

Samuel Brineman

428 Chemistry Building

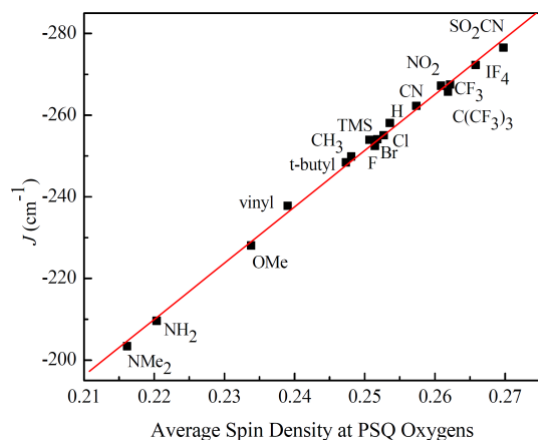
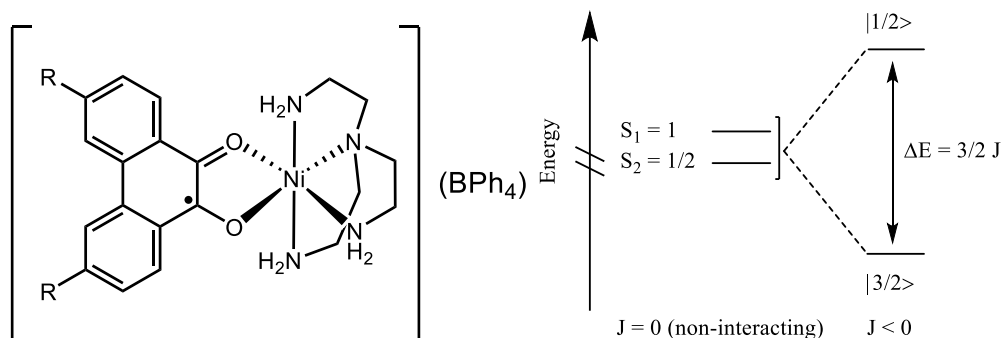
Research Summary

One of the major physical manifestations of spin is in magnetism, which is governed by the spin exchange interaction. The spin exchange interaction is a quantum mechanical phenomenon with no classical analogue, and it dictates the relative alignment of unpaired spins between paramagnetic centers. The magnitude of the exchange interaction determines the energy gap between spin states in exchange-coupled compounds. The magnitude of the exchange interaction, parameterized by the exchange coupling constant, J , is in part a product of the spin density at interacting paramagnetic centers.¹

The movement, or polarization, of unpaired spin currently has no unified model that can be applied to transition metal-radical ligand systems. This is in stark contrast to the movement of charge in molecular systems, which has been well-parameterized by the empirical Hammett-type parameters. As the spin density at interacting magnetic centers dictates the magnitude of the exchange interaction, it will be beneficial to demonstrate that spin polarization can be predictably controlled through synthetic means.²

The system used to study synthetic modulation of spin density is $[\text{Ni}(\text{tren})(3,6\text{-}(\text{R})_2\text{-PSQ})](\text{BPh}_4)$ (where tren = tris-(2-aminoethyl)amine, PSQ = phenanthrenesemiquinone, and BPh_4 = tetraphenylborate). Density functional theory (DFT) calculations suggest that, by substituting the PSQ ligand at the 3- and 6- positions, the amount of spin density at the ligating oxygen atoms can be altered across a substitution series.^{3,4} It is hoped that magnetic and EPR experiments will demonstrate changes in the spin density of the ligating oxygen atoms as a function of substitution of the ligand, manifesting in changing values of J and differentiated line shapes of the EPR spectra across the series.

Ultimately, this project seeks to establish that spin density, and thus magnetic properties, of exchange-coupling complexes can be modulated in a predictable fashion via synthetic means. If the project is successful in this goal, then it can serve as a basis for future studies seeking to demonstrate the broad applicability of synthetic modulation of spin in controlling the magnetic properties of exchange-coupled systems.



Top left: structure of $[\text{Ni}(\text{tren})(3,6\text{-}(\text{R})_2\text{-PSQ})](\text{BPh}_4)$. Top right: spin ladder of the complex showing energy gap between quartet and doublet spin states due to the exchange interaction. Bottom: plot of DFT-calculated J vs. spin density at PSQ ligand oxygen atoms (calculated at UB3LYP/6-311G**).

References:

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MICHIGAN STATE
UNIVERSITY

Department of Chemistry