

The superparamagnetic limit defines a minimum magnetizable area and places an upper bound on the density of magnetic storage. In order to condense magnetic memory further, paradigms for new regimes in mesoscopic physics must be forged.

My Ph.D. work aimed to reduce the minimum magnetizable area below the superparamagnetic limit using a bottom-up approach. We proposed that individual molecules with specific magnetic properties (single-molecule magnets) could be used as data storage media with each cluster representing an individual bit of information. In particular, my thesis, "Magnetic Properties of High-Spin Metal-Cyanide Clusters and the Directed Assembly of a Single-Molecule Magnet", focuses on the metal-cyanide chemistry of single molecules. It reports syntheses of high-nuclearity examples of these species and detailed investigations of the magnetic properties of such clusters.

Single-molecule magnets are high-spin clusters capable of sustaining a remnant magnetization at low temperatures upon removal from a polarizing field.¹ These clusters possess an axial magnetic anisotropy ($D < 0$) that gives rise to an energy barrier for magnetic moment reversal. Thus, magnetic hysteresis results from an extremely long paramagnetic relaxation time, rather than from magnetic domain wall motion of bulk magnets. The largest barrier observed is approximately 50 cm^{-1} , occurring in the $S = 10$ cluster $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$,² which exhibits a magnetic relaxation half-life of two months at 2 K.^{1b} To realize marketable data storage applications, an increase in the barrier height is of obvious benefit to the temperature and duration of storage.³

All of the single-molecule magnets reported before our work were metal-oxo cluster systems, wherein enormous structural variability limited synthetic control over geometric and magnetic properties. Our approach yields cyanide bridged moieties which

usually present a linear arrangement spanning just two metal centers. Consequently, it is easier to predict the structural outcome of assembly reactions. Additionally, the nature of the magnetic exchange interaction between pairs of metal centers through cyanide is also well known. Expected molecular spin states are based on coupling rules previously established for Prussian blue-type solids.⁴ With this added control, we tune the spin and magnetic anisotropy of our molecules more adeptly than possible with metal-oxo systems, ideally increasing the barrier to magnetization reorientation given by $S^2|D|$.⁵

Employed in the design of molecular clusters, a measure of influence similar to that exerted in the preparation of solids has greatly facilitated the synthesis of new metal-cyanide clusters. Previous workers isolated molecular Prussian blue analogues by employing a synthetic approach parallel to that for solids, but used tridentate ligands to block coordination sites of metal, effectively limiting extended framework growth.^{6a} This approach was extended resulting in higher nuclearity molecules such as $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$ ($\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane), a fourteen-metal cluster with a unique face-centered cubic geometry.^{6b}

My research began with the analysis of the magnetic properties of this molecule. The expected spin of $S = 18$ (ferromagnetic coupling: $8(3/2) + 6(1) = 18$) was not observed. Experiments revealed it was a simple paramagnet, implying that the Ni^{II} centers were diamagnetic. A thermally activated linkage isomerization had occurred wherein the carbon end of cyanide shifts from ligating Cr^{III} in the $[(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3]$ reactant to ligating Ni^{II} in the $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$ product. In the resulting complex, the Ni^{II} centers are square planar and diamagnetic, as opposed to octahedral and

paramagnetic. Similar isomerizations had been observed in NiCr-cyanide systems previously.^{7,8}

I began trying to isolate the cluster prior to cyanide ligand rearrangement, thereby maintaining a high spin configuration of Ni^{II}, and prompting ferromagnetic coupling with the surrounding Cr^{III} centers. Performing the reaction at reduced temperatures yielded a green solid displaying magnetic behavior suggestive of a $S = 18$ ground state⁹ expected for a putative $[(\text{Me}_3\text{tacn})_8(\text{H}_2\text{O})_{12}\text{Ni}_6\text{Cr}_8(\text{CN})_{24}]^{12+}$ cluster,¹⁰ but its identity could not be verified in X-ray analyses. Alternative preparations were sought employing various nickel salts as starting materials, in the hope that a coordinating counterion would stabilize the octahedral geometry of Ni^{II}. The use of NiI₂ led to the formation of an incomplete $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_5(\text{CN})_{24}]^{10+}$ cluster. Its framework was very similar to $[(\text{Me}_3\text{tacn})_8\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$ although one nickel ion was missing from a face center and an iodide ion was contained within the cluster cage. Further reactions of this molecule yielded yet another metal-cyanide cluster, $[(\text{Me}_3\text{tacn})_{10}\text{Cr}_{10}\text{Ni}_9(\text{CN})_{42}]^{6+}$ which was the first structure to contain trigonal bipyramidal, square planar, and square pyramidal Ni^{II} ions exclusively coordinated to cyanide.¹¹ Refinement of synthetic methods to produce these molecules in higher yields resulted in the isolation of further unique species. The crystal structures of two new metal-cyanide clusters, an edge-bridged 24-metal $[(\text{Me}_3\text{tacn})_{12}\text{Cr}_{12}\text{Ni}_{12}(\text{CN})_{48}]^{12+}$ and a still larger cluster, $[(\text{Me}_3\text{tacn})_{14}\text{Cr}_{14}\text{Ni}_{13}(\text{CN})_{48}]^{20+}$, an apparent fusion of two face-centered cubic structures at an apex, were obtained.¹² To date, this 29-metal complex remains the highest-nuclearity metal-cyanide cluster yet identified.

Although these molecules were of great structural interest, they were simple paramagnets. The bulk of my work was the collection and analysis of magnetic data on several Mo-containing metal-cyanide clusters synthesized by my colleagues.^{13, 14} The strong magnetic anisotropy observed in magnetization experiments^{6, 13} prompted my composition of specialized software to quantify such phenomena. I wrote the program, Anisofit 2.0, to model the magnetization of an 'isolated' spin ground state and allow the extraction of zero-field splitting parameters from empirical data.

The program modeled the behavior of the molybdenum analogue of a Mn-Cr metal-cyanide complex, itself the subject of intense scrutiny. After careful experimentation and analysis, the trigonal prismatic cluster, $[(\text{Me}_3\text{tacn})_6\text{MnMo}_6(\text{CN})_{18}]^{2+}$, was identified as the first cyano-bridged single-molecule magnet.¹⁴

Collaboration with a group at the National High Magnetic Field Laboratory led to spectroscopic studies of several other molybdenum-containing clusters¹³ using high-field, high-frequency electron paramagnetic resonance. This technique directly probes magnetic anisotropy, as opposed to deducing zero-field splitting parameters from bulk measurements alone. Conventional EPR spectrometry did not provide enough information about these transition metal complexes due either to large molecular spins ($S = 4$) or axial anisotropy larger than the X- or Q-band quanta. The results derived through this collaborative work revealed that several of our molecules which did not display out-of-phase AC susceptibility signals, a hallmark of single-molecule magnets, in fact possessed barriers to magnetization reorientation which were not probed at the temperatures and frequencies of the susceptibility experiments we previously performed.

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- 10 Krzystek, J.; Sokol, J. J.; Ozarowski, A.; Zvyagin, S. A.; Long, J. R.; Brunnel, L.-C.; Telsler, J., "EPR Spectra from "EPR-Silent" Species: High-Frequency and -Field EPR Spectroscopy of Pseudo Octahedral Complexes of Vanadium(III)", submitted.
- 9 Choi, H. J.; Sokol, J. J.; Long, J. R., "High-Spin Metal-Cyanide Clusters: Species incorporating $[Mn(salen)]^+$ Complexes as a Source of Anisotropy", *J. Phys. Chem. Solids*, in press.
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