu, Complexes Probed**
- **Mn, Co, Ni: AFM M-Ligand Coupling**
- **Cu: FM M-Ligand Coupling**
- **Intraligand exchange FM in all complexes**

Shultz, D. A. et al. *J. Am. Chem. Soc.* **2003**, *125*, 1607

Summary

- Semiquinones are viable as SCUs for high-spin systems
- Bis(Semiquinones) linked with FCUs have triplet ground states
- Semiquinone-Metal Complexes typically hard to analyze
- Higher spin systems possible
- Semiquinones can be combined with other SCUs to form high-spin systems

Acknowledgements

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