



# Magnetic spin state characterization of dysprosium(III) metallocenium single-ion molecular magnets using density-functional theory

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## Background

Single-molecule magnets (SMMs) are a group of large metallo-organic compounds that exhibit superparamagnetic behavior below a specific magnetic blocking temperature (~4K). Their unique molecular symmetry and spin configuration induce magnetic hysteresis, making them ideal for compact and information-dense qubit storage in quantum computing<sup>1</sup>.

Of particular interest are a set of dysprosium(III) metallocenium single-ion molecular magnets,  $[\text{Dy}(\text{Cp}^{\text{iPr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$  which exhibit very large magnetic blocking temperatures, ranging from 20K-70K, and differ only in their choice of functional group R<sup>2</sup>. Computationally investigating the spin states of these molecules may provide insight into their magnetic properties and high blocking temperatures.

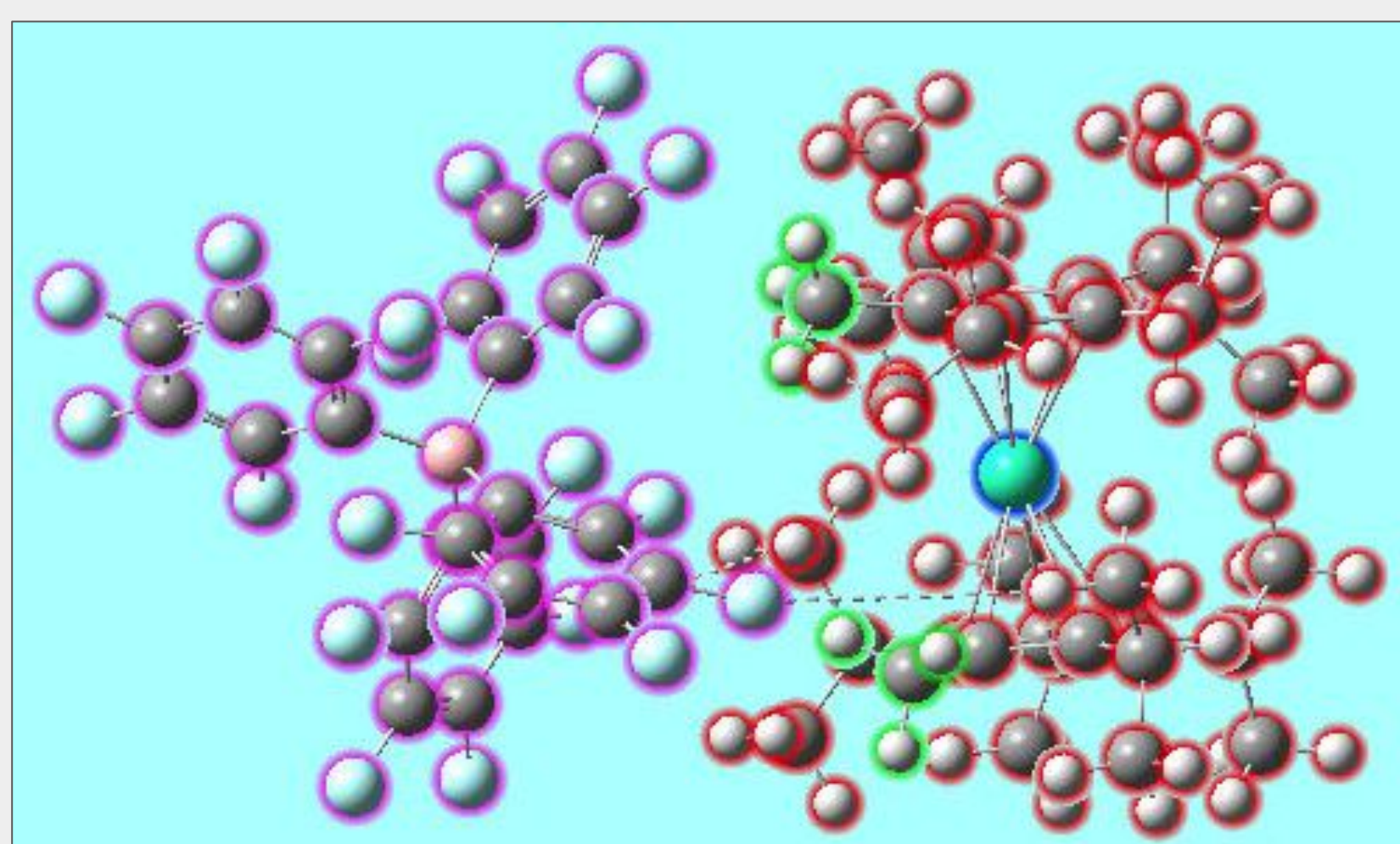


Figure 1: GaussView representation of  $[\text{Dy}(\text{Cp}^{\text{iPr}4\text{R}})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ , R=Me (green)

## Objectives

1. Extract raw X-ray crystallographic data for all six molecules and convert into a GaussView readable file
2. Find the most stable spin state of each molecule
3. Optimize each molecular geometry with the stable spin state
4. Model each antiferromagnetic spin state with fragment guesses using broken symmetry density-functional theory (DFT-BS)
5. Calculate each magnetic exchange coupling

## Method

Density-functional theory (DFT) is a comparatively low-cost and high-accuracy computational electronic structure method that expresses the total energy of a system as a functional of its specific electron density function ( $n_0$ ).  $E_S[n_0] = \langle \Psi[n_0] | \hat{T} + \hat{V}_S | \Psi[n_0] \rangle$

Minimizing the energy functional presents a variational problem solved with Lagrange multipliers<sup>3</sup>. The Kohn-Sham equations are then derived, which describe non-interacting particles in a fictitious effective potential ( $v_{\text{eff}}$ ):

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

Solving for the lowest energy solutions to the Kohn-Sham equations yield the desired set of Kohn-Sham orbitals  $\varphi_i$ . This is an intense computational process and requires high-performance computing resources.

## Results

The Heisenberg Hamiltonian is used to derive an expression for the magnetic exchange coupling constant  $J$  seen here, between spins  $i$  and  $j$ :

$$\hat{H} = - \sum_{i < j} J_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j$$

The expression for  $J$  simplifies to the energy difference between the stable, high-spin magnetic state and low-spin antiferromagnetic state<sup>4</sup>. Two approaches were used in Gaussian 16: a manual BS fragment approach and a stability job to also break spin symmetry. These magnetic exchange couplings were plotted against corresponding magnetic blocking temperatures from literature. Positive  $J$  values correspond to ferromagnetic states, and negative  $J$  values correspond to antiferromagnetic states.

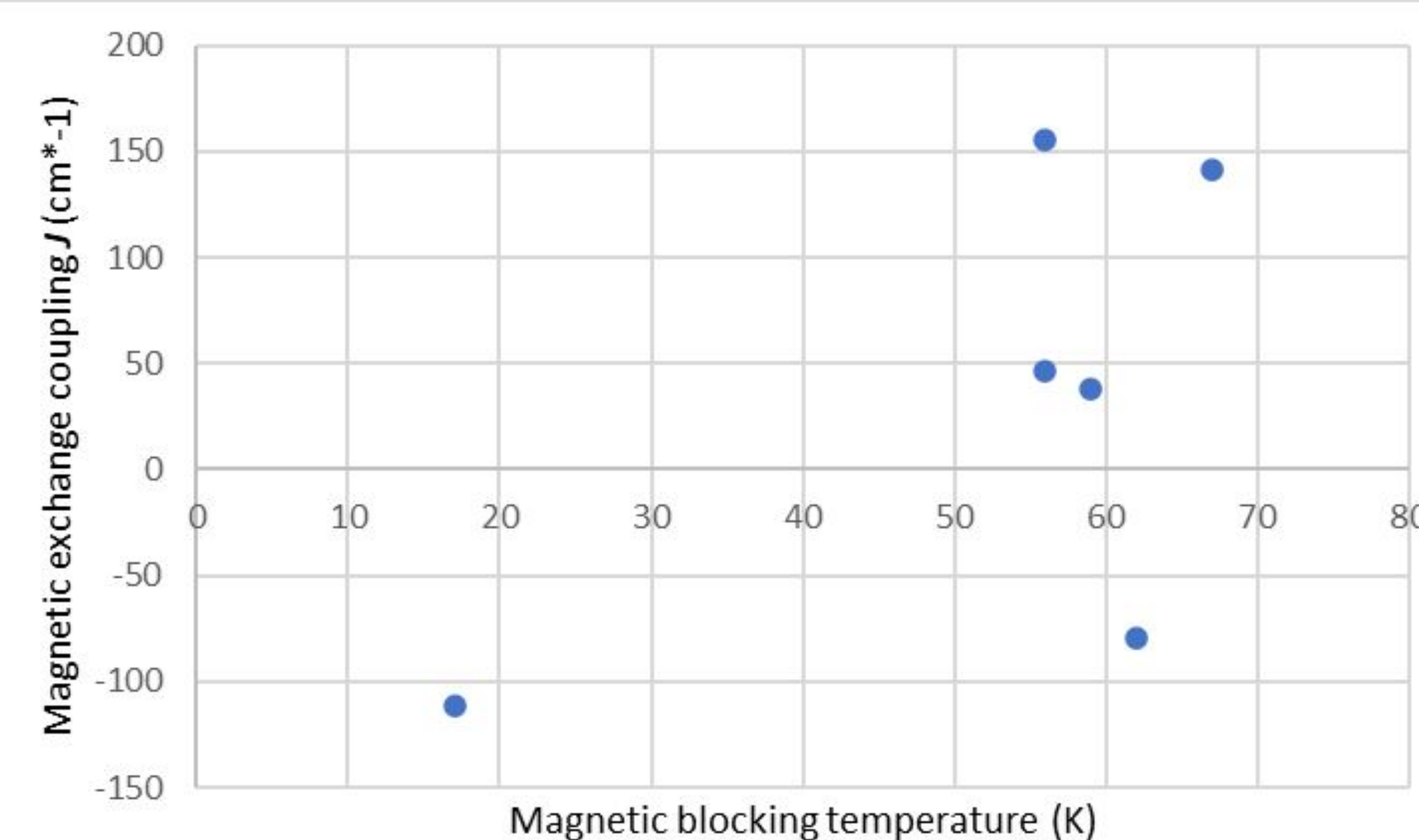


Figure 2: The magnetic exchange coupling constants of each molecule calculated using BS-DFT (UTPSSh/CEP-31G), plotted against literature magnetic blocking temperatures.

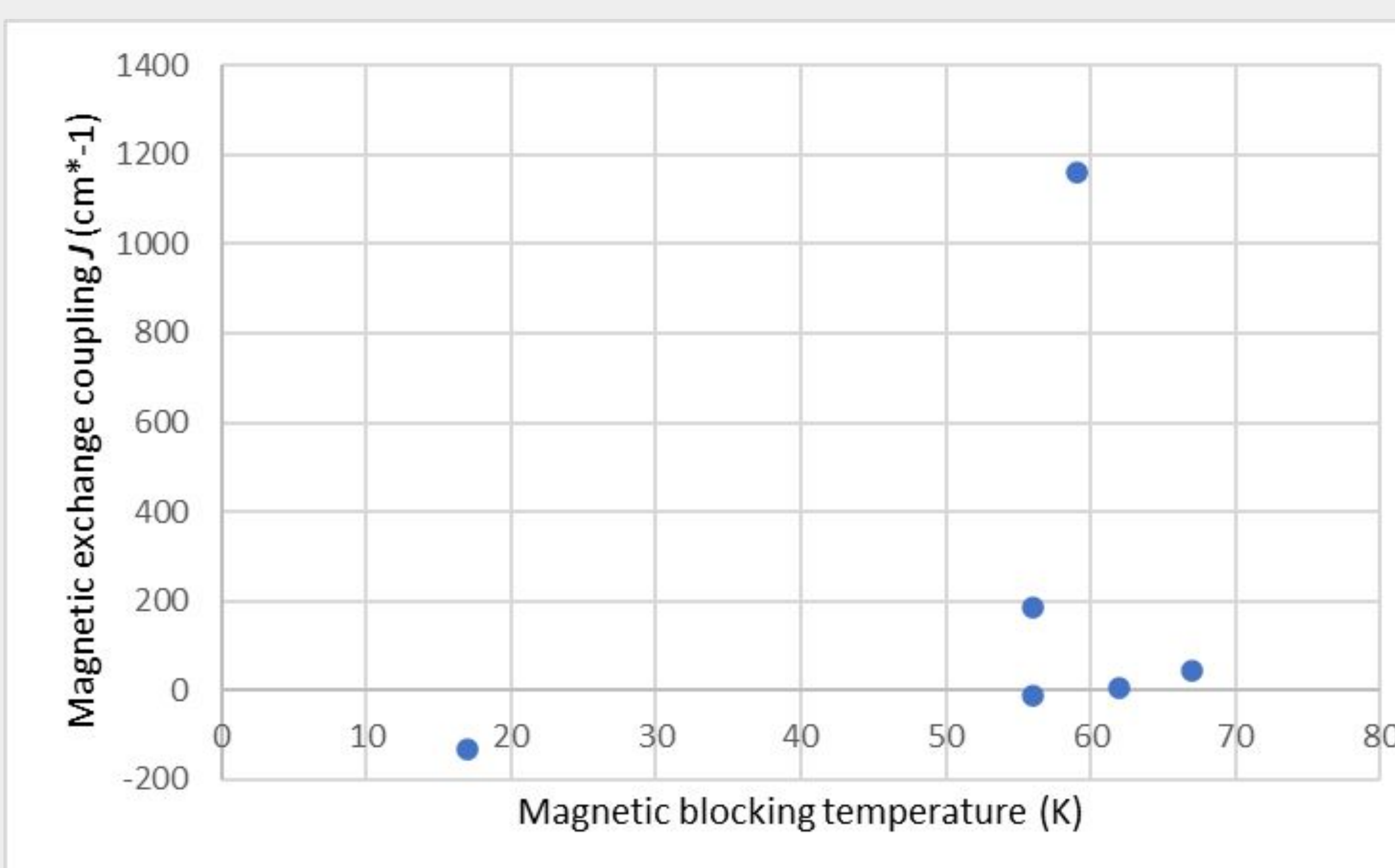


Figure 3: The magnetic exchange coupling constants of each molecule calculated by the optimizing the wavefunction (UTPSSh/CEP-31G) using stability tests, plotted against literature magnetic blocking temperatures.

## Discussion & conclusion

All calculations in this procedure were undertaken using Gaussian 16 and submitted to the Mesabi cluster with the Minnesota Supercomputing Institute (MSI) via OnDemand.

This project began with a series of single-point energy calculations (UHF/CEP-31G) on inputted X-ray crystallographic data. The data from those files contained invisible and overlapping identical atoms, which were deleted. These calculations were performed on S=2,4,6,8,10 multiplicities, and resulted in all states being most stable in the S=6 configuration, except for one in the S=8 (R=Et). The molecular geometries of each molecule were then optimized using the TPSSh exchange-correlation functional and unrestricted Kohn-Sham. This was an incredibly time-consuming process, and some molecules did not optimize within many weeks of running.

The antiferromagnetic singlet state energies were approximated using DFT-BS, using a 3-fragment guess: the single dysprosium atom, its entire coordination environment, and the entire boron counteranion. These fragments are illustrated in Figure 1, although the R group is highlighted green instead of red. These jobs all completed within 24 hours. Energies were also approximated using a wavefunction stability/optimization job.

The results of these calculations were surprising. Neither method matches one another or illustrate a trend between the magnetic blocking temperature of each molecule and its magnetic exchange coupling. Every value of  $J$  was also expected to be negative, corresponding to an antiferromagnetic state, yet positive values are observed. Some future directions to take with this research that may avoid some of these issues include:

- Surveying exchange-correlation functionals beyond TPSSh with a pseudopotential that may better model  $f$  electrons
- Investigate the effect of the R group on the magnetic exchange coupling
- Repeat a manual BS-DFT calculation with boron as a second metal center

## References

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