

**MAGNA**  **2020**

# **Book of Abstracts**

**February 21-24, 2020**



**St. Simon's Island, GA**

# Is Spin-Orbit Coupling Always the Dominate Factor in the Electronic Structure of Actinide Compounds?

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The magnetic behavior of actinide compounds often differs substantially from formally isoelectronic lanthanide compounds. While there are many factors that contribute to this, the single largest one is that the magnitude of spin-orbit coupling doubles between the 4*f* and 5*f* series and rises from ~1 eV to 2 eV. Many of our predictive rules concerning the ground states of metal ions assumes that the energy of e<sup>-</sup>... e<sup>-</sup> repulsion ( $H_{ee}$ ) is  $\gg H_{SO}$ . However, in the 5*f* series  $H_{ee} \approx H_{SO}$ . Furthermore, the magnitude of ligand-field splitting is also unusually large in the second half of the actinide series, and  $H_{ee} \approx H_{SO} \approx H_{LF}$ . In this talk, we will examine the consequences of these energetic factors being on similar scales through a variety of measurements on americium, curium, berkelium, californium, and einsteinium materials and coordination complexes.

# **Fermi-Lowdin orbital self-interaction correction in density functional theory calculations of magnetic properties**

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The self-interaction error in density functional approximations is attributed to a number of errors in calculated properties. We employ the Fermi orbital based self-interaction correction method with density functional approximations of increasing complexities – local density approximation, generalized gradient approximation, and SCAN meta-GGA functional to calculate a number of properties. The self-interaction correction is needed for barrier heights or for accurate description of stretched bond cases. The application of SIC however can degrade the already good predictions of semi-local functionals, especially for equilibrium properties. In this talk I will present the recent developments in the Fermi-Lowdin orbital self-interaction correction method and benchmark calculations for a number of properties including the magnetic properties. Results of calculations on transition metal oxide molecules and on a  $\text{Cu}_2$  molecular magnet will be discussed.

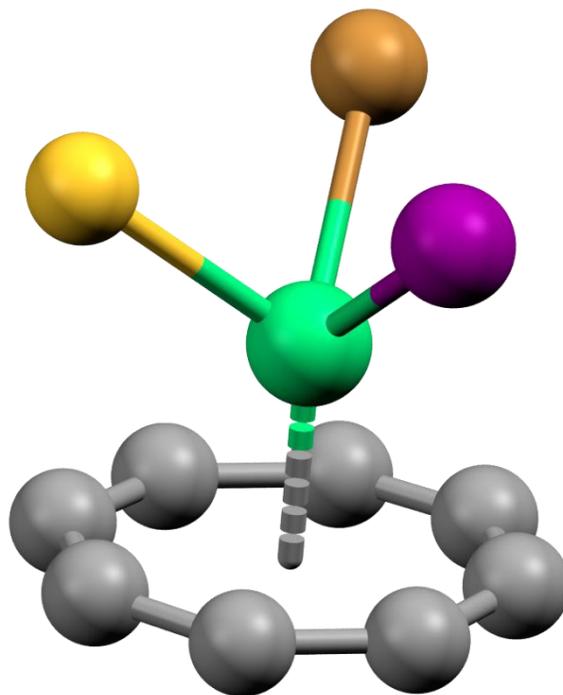
## ErCOT – An magnetic building block for ground-up structural design and understanding multinuclear anisotropy

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Lanthanide-based single-molecule magnets (SMMs) have captivated the field by the impressive single-ion relaxation behavior resulting from their strong single-ion anisotropy. Extending these systems to systems to incorporate multiple coupled metal centers has been challenging due to the difficulty of balancing the stringent crystal field requirements of each ion and the strength of interactions between them. We have employed the use of a magnetic building block consisting of  $\text{Er}^{3+}$  stabilized by the cyclooctatetraenyl dianion and its derivatives (ErCOT) to construct both highly anisotropic single-ion units and ferromagnetically coupled multinuclear complexes displaying slow relaxation. Deeper analysis of these systems through the lens of considering their individual ions' environments combined with insight into the strength of interactions between them, we hope both to illustrate the key difficulties in expanding lanthanide molecular magnets and illustrate some design principles to overcome them.



**Figure.** An ErCOT unit, displaying connectivity to arbitrary ligands.

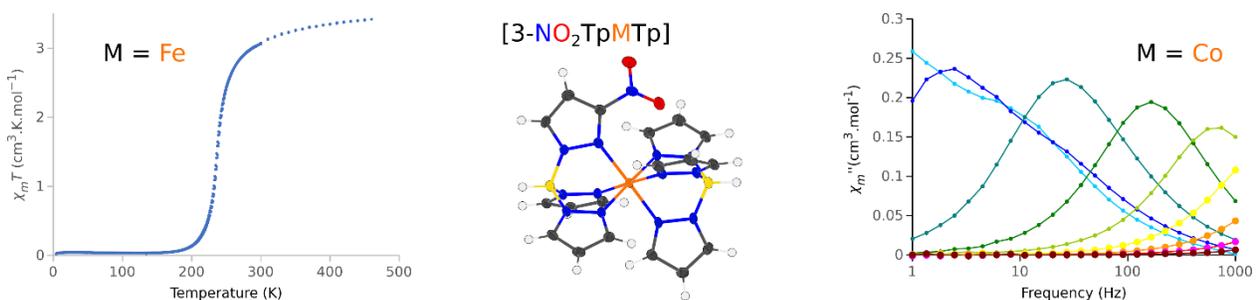
# Solid-state and solution magnetism of some functionalized trispyrazolylborate complexes of iron and cobalt

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Trispyrazolylborate (Tp<sup>-</sup>) ligands have long been part of the toolbox of the magnetochemist. The temperature-induced spin crossover properties of the iron complex [FeTp<sub>2</sub>] have been known since 1967 [1]. Since then, numerous derivatives and analogues of this species have been thoroughly investigated, demonstrating in particular the crucial importance of the ligands geometry and steric requirements on the spin transition temperature. The analogue [CoTp<sub>2</sub>] species also shows spin crossover properties, though in that case the transition is induced by pressure and not temperature. The cobalt complex was also recently shown to be a single molecule magnet [2].

Our work presented here builds on and complements those previous studies while putting emphasis on three thus far unexplored areas: 1. The synthesis of derivatives presenting reactive functionalities (e.g. amine) allowing subsequent integration of the magnetic complex into a device. 2. The investigation of electronic effects on the magnetic properties by introduction of strongly electron donating (e.g. amine) or withdrawing (e.g. nitro, cf. Figure) groups on the ligand backbone. 3. The synthesis of asymmetric derivatives incorporating different pyrazole rings in the same complex.

We recently developed a convenient access route to such molecules via an exchange reaction between a preformed ligand or complex and a functionalized pyrazole [3]. This gave us access to a wide range of iron and cobalt complexes bearing one to four substituents in positions 3, 4 or 5 on the pyrazole. We will report here the structures and magnetic properties of those complexes, in the solid state (cf. Figure) as well as in solution.



**Figure.** Magnetic properties of [3-NO<sub>2</sub>TpMTp] (center)  
for M = Fe (left) and M = Co (right, 1.8 to 9.8 K, H<sub>ext</sub> = 500 Oe)

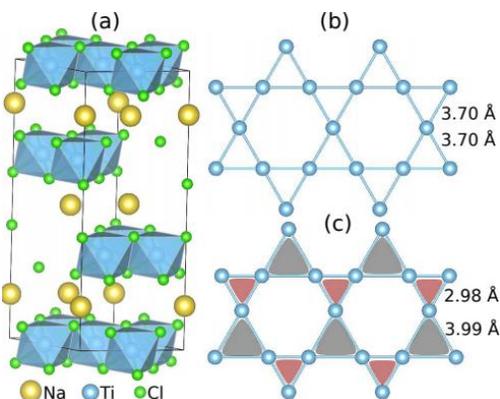
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[2] J. Zhang, J. Li, L. Yang, C. Yuan, Y.-Q. Zhang, Y. Song, *Inorg. Chem.* **2018**, *57*, 3903.  
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# Spin-Phonon and Spin-Lattice Couplings in Crystals (And Connections to Molecular Magnetism)

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The couplings between the lattice vibrations or static distortions and the magnetic Hamiltonians (the spin-phonon and spin-lattice couplings) are ubiquitous in transition metal oxide crystals. These effects give rise to phenomena such as spin-splitting of phonon modes, or breaking of the degeneracy of elastic constants below magnetic ordering temperatures. Historically, first principles computational approaches have been extremely successful in predicting and explaining the coupling between the crystal structure, its excitations, and the magnetic properties. In this talk, after giving a brief introduction to the idea of spin-lattice coupling [1], I am going to discuss two case studies from a first principles theory point of view:  $\text{Sr}_3\text{NiIrO}_6$  is a mixed 3d-5d transition metal oxide with one dimensional chains of magnetic ions [2]. This interesting compound displays a canting of ferromagnetically ordered moments when the ions are displaced according to polar normal modes - which is observed as a large change in the IR absorption under magnetic fields. I will then move on to a 2 dimensional frustrated spin-1 Kagome antiferromagnet,  $\text{Na}_2\text{Ti}_3\text{Cl}_8$ . This compound undergoes a structural phase transition at 200 K, below which the system develops a switchable ferroelectric polarization, and the magnetic moments are suppressed. Our combination of first principles density functional theory and exact diagonalization calculations show that this compound not only has a magnetic Hamiltonian with unexpected higher order 'ring exchange' terms, but also that the coexisting structural and magnetic phase transition is driven by the strong spin-lattice coupling [3]. I will conclude by a discussion on how the lower-T electronic structure of this compound is better explained from a molecular point of view, rather than the usual approach of well defined atomic moments in a solid.



**Figure.** (a) Structure of  $\text{Na}_2\text{Ti}_3\text{Cl}_8$ . (b) The Kagome lattice formed by the Ti ions above, and (c) below the transition temperature.

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[2] O'neal et al., *npj Quantum Materials*, **2019**, 4, 48.

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# Investigating decoherence pathways in $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$ via magneto-infrared spectroscopy

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We have identified  $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$  as a material of interest as it is both a single molecule magnet and a promising candidate for use as a spin qubit in quantum computing. A limitation found regarding the spin qubit application of this material is the presence of quantum decoherence. In order to reveal the decoherence pathways related to spin-phonon interactions, we investigated the vibrational properties of and its non-magnetic analog,  $[\text{Y}(\text{W}_5\text{O}_{18})_2]^{9-}$ , as a function of temperature and magnetic field and compared our findings to complementary lattice dynamics calculations. Our magneto-infrared studies up to 35 T revealed field-induced changes at 63, 351 and 373  $\text{cm}^{-1}$  that we attributed to a combination of crystal field splitting within the f-orbitals and spin-vibrational coupling.

# The Use of Pseudo-Carboxylates in Homometallic Cobalt Cluster Chemistry

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The development of cobalt-oxo cluster chemistry has been explored over many years and has led to an array of clusters of various nuclearities with relevance to bioinorganic chemistry, magnetism, and catalysis [1][2]. Typical ligation environments for cobalt-containing clusters are bridging carboxylate groups and nitrogen-containing ligands such as pyridine or 2,2'-bipyridine. Although metal-oxo-carboxylate chemistry has afforded numerous clusters for many transition and lanthanide metals, the utilization of 'pseudo-carboxylates' in such chemistry has been under-explored. Recently, di-alkyl(aryl)phosphinates have emerged as attractive pseudo-carboxylate groups to investigate in cluster chemistry because they mimic carboxylate ligand binding modes but are more bulky [3][4]. We have therefore begun to investigate the use of diphenylphosphinic acid ( $\text{Ph}_2\text{PO}_2\text{H}$ ) in  $\text{Co}^{\text{II}}$  and/or  $\text{Co}^{\text{III}}$  cluster chemistry in the search for new clusters with interesting structural features and physical properties. The synthesis, structure, and magnetic properties of a new cobalt diphenylphosphinate cluster will be presented.

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# First-principles Investigation of the Magnetic Properties of the Giant $\text{Mn}_{84}$ Torus

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## Abstract

The giant single-molecule magnet  $\{\text{Mn}_{84}\}$  has a shape of torus of eighty-four  $\text{Mn}^{3+}$  ions ( $S=2$ ). As the manganese atoms in  $\{\text{Mn}_{84}\}$  are all bridged by  $\text{O}^{2-}$  or  $\text{MeO}^-$  groups, strong pairwise exchange interactions between these manganese atoms are expected. In this work, we investigate these interactions using first-principles calculations, from which a Heisenberg model is developed. The exchange coupling constants are extracted by fitting to the total energies of different spin configurations of  $\{\text{Mn}_{84}\}$ . In addition, we compute the magnetic anisotropy energy by including spin-orbital couplings.

# Decoherence in Molecular Electron Spin Qubits: Insights from Quantum Many-Body Simulations

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Quantum states are described by wave functions whose phases cannot be directly measured, but which play a vital role in quantum effects such as interference and entanglement. The loss of the relative phase information, termed decoherence, arises from the interactions between a quantum system and its environment. Decoherence is perhaps the biggest obstacle on the path to reliable quantum computing. Here we show that decoherence occurs even in an isolated molecule although not all phase information is lost via a theoretical study of a central electron spin qubit interacting with nearby nuclear spins in prototypical magnetic molecules. The residual coherence, which is molecule-dependent, provides a microscopic rationalization for the nuclear spin diffusion barrier proposed to explain experiments. The contribution of nearby molecules to the decoherence has a non-trivial dependence on separation, peaking at intermediate distances. Molecules that are far away only affect the long-time behavior. Because the residual coherence is simple to calculate and correlates well with the coherence time, it can be used as a descriptor for coherence in magnetic molecules. This work will help establish design principles for enhancing coherence in molecular spin qubits and serve to motivate further theoretical work.

# Molecular Cerium/Manganese Chemistry: a Marriage made in Heaven

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It could not have been predicted when we reported the first Ce/Mn oxo cluster in 2003 [1] just how greatly this field would expand in subsequent years and how interesting it would become. Since Ce-O<sup>2-</sup> chemistry is dominated by the very oxophilic and diamagnetic Ce<sup>IV</sup> oxidation state, the primary stimulus of the original work was not just molecular magnetism but certain other areas that had caught our eye. In particular, Ce/Mn composite oxides have been used in a variety of industrial and catalytic applications such as, for example, environmental abatement of wastewater pollution by catalytic wet oxidation (CWO) of dissolved organic and inorganic pollutants, and low temperature oxidation of phenol. As it turned out, once Ce/Mn clusters had become available, both new single-molecule magnets (SMMs) and oxidation catalysts ensued, such as the identification of [Ce<sup>IV</sup>Mn<sup>III</sup><sub>8</sub>O<sub>8</sub>(O<sub>2</sub>CMe)<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>] with *S* = 16 as the first Ce/Mn SMM [1], and the use of [Ce<sup>IV</sup>Mn<sup>IV</sup><sub>6</sub>O<sub>9</sub>(O<sub>2</sub>CMe)<sub>9</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>] for catalytic oxidation of benzyl alcohol to benzaldehyde [2].

Ce/Mn-oxo chemistry has now grown extensively and spans clusters with a large variety of total metal nuclearities and Ce:Mn ratios, from mainly-Ce to mainly-Mn, and everything in-between. In our own work as it has expanded, we have also found Ce/Mn/O clusters that represent repeating units of the AMnO<sub>3</sub> manganites (A = lanthanide or main group metal) with the perovskite structure and fascinating magnetic properties, as well as higher nuclearity clusters that represent a molecular bottom-up approach to the composite Ce/Mn composite oxides and thus to ultra-small nanoparticles of such materials. This talk will describe a selection of the above clusters and their structural and magnetic properties.

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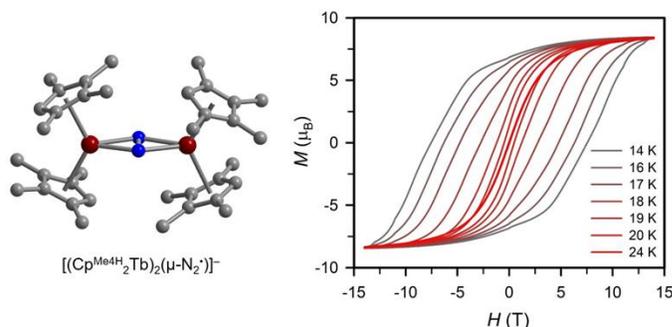
[2] Maayan *et al.*, *Inorg. Chem.* 2011, *50*, 7015-7021.

# Magnetic Blocking in Lanthanide-Based Radical-Bridged Single-Molecule Magnets

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Lanthanides have been demonstrated to be especially well-suited for the design of single-molecule magnets owing to their large magnetic moments and magnetic anisotropy that stem from strong spin-orbit coupling of the 4f orbitals. By employing lanthanide ions such as  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Er}^{3+}$  which possess intrinsically large orbital angular momentum, significantly higher spin-reversal barriers and blocking temperatures can be attained. One effective methodology to increase blocking temperatures is to generate strong magnetic exchange between lanthanide centers using radical bridging ligands. If the magnetic exchange coupling is large enough then quantum tunneling of the magnetization can be suppressed. Here, the synthesis of multiple bimetallic radical-bridged lanthanide single-molecule magnets and the effective suppression of quantum tunneling pathways using various organic and inorganic radical bridging ligands will be presented [1-4]. In particular, the combination of axial magnetic anisotropy provided by the cyclopentadienyl ligands with the strong magnetic exchange coupling enabled by the inorganic  $\text{N}_2^{3-}$  radical gave rise to exceptionally large magnetic hysteresis loops which remain open up to high temperatures, Figure 1, [5].



**Figure 1.** Structure and magnetic hysteresis data for  $[(\text{Cp}^{\text{Me}_4\text{H}_2\text{Tb}})_2(\mu\text{-N}_2^{\prime})]^{-}$ .<sup>5</sup>

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- [3] S. Demir, I.-R. Jeon, J. R. Long, T. D. Harris, *Coord. Chem. Rev.*, **2015**, *289–290*, 149.
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# Investigation of LIESST effect in homoleptic Fe(II) complexes with thiazole-containing diimines

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Spin crossover (SCO) complexes exist in two spin states (high spin, HS, and low spin, LS) that can be interconverted by applying an external stimulus, such as temperature, pressure, or light irradiation. Recent interest to SCO materials is driven by their possible application in molecular electronics, spintronics, and quantum information processing. Perhaps, one of the most appealing properties is light-induced excited spin state trapping (LIESST), which can be used to design new photo-switchable materials. The LIESST effect has been studied extensively for the last three decades, but further fundamental research is required to establish general criteria that lead to effective light-induced transition from the LS to HS state and to increased thermal stability of the trapped HS state. Among ligands that provide appropriate ligand field strength to implement SCO, our attention was attracted by chelating derivatives of thiazoles. Despite reports of SCO behavior in Fe(II) complexes of such ligands [1], there is no any information about the occurrence of LIESST in these materials. This gap led us to investigate homoleptic Fe(II) complexes with three thiazole-based ligands, 2,2'-bithiazole (2bt), 4,4'-bithiazole (4bt) and 2-(1H-pyrazol-3-yl)thiazole (3tpH). These ligands were also chosen due to their conformity to the recently formulated rule for observing SCO in homoleptic Fe(II)-diimine complexes [2]: the distance between the chelating N atoms of the ligand should be within 2.78 – 2.93 Å, and these three ligands meet this requirement. Complexes Fe[(4bt)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**), Fe[(2bt)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**), and Fe[(3tpH)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> (**3**) were synthesized and characterized by single-crystal X-ray diffraction to confirm their mononuclear structures and to establish the changes in the Fe–N bond lengths that might accompany the spin transition. Magnetic measurements revealed a gradual SCO in complex **1** above the room temperature. It is unlikely that this compound will exhibit a measurable LIESST effect. Complex **2** showed an abrupt irreversible SCO at  $T_{1/2} = 360$  K upon initial heating, followed by an abrupt hysteretic SCO at  $T_{1/2,\downarrow} = 225$  K and  $T_{1/2,\uparrow} = 232$  K in the subsequent heating-cooling cycles. Such behavior might be due to the loss of interstitial solvent molecules, which was observed in the crystal structure of **2**. The complex subjected to initial heating also showed a LIESST effect, with the relaxation temperature of ~80 K. Complex **3** also showed an abrupt hysteretic SCO, with  $T_{1/2,\downarrow} = 151$  K and  $T_{1/2,\uparrow} = 154$  K, and a LIESST effect with the relaxation temperature of ~70 K. Thus, complexes **2** and **3** represent interesting light-responsive materials, and it is worthwhile to continue the study of their behavior under irradiation. The results of such studies and further plans will be discussed.

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## Supramolecular aggregates of single-molecule magnets

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Manganese-cluster chemistry has attracted many research groups because of its impact on bioinorganic chemistry and molecular magnetism. In the latter area, many Mn clusters have been found to be single-molecule magnets (SMMs), which are molecules with a large ground-state magnetic moment and a magnetoanisotropy of the Ising-type (easy-axis). Consequently, they display the classical diagnostic property of a magnet, hysteresis loops in magnetization vs applied dc magnetic field scans. SMMs represent a molecular approach to nanoscale magnetic materials and display interesting quantum properties, such as quantum tunneling of magnetization (QTM). In recent years, we have been linking two or more SMMs together to introduce weak exchange interactions between them that yields exchange-biased QTM, quantum superposition states and entanglement: this is important for potential applications, such as for qubits in quantum computing. In the present work, we have obtained three new supramolecular clusters, a  $[\text{Mn}_3]_2$  dimer and two  $[\text{Mn}_3]_8$  octamers, with very interesting structures formed by using three new bis-oxime linkers, 1,3-phenylenebis(pyridin-2-ylmethanone)dioxime (1,3-ppmdH<sub>2</sub>), 1,4-phenylenebis(pyridin-2-ylmethanone)dioxime (1,4-ppmdH<sub>2</sub>), and 1,4-naphthalenebis(pyridin-2-ylmethanone)dioxime (1,4-npmdH<sub>2</sub>) respectively. The synthesis, supramolecular structures, and magnetic characterization of these supramolecular aggregates of SMMs will be described.

# Applications of Advanced Electron Paramagnetic Resonance Techniques to Actinide-Based Coordination Complexes

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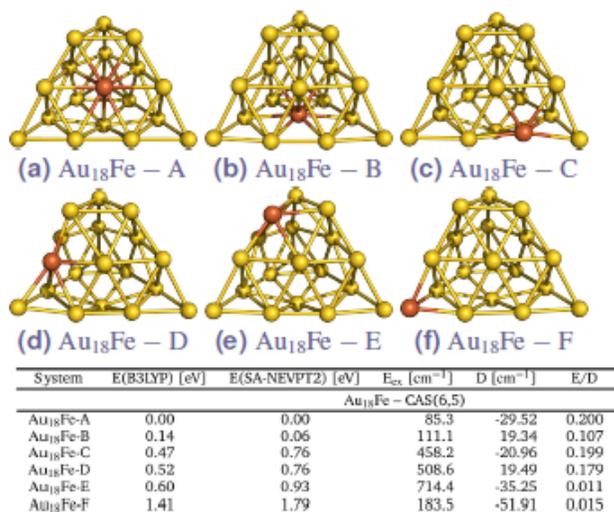
Electron Paramagnetic Resonance (EPR) methods have been used extensively to unravel the origin of physical properties in transition metal coordination complexes. Despite this success few studies have applied EPR techniques to actinide-containing compounds. At the same time our understanding of bonding and the relationship between physical and electronic/magnetic properties in actinides remains anemic compared to the rest of the periodic table. Here, we present on our efforts using continuous wave- and pulse- EPR methods to probe the magnetic properties of actinide-based coordination complexes. These efforts include the deployment of a benchtop x-band EPR spectrometer in a facility equipped to handle the unique challenges posed by radiological materials. We have also established procedures for the study of actinide coordination complexes using the high-frequency/high-field EPR spectrometers at the National High Magnetic Field Laboratory in Tallahassee, Florida. This unique combination of capabilities forms a powerful approach for probing the interplay between spin-orbit coupling, the ligand field, and their combined influence on the magnetic properties of molecules. We will present some of our procedures as well as our initial results from both of these new capabilities.

# Iron doped gold cluster nanomagnets: ab initio determination of barriers for demagnetization

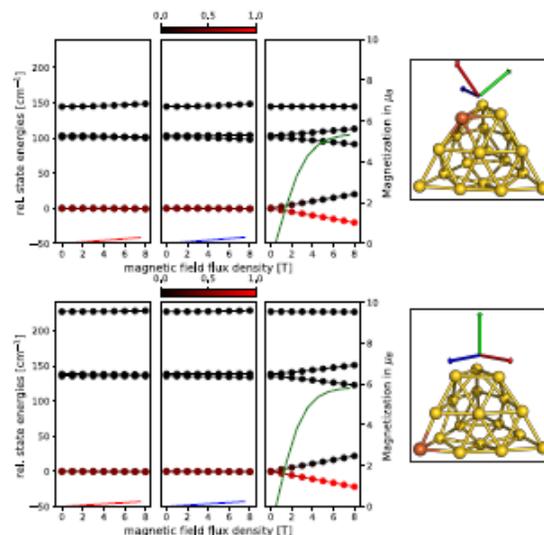
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Gold clusters,  $Au_n$ , have low spin ( $S = 0$  for even  $n$  and  $S = 1/2$  for odd  $n$ ). However, iron doped gold clusters have high spin. Because of the large electronegativity of gold, the iron atom is positively charged and these species would therefore be a type of single molecule magnets (SMMs) termed single ion magnets. The cornerstone of our study is the extremely stable  $Au_{20}(Td)$  compact structure. The axial ( $D$ ) and equatorial ( $E$ ) zero-field splitting parameters are calculated for  $Au_{19}Fe$  ( $S = 3/2$ ) and  $Au_{18}Fe$  ( $S = 2$ ) at the level of second order multireference perturbation theory.[1] The requirements for a SMM are  $D \ll 0$  (so the ground spin states have  $|M_S| = S$ ) and  $E/D \approx 0$  (to limit tunneling and mixing of states with different  $|M_S|$ ). If there is a large magnetic anisotropy, the SMM can be easily magnetized along the axial direction. We find that none of the three odd electron count structural isomers of  $Au_{19}Fe$  is magnetic. However, two of the six even electron count  $Au_{18}Fe$  structural isomers exhibit strong axial magnetic anisotropy and, for the corner substituted structural isomer  $Au_{18}Fe-F$ , the barrier for demagnetization is close to room temperature. In future studies we plan to examine (i) doping with other d-metal (Co, Mn) or f-metal (Tb, Dy) atoms; (ii) doping on/in the  $Au_n$  cage structures; (iii) the effect of charge on magnetic properties- cationic and anionic species; (iv) the effect of ligands on magnetic properties. Our goal is the rational design of doped gold nanoclusters to achieve optimum magnetic properties.



► For  $Au_{18}Fe - F$ , a  $208\text{ cm}^{-1}$  ( $\approx 300$  Kelvin) barrier for demagnetization.



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# **Giant molecules: exploring synthetic parameters on the path to new Mn/O torus-like clusters**

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The discovery of giant molecular clusters of paramagnetic metal ions, with metal nuclearities of 30 or greater and diameters up to 6.0 nm, has garnered immense interest due to their relevance to chemistry, physics, and materials science. The allure of giant clusters is rooted in their fascinating properties, such as their aesthetically-pleasing architectures, their nanoscale size regime, and their often remarkable physical properties. These features position giant clusters as truly mesoscale particles at the interface between the classical and quantum realms. Mn/O clusters are at the forefront of 3d transition metal giant clusters, owing to the relevance of Mn to molecular magnets, especially single-molecule magnets (SMMs). The largest homometallic Mn/O clusters and SMMs to date were synthesized by our group beginning over a decade ago: the Mn<sub>70</sub> and Mn<sub>84</sub> clusters with a torus structure and a diameter of ~4 nm truly straddle the classical-quantum interface both in terms of their size and their magnetic properties. In this presentation, we shall describe the results of an exploration of the factors that determine the Mn<sub>70</sub> vs Mn<sub>84</sub> nuclearity of the products, in order to pave the way for targeted synthesis of new giant Mn-O clusters.

# Molecular Spins for Next Generation Quantum Technologies

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Electron and nuclear spins in molecules possess discrete energy levels, and the associated quantum states can be tuned and coherently manipulated by means of external electromagnetic fields. Such systems therefore provide one of the simplest platforms to encode a quantum bit (qubit), the elementary unit of future quantum computers. Performing any useful computation demands much more than realizing a robust qubit—one also needs a large number of qubits and a reliable manner with which to integrate them into devices that can store and process information and implement quantum algorithms. This ‘scalability’ is arguably one of the challenges for which a chemistry-based bottom-up approach is best-suited [1]. Molecules, being much more versatile than atoms, and yet microscopic, are the quantum objects with the highest capacity to form non-trivial ordered states at the nanoscale and to be replicated in large numbers using chemical tools.

This talk will describe continuous-wave and pulsed electron paramagnetic resonance (EPR) studies of various families of lanthanide (Ln) containing molecules that have attracted our recent interest as potential next-generation spin qubits. Examples include Ln<sup>III</sup> bis-phthalocyanine complexes, where weak coupling between the spin density on the radical bearing (Pc)<sub>2</sub> ligands provides a means of addressing the electron and nuclear quantum states associated with the Ln<sup>III</sup> ion [2]. Another example involves the protection of spin qubits against decoherence processes caused by magnetic noise associated with the surrounding electron and nuclear spin baths [3]. Time permitting, I will describe several other new directions under exploration in the group.

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# Structure-Property Relationships in Molecule-Based Magnets and Photochromic Clusters

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Low coordination number complexes display magnetic properties that are among the most promising single-ion magnets known for to date. While weak ligand fields and relatively small spin orbit coupling parameters are generally encountered for first row transition metal complexes, second and third row analogues are expected to display considerably higher ones, possibly leading to magnetically anisotropic intermediate or low spin electronic configurations. Orbital degeneracy may be exploited to introduce first-order angular momentum contributions into the magnetic ground state. The key feature of this electronic configuration is that doubly degenerate spin ground states are retained regardless of the sign of the zero-field parameter, while less efficient second-order interactions, arising from mixing of spin-orbit coupled excited states, become less important for magnetic anisotropy.[1]

A series of single-molecule magnets (SMMs) containing sterically demanding tris(3-phenylpyrazolyl)borate ligands, namely (Tp<sup>Ph</sup>)MX analogues (M<sup>II</sup> = Mn, Fe, Co, Ni, Zn), were prepared and characterized via UV-vis, X-ray structural, electrochemical, and magnetic techniques. Spin ground states ranging from  $S = 5/2$  (Mn<sup>II</sup>) to zero (Zn<sup>2+</sup>) were found for the series. Tunable slow magnetic relaxation is seen with halide substitution in several mononuclear [(Tp<sup>Ph</sup>)M<sup>II</sup>X] (M<sup>II</sup> = Ni, Co; X = Cl, Br, I) complexes—a first for 4-coordinate Ni<sup>II</sup>. Interestingly, despite considerable magnetic anisotropy, five-coordinate (Tp<sup>Ph</sup>)Ni<sup>II</sup>Cl(3-phenylpyrazole), does not display slow magnetic relaxation even under an applied magnetic field. Density-functional theory, spectroscopic, and magnetic studies clearly demonstrate the importance of in-state orbital contributions in single-molecule magnets.

In part two, the rational design of structurally related multifunctional materials relies heavily on a thorough understanding of the optical and magnetic properties of their components. Over the past decade, we have exploited the pyrazolylborate family of building blocks, to serve as vehicles for the preparation of many single-molecule magnets and photochromic materials.[2] While numerous Fe/Co complexes and chains are known to display thermo- and photochromic behavior the analogous Fe/Mn ones remain unknown.[3] Using a modular approach, the magnetic and optical properties of tri- and tetranuclear clusters may be tuned via three general approaches: (1) ancillary ligand replacement, (2) anion substitution, and (3) electrophile addition. Recent efforts to prepare new bistable derivatives will be described.

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# Density Functional Theory Investigation of The Multiferroic Behavior in $[\text{Mn}_3]_2$ Single Molecular Magnet

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Relative to molecular magnets composed of three spin  $\frac{1}{2}$  ions, the understanding of spin-electric behavior in systems with higher spins, such as the  $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_3(\text{dpd})_{3/2}]_2$  molecule, also known as  $\text{Mn}_3$  dimers, is less well studied and deserving of more attention since on-site electronic excitations may be lower in energy than the charge transfer excitations associated with three spin  $\frac{1}{2}$  systems. Further it has been shown that with appropriate ligation, the  $\text{Mn}_3$  dimers can reside in a ferromagnetic ground state composed of three  $S=2$  spins, resulting in a single molecule magnet with total  $S=12$  [1]. Such FM behavior is expected to be unusual based upon generalizations of the Goodenough-Kanamori rules and the details associated with spin-electric behavior will be qualitatively different than for triangular-spin molecules with antiferromagnetic ordering. In this work we investigate these details using standard density functional theory calculations. In addition to studying the spin-electric behavior calculations analogous to those on a similar investigation of  $\text{Fe}_3\text{O}(\text{NC}_5\text{H}_5)_3(\text{O}_2\text{CCH}_5)_6$  [2], the results are reported to address the possible existence of multiferroic behavior in the  $[\text{Mn}_3]_2$  dimers. We report simulated electronic and magnetic structures that could be used to search for a different type of spin electric behavior and possible high-spin/low-spin transitions on the Mn centers. The methods we used are based on density functional theory at the level of generalized gradient approximation (GGA). We obtained the electronic and magnetic structure of the molecule using NRLMOL computational code which employs Gaussian orbitals to represent the Kohn-Sham orbitals. The self-consistent field (SCF) calculations are performed using the Perdew-Burke-Ernzerhof GGA approximation to describe exchange-correlation interactions. The conjugate-gradient scheme has been used for optimization of structures with the energy and force threshold of  $0.1 \times 10^{-5}$  hartree and 0.001 hartree/bohr, respectively. Spin excitation energies associated with the calculated Heisenberg Hamiltonians are determined from exact diagonalization techniques.

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## FLOSIC: Progress towards efficient density functional theory calculations without self-interaction

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Density Functional Theory (DFT) is the method of choice for the atomistic modeling of materials from first-principles, including molecular magnet compounds. Modern density functionals can be remarkably accurate in describing properties when atoms are near their equilibrium positions, yet all semi-local functionals are subject to self-interaction errors that appear in stretched-bond situations and in some interactions involving charge transfer. The Fermi-Löwdin orbital self-interaction correction (FLOSIC) method was developed to remove such errors efficiently by implementing the Perdew-Zunger self-interaction correction (PZ-SIC) without imposing computationally costly constraints. In this talk we outline the FLOSIC formalism and present results from several recent studies that demonstrate its success in removing self-interaction errors in practical calculations. For example, we show that FLOSIC: i) improves the description of magnetic exchange couplings; ii) shifts orbital energies to bring them into better agreement with electron removal energies; iii) yields more accurate dielectric properties such as dipole moments and polarizabilities; and iv) repairs the too-strong hydrogen bonds that plague DFT treatments of water. Finally, we discuss recent work[1] aimed at resolving the “paradox of SIC” – the fact that DFT-SIC can degrade the description of equilibrium properties, while improving predictions when self-interaction errors are dominant. We present new insights into the origin of this paradox and our initial success in developing a self-interaction free method that works in all settings. This research is being conducted in the FLOSIC Center, funded by U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences as part of the Computational Chemical Sciences Program under award number #DE-SC0018331.

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# Synthesis and EPR Studies of Pyrazine-Bridged Copper (II) Complexes

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The family of compounds synthesized and analyzed is comprised of pyrazine-bridged copper (II) chain complexes of two varieties: one with four methyl-substituted 2-pyridone ligands on each copper ion and the other with two of these ligands and two water molecules coordinated to each copper ion. Within both types of compounds, there are four variations due to the four possible positions of the methyl substituent on the 2-pyridone ligand. This family was selected for analysis via powder and single crystal EPR studies, in addition to SQUID magnetometry, due to its moderate superexchange interactions and significant isolation between chains. Preliminary EPR studies demonstrated drastic variation in electronic structure between compounds. Moreover, one compound, for which a Jahn-Teller elongation effect has been identified via single-crystal X-ray diffractometry, yielded particularly interesting results. While its geometry agrees with a rhombic system, EPR data for powder (collected at X-band and Q-band) and single-crystal (collected at X-band) samples indicate that its electronic structure agrees with an axial system. In two compounds, powder EPR results agree with the presence of a Jahn-Teller compression effect, but single-crystal X-ray diffractometry for these compounds are still in process. Although the chemical formulae across compounds in this family are analogous, their crystal packing varies greatly. Of the five compounds for which crystal structures have been solved, four of them are in distinct space groups. The consistent morphology of the crystals allowed for development of a methodology for orienting single-crystal EPR samples that was applicable throughout the family. The unit cell appeared to be aligned with the crystal frame;  $g_x$ ,  $g_y$ , and  $g_z$  all aligned well with bond axes, with g-factor values inversely correlated to bond length. The consistent morphology of the analyzed crystals allowed for a methodology to be devised for mounting each crystal and beginning data collection, which fortuitously made bond angle predictions from single crystal EPR data possible.

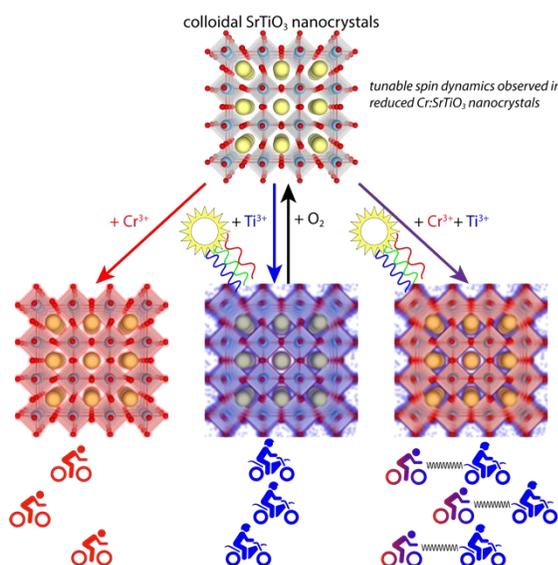
## Defect-controlled Magnetism in Metal Oxide Nanocrystals

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Manipulating the spin-polarization of free charge carriers in semiconductors is at the heart of spin-based electronics applications. Diluted magnetic semiconductors (DMSs) constitute one class of materials that impart magnetic exchange interactions between localized paramagnetic dopants and the charge carriers in the typically diamagnetic semiconductor. The archetypal DMS demonstrating ferromagnetism with a tunable critical temperature is  $\text{Mn}^{2+}$ -doped GaAs where  $\text{Mn}^{2+}$  ( $S = 5/2$ ) both substitutes at the  $\text{Ga}^{3+}$  site and serves as a shallow acceptor. This design principle of targeting *magnetic aliovalent* dopants has been extended to colloidal metal oxide semiconductor nanocrystals (NCs), namely  $\text{Fe}^{3+}$ -doped ZnO [1] and  $\text{Cr}^{3+}$ -doped  $\text{SrTiO}_3$  [2]. We will explore the electronic structures of these doped metal oxide NCs by electron paramagnetic resonance (EPR) and optical spectroscopy. In addition, we will demonstrate control over the magnetic properties of the dopant ions inside the NCs through an anaerobic photodoping procedure. In the case of  $\text{Cr}^{3+}$ -doped  $\text{SrTiO}_3$ , we demonstrate changes in the spin relaxation dynamics that persist above room temperature. The observed control over the magnetic properties can be quantitatively reversed by simple reoxidation of the charge carriers with air. The observed changes in the magnetic properties are optimized in the NCs by the inherent spatial confinement of the photodoped charge carriers and provide a potential use of these materials in quantum information processing technologies.



**Figure.** Schematic depiction of the spin relaxation rates of  $\text{Cr}^{3+}$  dopants in doped  $\text{SrTiO}_3$  before and after the introduction of  $\text{Ti}^{3+}$  defects with light.

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# **Synthesis and characterization of a Mn<sub>16</sub>Ba<sub>2</sub> cluster from reductive aggregation: influence of Ba on the magnetic properties of the corresponding homometallic Mn<sub>16</sub> cluster**

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The capability of Mn-oxo clusters to behave as nanoscale magnets has greatly interested the scientific community and leads to the need to develop new synthetic routes to new high nuclearity Mn-oxo clusters. Using the new synthetic approach, “reductive aggregation”, developed by our group in which a high oxidation state Mn source (MnO<sub>4</sub><sup>-</sup>) is reduced by MeOH in the presence of excess carboxylate, we have previously reported a family of Mn<sub>12</sub> and Mn<sub>16</sub> clusters with various topologies and interesting structural and magnetic properties. Until recently, reductive aggregation had not been explored in heterometallic chemistry, but our group recently had success in synthesizing a family of Mn<sub>5</sub>Ce<sub>3</sub> clusters using this method. In the present work, we have extending this method Mn/Ba heterometallic chemistry and have synthesized a Mn<sub>16</sub>Ba<sub>2</sub> cluster that reveals a surprising influence of the Ba on the magnetic properties vs the corresponding homometallic Mn<sub>16</sub> cluster.

# Redox-active ligand complexes: Scaffolds for multifunctional materials

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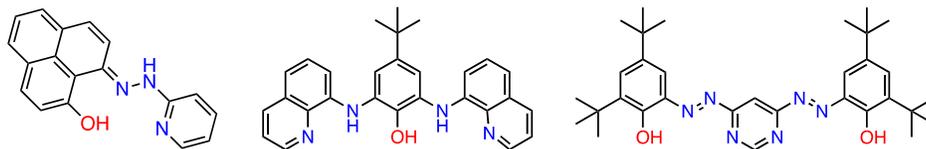
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Redox-active ligands (RALs) that can be readily oxidized or reduced to produce stable, open-shell species, are an ideal scaffold for the creation of multifunctional molecule-based materials. The coordination of RALs to metal ions has been demonstrated to be a successful strategy toward the preparation of valence tautomers [1], single molecule magnets (SMMs) [2], and recently, electrically conducting metal-organic frameworks (MOFs) [3]. Open-shell ligands have been shown to mediate strong magnetic exchange coupling with metal ions, resulting in well-isolated high spin ground states and better SMM properties. When open-shell ligands are incorporated into spin-crossover materials, the potential for new multifunctional behaviours is great (spin-crossover conductors, for example [4]). We have developed synthetic strategies to produce a range of RALs (some structures outlined below). In this presentation we will discuss coordination complexes formed with these and other RALs. We will highlight structures, electronic/magnetic properties, the range of different oxidation states featured by these ligands and recent efforts to synthesize new ligands and lanthanide complexes.



**Figure 1.** Redox-active ligands to be discussed in this presentation.

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# Cobalt-Manganese-Oxide Clusters as Potential Water Oxidation Catalysts (WOCs)

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The ability of Nature to achieve high-efficiency catalytic water oxidation in plants and cyanobacteria using the earth-abundant metals Mn and Ca is unmatched in any of the artificial systems known to date. Most of the latter rely on 4d and 5d metals such as Ru, Ir, etc. Thus, efficient catalytic oxidation of water using 3d metals such as Mn, Co and Cu remains a long-standing challenge for synthetic chemists. Homometallic, high oxidation state Mn and Co systems have been extensively researched as WOCs over the past 20 years, but only recently has an efficient water oxidation catalyst of Mn been reported – the very recent report of water oxidation electrocatalysis with a remarkably low overpotential of only 0.33 V by a member of the well-known  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  family of clusters [1]. While very active, the catalysis begins to decay within a few hours, assigned to slow decomposition of the  $\text{Mn}_{12}$  cluster. Since several robust Co/O clusters containing kinetically-inert CoIII have also been reported in the literature and shown to be good WOCs, we have initiated a program seeking to amalgamate the benefits of the two areas by developing mixed-metal Co/Mn/O/ $\text{RCO}_2^-$  clusters. In this presentation will be described the development of a synthetic route to a new family of high oxidation state  $\text{Co}^{\text{III}}/\text{Mn}^{\text{IV}}/\text{O}$  clusters and their characterization by X-ray crystallography, magnetic studies, and other techniques.

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# Spectroscopic Evidence of Spin-Phonon Coupling in an Yb(trensals) Single-Molecule Magnet

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Recently, the development of single molecule magnets has shifted rapidly away from the use of transition metals in favor of lanthanides due to their large single ion anisotropy. This is a direct consequence of the relatively strong spin-orbit coupling inherent to lanthanides, which, in the presence of the appropriate crystal field, gives rise to well separated spin-orbit project states that can permit slow relaxation of the magnetization. The motivation for studying such systems presumes that the so-called 'slow' Orbach process, involving thermal activation to excited magnetic states, provides the primary pathway through which the magnetization relaxes. However, previous AC-susceptibility measurements of the Yb(trensals) complex demonstrated a rather extreme case where, despite possessing a relatively large zero-field energy barrier to magnetization reversal of  $\sim 900 \text{ cm}^{-1}$ , a straight forward Arrhenius fit to the temperature dependent relaxation yielded an unrealistic activation energy of just  $38 \text{ cm}^{-1}$  [1]. This suggests a rather sizeable contribution from Raman relaxation, which can be attributed to strong coupling between the crystal field and the vibration degrees of freedom available to the system. Here, we present frequency domain magnetic resonance (FDMR) measurements in the far-infrared (FIR) range in an attempt to spectroscopically characterize the spin-vibron coupling associated with the previously observed Raman relaxation in Yb(trensals).

# Magnetism and structure of 6- and 4-coordinate nickel complexes with substituted aniline ligands

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The scientific community is interested in the structure, coordination, and the magneto-structural correlation principles of coordination complexes. In order to expand our understanding of such magneto-structural correlations, it is necessary to prepare and analyze families of compounds where the effect of small changes in structure on the metal can be observed. Although a variety of compounds of substituted aniline ligands with transition metal halides  $ML_2X_2$  [M = Zn, Cu, Co, Fe; X = Cl, Br] have been reported, less is known regarding the corresponding nickel halide complexes. There is current interest in nickel(II) because of its applications with antimicrobial activity, molecular sensors, and superconductors. In the magnetism community, nickel(II) is of interest because it is the prototypic metal for studying the Haldane Gap and because of its single ion anisotropy.

We have undertaken a study of the nickel halide complexes of 4-chloroaniline, 4-methylaniline, and 4-methoxyaniline to determine the effects the different functional groups have on the bonding and coordination of the complexes. In the course of this work, we have found a distinct preference of the nickel(II) ions to be 6-coordinate in a distorted octahedral configuration. We have isolated six of these complexes that appear to crystallize only as 6-coordinate species, regardless of the ligand stoichiometry. There are a variety of structures, including 4:1 complexes as well as 2:1 complexes with varying coordinated solvents and halides to ensure nickel(II) was 6-coordinate. In addition to these 6-coordinate complexes, we have also isolated four 4-coordinate species. We have been unable to isolate these compounds as crystals because of their instability, but their composition has been confirmed through X-ray powder diffraction patterns and a superconducting quantum interference device (SQUID). These 4-coordinate species are very interesting because they are all metamagnets, where they behave as ferromagnets through the chains of the complex and have weaker antiferromagnetic interactions in between the chains. We will present the synthesis of several members of this family of compounds as well as the structural and magnetic data for each compound, which will help show the effects the ligands and halides have on the magnetism and coordination of nickel(II).

# Unusual Magnetic Response of the Anisotropic $S = 1$ Spin Chain $[\text{Ni}(\text{HF}_2)(3\text{-Clpyridine})_4]\text{BF}_4$ : Inelastic Neutron Scattering Results

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$[\text{Ni}(\text{HF}_2)(3\text{-Clpyridine})_4]\text{BF}_4$  (hereafter NBCT) is a one-dimensional,  $S = 1$  spin chain material that has been identified to possess nearest-neighbor intrachain superexchange energy  $J/k_B = 4.86$  K and single-ion axial anisotropy energy  $D/k_B \approx 4.3$  K, while exhibiting no evidence of long-range magnetic order down to 25 mK [1]. These results placed NBCT in the unique position of being a real system potentially being located near the  $D/J \approx 1$  quantum critical point between the Haldane phase and the Large- $D$  quantum paramagnetic phase.

To further explore this exciting assignment, inelastic neutron scattering (INS) studies were performed on partially deuterated, partially  $^{11}\text{B}$  enriched NBCT polycrystalline samples in zero magnetic fields and down to 0.3 K. By comparing density matrix renormalization group calculations to the INS data, which provide microscopic insight, the magnetic properties of NBCT are more comprehensively identified, where  $J/k_B = 4.06$  K ( $0.35 \pm 0.01$  meV),  $D/k_B = 6.15$  K ( $0.53 \pm 0.01$  meV), and a non-negligible, finite rhombic single-ion anisotropy energy  $E$  exists, thereby yielding  $D/J = 1.51$  and  $E/J \approx 0.05$ . In contrast to the initial identification [1], our results and interpretations indicate that NBCT exists in the Large- $D$ , rather than Haldane, phase while still being close to a quantum critical phase transition. However, the existence, albeit small, of a finite  $E$  anisotropy appears to place NBCT closest to a  $\gamma$ -Néel long-range phase [2].

Future work on this interesting system will require sizable single crystals that will allow a more complete study of the underlying magnetocrystalline anisotropy.

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**Acknowledgements:** D.M. Pajerowski and A.P. Podlesnyak are supported through the Scientific User Facilities Division of the Department of Energy (DOE) Office of Science, sponsored by the Basic Energy Science (BES) Program, DOE Office of Science. This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory (ORNL). J. Herbrych was supported by the US DOE Office of Science, sponsored by the BES Program in Materials Sciences and Engineering Division of ORNL and by the Polish National Agency of Academic Exchange (NAWA) under contract PPN/PPO/2018/1/00035. Aspects of this work were partially supported by funding provided by the National Science Foundation (NSF) via DMR-1703003 (JLM) and DMR-1708410 (MWM). A portion of this work was performed at the National High Magnetic Field Laboratory (NHMFL), which is supported by NSF Cooperative Agreement No. DMR-1644779 and the State of Florida. We acknowledge enlightening conversations with C. Batista, G.E. Granroth, D.R. Talham, and A. Tsvetlik, and contributions from M. Whangbo for a calculation of the single-ion anisotropy. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

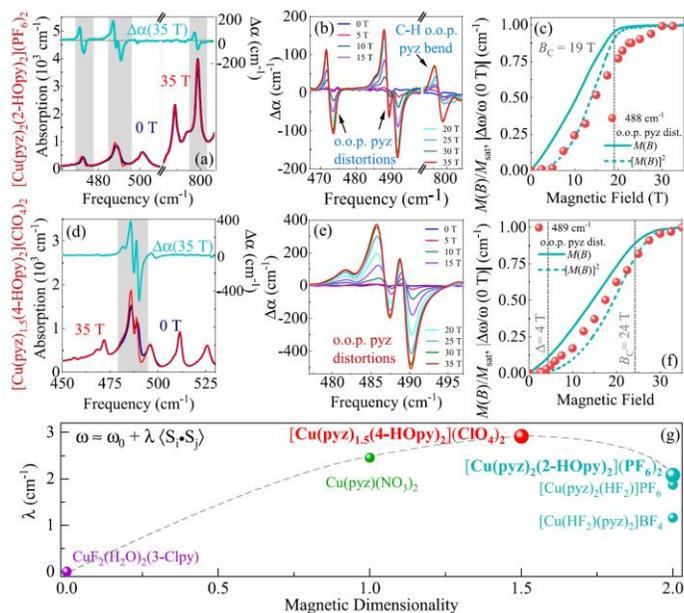
# Spin-phonon coupling in molecule-based materials and beyond

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In this presentation, I will review the mechanism of spin-vibrational coupling and discuss how this type of interaction can be understood in several different physical systems. The first case study will focus on a family of copper-containing coordination polymers with magnetic quantum phase transitions where structure-property relations can be developed to reveal how the coupling constant changes with dimensionality [Fig. 1].<sup>1</sup> The second example will examine a molecular multiferroic with hydrogen bonding interactions that give rise to magnetic exchange and a quantum phase transition to control the spin state. Here, we use vibrational spectroscopy to uncover the modes that couple to this transition and extract their coupling constants.<sup>2</sup> Finally, we will consider a 3d/5d hybrid system with record-high coercive field – up to an incredible 55 T. Here, we again unveil the fundamental excitations of the lattice that are sensitive to changes in the microscopic spin state + how and why this information impacts the developing magnetic model for ultra-high coercivity.<sup>3</sup> Together, these findings demonstrate the foundational role of spin-lattice entanglement in molecule-based quantum materials and beyond.

**Fig. 1:** Spin-lattice coupling across the magnetic quantum phase transitions in a series of copper-containing coordination polymers and the structure-property relations that can be unraveled in these materials. Coupling is maximum in the ladder-like system.<sup>1</sup>



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# Organic Cation Engineering for Low-dimensional Hybrid Perovskite Magnet

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Being able to control spin orderings in a magnetic material with tailored structures will bring in significant implication in both condensed matter physics and practical magnetic device applications. In this talk, I will introduce a series of Ruddlesden-Popper (RP) phase hybrid perovskites containing metal-halide octahedrons stabilized by organic spacers. The metal core used is manganese. We found by tuning the organic spacers alters the crystalline structure and unit cell volume, which subsequently impact the magnetic properties. Specifically, the perovskites containing linear shaped organics form orthorhombic phase that maintain the 2-dimensional RP phase structure. When using with bulky organics in the structure, the lattice form monoclinic phase, distorting the layered structure into 1-dimensional trimmer, where face sharing octahedron cages are observed. The temperature dependent magnetic susceptibility curves for those 2-dimensional structured perovskites show typical broadened inter-layer antiferromagnetic coupling near 100 kelvins, followed by a sharp phase transition around 40 kelvins. In two typical 2D RP structures, magnetic anisotropy was observed when field was applied along ab axis as opposed c-axis. On contrary, the 1-D systems do not show ordering till the temperature reaches below 10 kelvins. Interestingly, the trimmer system showed non-linear field dependent magnetization, where multiple plateaus are observed at low temperature. Our study reveals the magnetic orderings in the hybrid perovskite system can be tuned by the choice of organic cations, and more exotic spin states can be discovered by rational structure design.

# Molecular Platforms for Manipulating Magnetic Anisotropy and Coupling of Lanthanide Ions

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Recognizing the large single-ion anisotropy of several lanthanide ions, the coordination chemistry of the 4f<sup>n</sup> elements continues to be a lively area of research and has yielded single-molecule magnets (SMMs) with fairly high blocking temperatures. In this talk, we will discuss trends in structure and magnetic properties of relatively new classes of organometallic lanthanide complexes. We will present an overview of our recent results in the area of mononuclear lanthanide-metallocenophanes which resulted in the generation of optimized mononuclear lanthanide SMMs with blocking temperatures well beyond 10 K. We will also discuss the use of metallocenophane chemistry to promote significant magnetic coupling between lanthanide ions which results in effective reduction of quantum tunneling of the magnetization. Finally, our newest results towards the generation of high energy barrier SMMs will be presented.

# Hyperfine and nuclear quadrupole interactions in TbPc<sub>2</sub> and DyPc<sub>2</sub> molecules

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Nuclear spin levels may play an important role in understanding magnetization dynamics and implementation and control of quantum bits in lanthanide-based single-molecule magnets. Recently, Tb and Dy-based single-molecule magnets have attracted attention due to the large magnetic anisotropy barrier and the realization and control of quantum bits via external electric field. We investigate the hyperfine and quadrupole interactions for <sup>159</sup>Tb nucleus in anionic and neutral TbPc<sub>2</sub> molecules and for <sup>161</sup>Dy and <sup>163</sup>Dy nucleus in an anionic DyPc<sub>2</sub> molecule (Pc=phthalocyanine), using multiconfigurational ab-initio methods including spin-orbit interaction. We identify the most dominant mechanism to the hyperfine interaction for TbPc<sub>2</sub> and DyPc<sub>2</sub> molecules. We compare the calculated hyperfine and quadrupole interactions and the resulting electronic-nuclear levels to the experiment data for both types of molecules. We also discuss consequences of the interactions on the quantum tunneling of magnetization.

Funded by the Department of Energy Basic Energy Sciences Grant number DE-SC0018326. Computational support by Virginia Tech ARC.

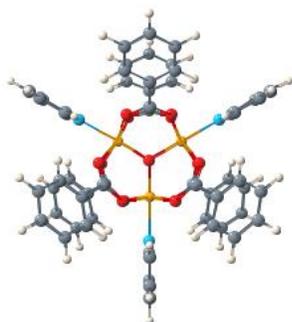
# Molecular Magnets for Quantum Sensing of Chemical Reactions and Qubits

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In this talk, the computational and theoretical challenges associated with the accurate quantum-mechanical computational description of molecular magnets[1] and recent quantum simulations[2-4] are presented within the context of recent experiments[5-7]. One example demonstrates that resonant tunneling of magnetization can deduce the chemical splitting of water into hydroxyl and hydrogen molecules. The second example demonstrates how computational density-functional-based methods are used to accurately determine the properties and complexities of putative molecular magnetic qubits that are composed of a perfect triangle of half-integer spin metal ions[3,4] and to suggest additional experiments.

The  $\text{Mn}_{12}\text{O}_{12}(\text{COOR})_{16}(\text{HOH})_4$  molecule, with  $S_4$  symmetry, has four of everything. Our recent calculations find that this system readily accepts four excess electrons at the cost of only 0.32 eV in vacuum. It exhibits a macro-spin with  $S=10$  and received significant past interest due to its quantum tunneling of magnetization (QTM). We show that the spectroscopic signatures associated with QTM are sensitive to the presence of the four HOH terminators (e.g. 4 waters vs.  $2\text{H}_2$  and  $2\text{OH}$ ) and to the number of added electrons (0 vs. 4). As such, QTM can provide an ultra-low-energy non-destructive technique for observation of water decomposition in a molecule that bears a striking similarity to the reaction center in the oxygen-evolving complex[2,7]

Recently, Boudalis *et al* have experimentally observed the magneto-electric effect in a chiral  $\text{Fe}_3\text{O}(\text{NC}_5\text{H}_5)_3(\text{O}_2\text{CC}_6\text{H}_5)_6$  molecule [5] and have noted further that this is the first possible spin-electric system based upon spin 5/2 metal centers. Our results [3], using standard density-functional methods, show that the spin-electric behavior of this molecule could be even more interesting as there are energetically competitive reference states with high and low local spins ( $S=5/2$  vs.  $S=1/2$ ) on the  $\text{Fe}^{3+}$  ions. We provide predictions of magnetic and x-ray spectroscopies to deduce the presence of both states. Possible uses for low-temperature quantum sensing of fields and pressure variations are suggested.

Recent efforts at improving quantum approximations for such systems will be highlighted[1].

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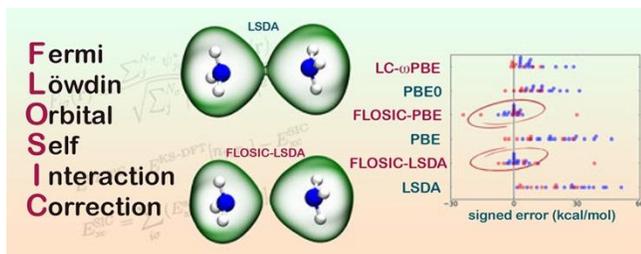
# Towards practical self-interaction free DFT: Recent advances and applications of the FLO-SIC method

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The effect of density functional theory (DFT) self-interaction error (SIE) on calculated molecular and solid-state properties has been known for a long time, and perhaps the most widely accepted framework for removing SIE in DFT is due to Perdew and Zunger (PZ) [1]. However, the high computational cost associated with minimizing the PZ energy expression makes the calculation of explicitly self-interaction free molecular properties still very challenging. Recently, an efficient implementation for SIE removal based on Fermi orbitals was proposed [2]. This method simplifies the computational bottleneck of optimizing a full unitary transformation, needed in standard PZ, by replacing it by a Fermi-Löwdin transformation, which depends only on one vector descriptor per orbital, or Fermi orbital descriptor (FOD). The Fermi-Löwdin orbital self-interaction correction (FLO-SIC) provides a computationally efficient alternative to the traditional PZ approach [2]. I will describe the FLO-SIC methodology and its advantages and caveats compared to standard PZ-SIC. I will also show our recent efforts to make FLO-SIC more efficient and user-friendly. As an illustration of the capabilities of the FLO-SIC method, I will review some recent results of the effect of SIE on several properties, such as dissociation energies and magnetic exchange couplings, and in other typical cases where SIC is important. This work is supported by the US Department of Energy DE-SC0005027 and DE-SC0001330.



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# Lanthanide-Radical Coordination Complexes: Trends in Isostructural Series

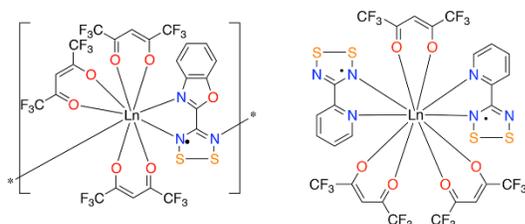
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The ability to manipulate supramolecular structure is a key element in the design of molecule-based magnets. Magnetic properties, including magnetic exchange (local) and magnetic ordering (bulk), rely on intermolecular interactions and thus on supramolecular architecture. Although we are still a long way from reliable Crystal Structure Prediction (CSP), many molecular systems are amenable to the incorporation of small alterations to the molecular structure that will manifest as modest, but important, changes in supramolecular structure. Systems that include lanthanide ions are particularly suited to the creation of isostructural series since bonding to lanthanides is primarily ionic in nature. Thus, the ionic radius is the key factor in determining structure, and small changes in ionic radius across the lanthanide period can generate a series in which the subtle role of specific intermolecular interactions is elucidated.

Our work using thiazyl radicals as paramagnetic ligands lends itself to the creation of isostructural series of lanthanide coordination complexes. Thiazyl radicals tend to exhibit a variety of intermolecular interactions, including strong, directional electrostatic contacts and pancake bonding. As a result, it is possible to create isostructural series of lanthanide-radical coordination complexes in which the interactions between thiazyl radicals are modified slightly by the changing ionic radii. Herein, two such series will be discussed, both of which have recently been completed.



**Figure.** Line drawings of Ln-radical coordination complexes.

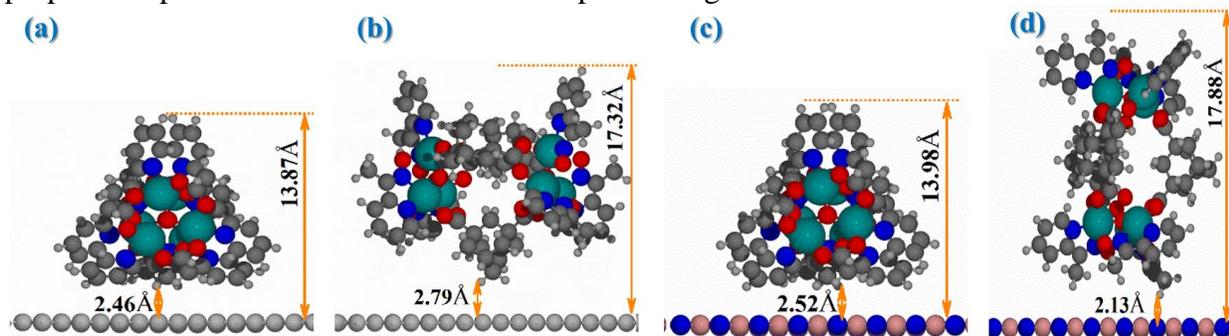
# Single-Molecule Magnets on Two Dimensional Materials: insights from ab initio calculations\*

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Single-molecule magnets (SMMs) continue to be attractive candidates as building blocks for a variety of quantum technologies. They possess high spin and their magnetic properties may be tuned. They may also be assembled as dimers for further applications. The  $Mn_3$  dimer is such an example in which the  $Mn_3$  triangles are connected via ligands to form either the ferromagnetic (FM) or the antiferromagnetic (AFM) ground state.<sup>1</sup> One challenge for SMMs is finding a suitable substrate that keeps their magnetic properties intact, helps stabilize their assembly, and allows access to probes. In this talk, after presenting results of our spin-polarized density functional theory based calculations of the electronic structure and magnetic properties of the  $Mn_3$  dimers themselves, we examine the modifications to these properties when the dimers are adsorbed on graphene and monolayer hexagonal boron nitride (*h*-BN), as well as when they are sandwiched between two layers of *h*-BN. Our calculations for the total spin of the FM ( $S = 12$ ) and AFM configurations of the isolated dimers agrees with the experimental results<sup>1</sup> only when the dimers are charged (+2) (similar to molecules in solvent) and these values are retained on both supports. We find that the calculated magnetic exchange interactions to be in reasonable agreement with those deduced from experiments, except for the case of the charged FM dimer. Furthermore, both the FM and AFM configurations of the  $[Mn_3]_2$  dimer retain their spin localization about the  $Mn^{3+}$  ions when deposited upon graphene. The binding energy for the system lies in the range 0.8 to 1.6 eV. We find very little charge transfer between the dimers and *h*-BN when the dimers are neutral and about  $0.28 e$  when they are charged (+2). Interestingly, for the dimers on graphene, the charge transfer is about  $0.3 e$  for the neutral dimers and about  $1.58 e$  when they are charged. We compare the effect of these two substrate on the magnetic properties and electronic structure of the  $Mn_3$  dimers and comment on the viability of the sandwiched structure for proposed experimental examinations of transport through the SMMs.



**Fig.** Supported  $Mn_3$  dimers: a) FM on graphene; b) AFM on graphene; c) FM on *h*-BN; d) AFM on *h*-BN

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\*This work is supported in part by DOE-DE-SC0019330.

# Quantifying multiple relaxation processes at magnetically “blocked” timescales

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Instrumental considerations dictate that the most common window for measurement of a single-molecule magnet's (SMM) characteristic relaxation time,  $\tau$ , falls within the timescale  $\tau = 1\text{ s} - 1\mu\text{s}$ . Within this time range, extensions of the Debye relaxation model allow extraction of magnetic relaxation information, even when more than one such process is present. The rapid and ongoing advancement of SMM strength has led to an abundance of systems with relaxation times exceeding 1 s and sometimes persisting in blocked states for minutes to hours or longer. In this long timescale regime (i.e.  $10^{-\infty}$  s),  $\tau$  is typically fit by modelling the zero-field magnetic relaxation profile to an exponential decay model. DC magnetization decay captures the dynamics of the overall ensemble but lacks many of the advantages of fitting in the frequency-domain. This presentation will focus on recent magnetic relaxation results made possible by a method described recently to extend frequency-dependent relaxation studies to arbitrarily long timescales.<sup>1</sup> A trinuclear Er(III) complex with multiple, noncolinear single-ion anisotropy axes serves as an example of complex relaxation dynamics that manifest outside of the normal range of measurement. Quantification of the time, temperature, and field-dependence of the operant relaxation processes can help to rationalize their origin and offer chemical strategies to alter or remove them -leading to better control and optimization of SMM behavior.

[1] Hilgar, J. D.; Butts, A. K.; Rinehart, J. D. *Phys. Chem. Chem. Phys.* **2019**, *21*, 22302.

# Molecular spin frustration in iron-oxo clusters leading to unusual high ground state spin

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The chemistry of polynuclear Fe(III) complexes continues to attract research interest due to its significance in bioinorganic chemistry, molecular magnetism, and material sciences. Metal-oxo clusters with a large number of unpaired electrons are desirable for building molecular-based magnetic materials. High spin Fe(III) ( $d^5$ ,  $S=5/2$ ) consists of five unpaired electrons, therefore, new polynuclear iron oxo-hydroxo complexes are synthesized to identify molecules with a large number of unpaired electrons. Literature precedence has shown that spin frustration in structural topologies observed in polynuclear iron-oxo complexes can serve as an effective medium to attain a significant number of unpaired electrons. Therefore, many researchers are interested in synthesizing new polynuclear iron-oxo complexes to discover interesting magnetic properties for the latter material. The use of chelating and bridging ligands in iron-oxo chemistry has led to several structural topologies in the past and have given nuclearities up to 34. Interestingly, the use of a combination of three or more ligands has been rare, and therefore we started an investigation combining carboxylic acid with triethanolamine, and picolinic acid in our search for new iron-oxo clusters. In this work, we describe the detailed syntheses, crystal structures and magnetic characterization of three new spin frustrated iron-oxo clusters.

# **Magneto-electric couplings in Quantum Materials**

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We have developed a new system for measuring the magnetic susceptibility in the presence of the external electric fields over a wide range of temperatures (1 K - 150 K). The changes to the magnetic susceptibility can be detected using a tunnel diode oscillator (TDO) circuit. TDO circuits have been shown to have a sensitivity on the order of 0.001ppm, making them a good candidate to measure small changes in magnetic susceptibility. In our design, the tunnel diode itself is separated from the sample chamber by 12 cm of low loss cryogenic cable to keep it at the constant temperature. The purpose of this study is to measure the magnetic response due to an applied electric field. Sample candidates for this experiment include spin crossover (SCO) materials and single-molecule magnets (SMM).

# Charge Transfer in Single-Molecule Magnetic Complexes



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Single-molecule magnetic (SMM) complexes  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ , with  $\text{R}=\text{-H, -CH}_3, \text{-CHCl}_2, \text{-C}_6\text{H}_5$ , have twelve Mn atoms in the core, eight of them are in 3+ charge state and located at peripheral ring of the molecule, while the four remaining Mn atoms in the center of the molecule are in 4+ charge state. When the SMM molecule is receiving the additional electron by excitation, this electron is localizing on one of the peripheral Mn atom, and the charge state of this atom is changing from  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$ , what is confirmed by experiment measuring the Mn-O bond lengths [Inorg. Chem. 2017, 56, 10706]. In order to develop the SMM with high catalytic activity, it is very important to know the energy barrier for electron transfer from  $\text{Mn}^{2+}$  atom to another  $\text{Mn}^{3+}$  atom located on diametral site of the molecule, in order to stimulate oxidation reaction. We are calculated the minimum energy pathway for electron transfer in tunneling regime calculating the energy barrier for electron motion by plotting the profile of electrostatic potential along possible pathways.

## Acknowledgements

US Department of Energy Basic Energy Sciences Energy Frontier Research Centers under Grant No. DE-SC0019330

# Interface and Matrix Effects on Spin Transition Solids

Daniel R. Talham,<sup>1</sup> John M. Cain,<sup>1</sup> Wanhong He,<sup>1</sup> Ashley C. Felts,<sup>1</sup> Ahmed Slimani<sup>2</sup>,  
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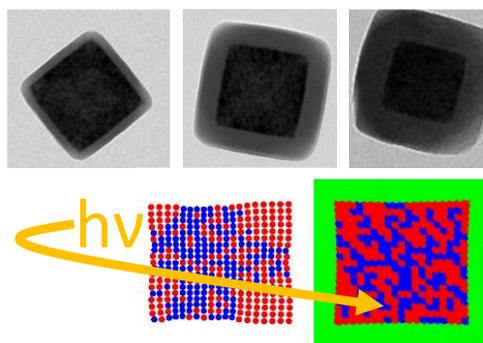
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If switchable spin transition magnetic networks are to be incorporated into complex architectures for applications ranging from spintronics to mechanical actuators, alterations in their behavior at surfaces or when coupled to other components must be understood. Earlier work showed that when spin-transition networks, such as the charge-transfer induced spin transition (CTIST) Prussian blue analogue,  $A_jCo_k[Fe(CN)_6]_l \cdot nH_2O$ , or LIESST-active Hofmann-like phases are incorporated into thin-film or particle heterostructures, thermally- or optically-induced spin changes couple across the interface to change behavior of the second material [1,2]. However, the response of the spin-transition network is also altered when included in a heterostructure. For example, volume changes associated with the  $A_jCo_k[Fe(CN)_6]_l \cdot nH_2O$  CTIST are inhibited when included in a core-shell particle, changing the elastic response of the phase transition. As a result, the transition temperature,  $T_{1/2}$ , of the thermally-induced transition and the hysteresis widths are altered, as is the relaxation from the light-induced state. Most notably, the rate of the light-induced CTIST increases by two orders of magnitude when the same particle is in a core-shell structure with  $K_{0.8}Ni_{4.0}[Cr(CN)_6]_{2.9} \cdot nH_2O$ . Experimental studies using magnetometry and synchrotron X-ray diffraction and nuclear resonant inelastic X-ray scattering (NRIXS) are combined with Monte Carlo simulations based on elastic models [2,3] to explain the new behavior.



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# Neutron scattering study of the coupled phenomena in molecular multiferroic $(\text{ND}_4)_2[\text{FeCl}_5(\text{D}_2\text{O})]$

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$(\text{NH}_4)_2[\text{FeCl}_5(\text{H}_2\text{O})]$  is a rare molecular magnet exhibiting direct coupling between magnetism and electric polarization as well as a very rich magnetic field versus temperature phase diagram [1-4]. Unlike its counterpart compounds where  $\text{NH}_4$  group is replaced by K, Cs, and Rb,  $(\text{NH}_4)_2[\text{FeCl}_5(\text{H}_2\text{O})]$  is the only system that undergoes two successive magnetic transitions at 7.3K and 6.8K, with the onset of ferroelectricity at 6.8K, suggesting  $\text{NH}_4$  plays a critical role in the unusual magnetic property of  $(\text{NH}_4)_2[\text{FeCl}_5(\text{H}_2\text{O})]$ . In order to study the magnetism, we grew large deuterated single crystals and performed both elastic and inelastic neutron scattering experiments to determine the magnetic structures and investigate the dynamics in this material. In this talk, I will present results of neutron-scattering experiments that provide insights on the nature of the coupled phenomena. Our inelastic neutron scattering results also reveal the role the  $\text{NH}_4^+$  ion played in the intriguing properties observed in  $(\text{NH}_4)_2[\text{FeCl}_5(\text{H}_2\text{O})]$ .

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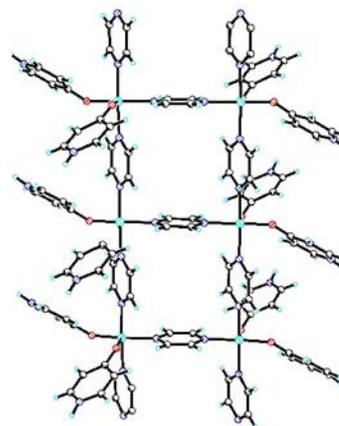
**Acknowledgments:** Research conducted at ORNL's Spallation Neutron Source and High Flux Isotope Reactor was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U. S. Department of Energy.

# Low-Dimensional Cu(II)-based Molecular Magnetic Materials; Benefits of hydroxypyridine/pyridone ligands

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The development of the lanthanum copper oxide-based superconductors and intrinsic relationship between the magnetic and electrical exchange in these materials has led to a renewed interest in Cu(II)-based magnetism over the past three decades, especially in materials where the magnetic interactions do not propagate equally in all dimensions. The very strong magnetic exchange observed in the copper oxides (typically  $\gg 600$  K) makes it impractical to study the magnetic exchange process in these materials. Hence, we have undertaken a program to prepare model compounds which exhibit a wide variety of magnetic lattices with moderate exchange where dimensionality of the magnetic exchange is limited. The preparation of families of such materials allows for structure-exchange correlations which can improve our understanding of the factors which control magnetic exchange. Examples of chains, layers and ladders based on a versatile family of hydroxypyridine ligands will be presented



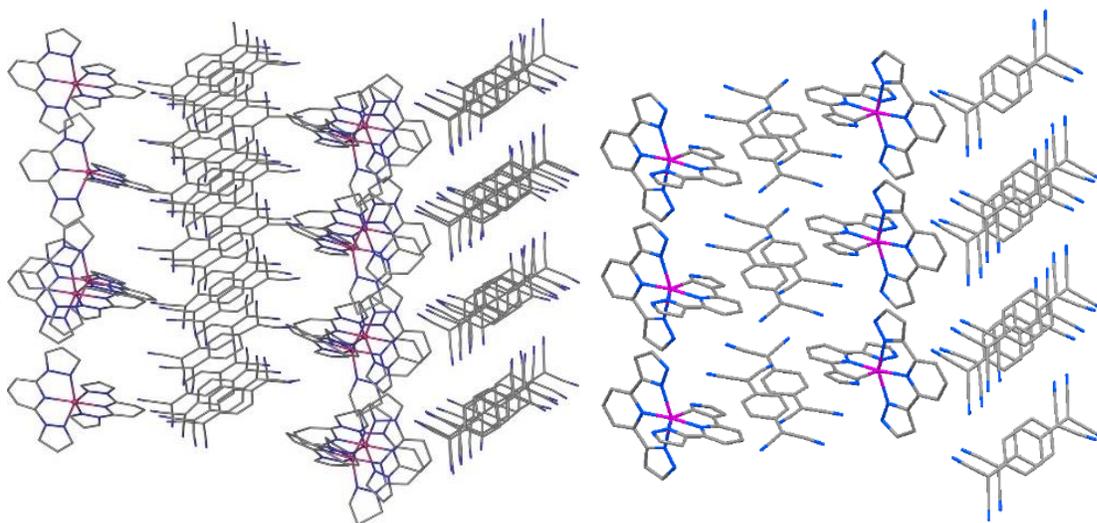
# Conducting Fe(II) Spin Crossover Complexes with TCNQ Radicals

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In recent year, extensive research efforts have been dedicated to the design of multifunctional materials<sup>1</sup> which exhibit spin-state switching and conductivity by combining Fe(II) spin-crossover (SCO) complexes and organic TCNQ-type acceptors. In such complexes, TCNQ<sup>• $\delta$ -</sup> radical anions ( $0 < \delta < 1$ ) are arranged in stacks that provide conducting pathways (Fig. 1). The stacking distances can be affected by structural changes induced by the change in the electronic configuration at the Fe(II) center, resulting in a synergy between SCO and electrical transport. The synthesis of such materials can be approached in two ways: (1) by coordinating TCNQ<sup>• $\delta$ -</sup> ligands directly to the Fe(II) center, which is partially protected by blocking ligands that limit the growth of extended structures; or (2) by co-crystallizing completely blocked Fe(II) centers with free TCNQ<sup>• $\delta$ -</sup> radicals.<sup>2</sup> We will discuss several examples of the second approach, in which homoleptic Fe(II) cationic SCO complexes with tridentate bis-pyrazolyl-pyridine (bpp) type ligands have been co-crystallized with fractionally-charged TCNQ<sup>• $\delta$ -</sup> radicals, resulting in complexes [Fe(3-bpp)<sub>2</sub>](TCNQ)<sub>3</sub>·3MeCN and [Fe(1-bpp)<sub>2</sub>](TCNQ)<sub>4</sub>·2MeCN. Both structures contain stacks of fractionally charged TCNQ<sup>• $\delta$ -</sup> radical anions organized in layers that alternate with cationic layers. To the best of our knowledge, these are the first examples of conducting molecular materials with abrupt temperature-driven spin transitions.



**Figure 1.** Crystal packing in [Fe(1-bpp)<sub>2</sub>](TCNQ)<sub>4</sub>·2MeCN (left) and [Fe(3-bpp)<sub>2</sub>](TCNQ)<sub>3</sub>·3MeCN (right), showing the layers of SCO cations alternating with the layers of TCNQ stacks. The interstitial solvent molecules and H atoms are omitted for clarity.

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# Coupled evolution of magnetic and ferroelectric states in $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$ under pressure

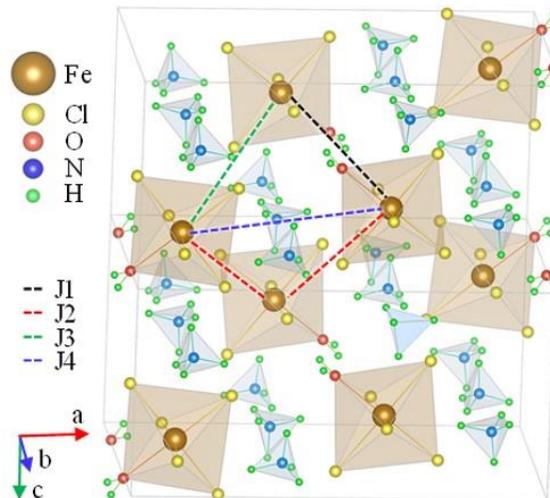
Yan Wu<sup>1</sup>, Na Su<sup>2</sup>, Bryan Chakoumakos<sup>1</sup>, Young Sun<sup>2</sup>, Jinguang Cheng<sup>2</sup>, Wei Tian<sup>1</sup> and Huibo Cao<sup>1</sup>

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Multiferroics have attracted tremendous research interests with their rich physics and potential in constructing next-generation multifunctional devices[1]. Metal-organic frameworks multiferroics have been one of the recent focus in single phase multiferroics investigations[2]. These materials are usually bonded with molecular force and their magnetic moments interacts through H-bond super-exchange couplings. As a result, pressure induced lattice change would lay a significant impact on the magnetic phase of these materials. We investigated the crystal structure, magnetism and ferroelectricity changes of  $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$  under pressure. Interesting magnetic transitions correlated with ferroelectricity is observed at systematic increased pressures. We identified the strong coupling between magnetic phase, ferroelectricity and the structure. The rich picture of the pressure effects on this molecular multiferroics system could bring new insights to the field.



**Figure.** Crystal structure of  $(\text{NH}_4)_2\text{FeCl}_5\cdot\text{H}_2\text{O}$ . Four of the strongest super-exchange coupling moments between Fe atoms in the structure are demonstrated, which is  $J1 \gg J2 \approx J4 > J3$ .

The research was supported by the U.S. DOE, Office of Science, Early Career Research Program Award KC0402010 and used the DOE User Facility operated by the ORNL.

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# Nature of hyperfine interactions in TbPc<sub>2</sub> and DyPc<sub>2</sub> single-molecule magnets

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Lanthanide-based single-ion magnetic molecules can have large magnetic hyperfine interactions as well as large magnetic anisotropy. Recent experimental studies reported tunability of these properties by changes of chemical environments or by application of external stimuli for device applications. In order to provide insight onto the origin and mechanism of such tunability, here we investigate the magnetic hyperfine and nuclear quadrupole interactions for the rare-earth nuclei in TbPc<sub>2</sub> and DyPc<sub>2</sub> single-molecule magnets using multiconfigurational *ab-initio* methods including spin-orbit interaction.

The microscopic Hamiltonian is mapped onto an effective Hamiltonian with an electronic pseudo-spin  $S=1/2$ . We discuss the physical origin of *ab-initio*-calculated hyperfine interaction parameters and their dependence on the experimental molecular geometry, rare-earth ion type, and structure distortions. We show the *ab-initio*-calculated electronic-nuclear spectrum and compare with experimental data. We further analyze the role of the non-axial quadrupole and off-diagonal magnetic hyperfine interactions in formation of avoided level crossings and magnetization dynamics.

Funded by the Department of Energy Basic Energy Sciences grant No DE-SC0018326. Computational support by Virginia Tech ARC.

# Spectroscopic Studies of Single-Molecule Magnets

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Large separations between magnetic ground and excited states in metal complexes are critical to the properties of single-molecule magnets (SMMs). However, there are few experimental methods to directly determine separations larger than  $30 \text{ cm}^{-1}$ . We have used inelastic neutron scattering (INS), far-IR and Raman spectroscopies to probe these separations in  $\text{Er}[\text{N}(\text{SiMe}_3)_2]_3$ ,  $\text{Fe}[\text{C}(\text{SiMe}_3)_3]_2$ ,  $(\text{NBu}^n_4)_2[\text{ReX}_4(\text{ox})]$  ( $\text{X}^- = \text{Br}^-, \text{Cl}^-$ ;  $\text{ox}^{2-} = \text{oxalate}$ ) and  $\text{Co}(\text{AsPh}_3)_2\text{I}_2$ . In addition, far-IR and Raman show spin-phonon couplings in several complexes.

## First-Principles study of an $S = 1$ quasi-1D quantum molecular magnetic material

Maier Yazbeck, Jie-Xiang Yu, Shuanglong Liu, Neil S. Sullivan and Hai-Ping Cheng

We use density functional theory to study the structural, magnetic and electronic structure of the organo-metallic quantum magnet  $\text{NiCl}_2 \cdot 4\text{SC}(\text{NH}_2)_2$  (DTN). Recent work has demonstrated the quasi-1D nature of the molecular crystal and its quantum phase transitions at low temperatures. This includes a magneto-electric coupling and, when doped with Br, the presence of an exotic Bose-glass state. We systematically show that, by using the generalized gradient approximation (GGA) with inclusion of a van der Waals term to account for weak inter-molecular forces and by introducing a Hubbard U term to the total energy, our calculations reproduce the magnetic anisotropy, the inter-molecular exchange coupling strength and the magneto-electric effect in DTN, which were observed in previous experiments. Further analysis into the electronic structure gives insight into the underlying magnetic interactions, including what mechanisms may be causing the ME effect. Using this computationally efficient model, we predict what effect applying an electric field might have on the magnetic properties of this quantum magnet.

# Designing materials with abrupt hysteretic spin transitions

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Spin crossover (SCO) is a magnetic bistability phenomenon, wherein a moderate ligand field strength leads to energetic similarity between two different spin states, which, as a result, can be interconverted by external stimuli such as temperature, pressure, or photoexcitation [1]. This spin-state switching is coupled to structural (Fe-N bond lengths, unit cell volume) and spectral changes, making SCO materials appealing for applications in spintronic devices, data storage, sensors, and mechanical actuators [2].

In this work, we report the synthesis and characterization of two new SCO complexes that exhibit abrupt hysteretic spin transitions. Heteroleptic  $[\text{Fe}(\text{tpma})(\text{xnap-bim})](\text{ClO}_4)_2$  (tpma = tris(pyridin-2-ylmethyl)amine, xnap-bim = 8,15-dihydrodiimidazo[1,2-a:2',1'-c]naphtho[2,3-f][1,4]diazocine) crystallizes in the  $P-1$  space group and contains two interstitial molecules of pyridine molecules per formula unit. Exposure to air results in rapid loss of the interstitial solvent, as shown by thermogravimetric analysis. The resulting material exhibits an abrupt spin transition at  $T_{1/2} = 127$  K and 1 K hysteresis loop. A homoleptic complex  $[\text{Fe}(\text{bpt})_2](\text{BF}_4)_2$  (bpt = bis(pyridin-2-ylmethyl)sulfane) exhibits abrupt spin crossover with a 7 K wide hysteresis. To the best of our knowledge, this is the first example of a *homoleptic* Fe(II) SCO complex with the  $\{\text{N}_4\text{S}_2\}$  coordination environment and also the first example of an abrupt spin transition in complexes with such coordination. Further studies of these materials will probe the possibility to observe spin-state conversion under irradiation.

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# **Jahn-Teller solid, liquid and gas in spin-crossover system Mn(taa)**

Jie-Xiang Yu

Jahn Teller (JT) distortions play important roles in many spin-crossovers (SCO) in molecule-based magnets. Long-range ordering of the JT distortions in the crystalline molecular magnet Mn(taa) has been shown to lead to magnetoelectric coupling, which is the interplay between magnetism and electric polarization or dielectric properties. Our theoretical study based on first-principles calculations and Monte Carlo simulations on Mn(taa) reproduces the SCO and magnetoelectric coupling. More importantly, a low-temperature Jahn-Teller ordered (solid) phase, an intermediate-temperature dynamically correlated (liquid) phase, and an uncorrelated (gas) phase are identified in the high-spin region. In particular, the Jahn-Teller liquid phase arises from competition between mixing with low-spin impurities, which drives the disorder, and inter-molecular strain interaction. The latter is a key factor in both the spin-crossover phase transition and the magnetoelectric coupling. Jahn-Teller liquids may exist in other spin-crossover materials and materials that have multiple equivalent Jahn-Teller axes.

# Nuclear-Spin-Based Strategies to Control Molecular Spin Coherence

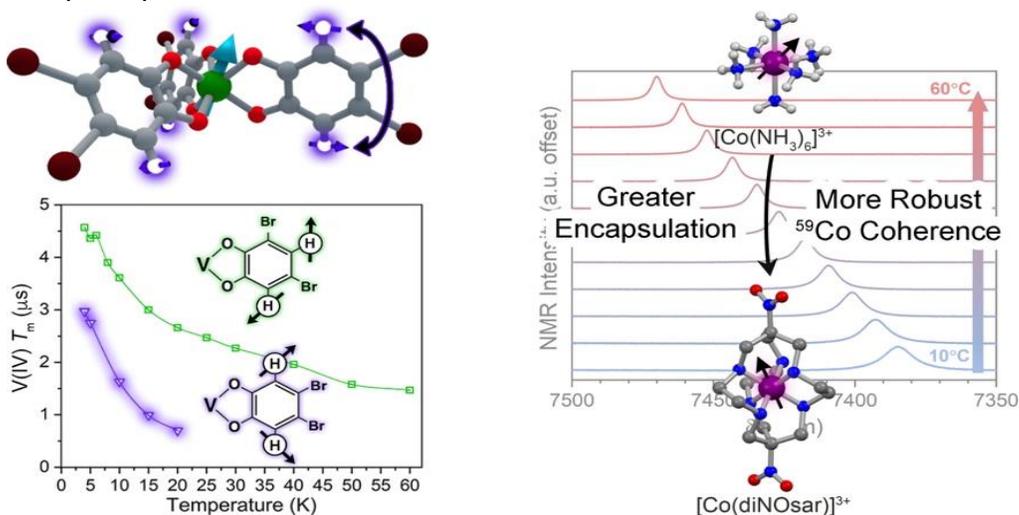
J. Zadrozny, C. Jackson, T. Ozvat, C. Lin, S. Johnson, M. Peña, A. Campanella

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The development of new qubit systems relies on the ability to create robust spin coherence in magnetic systems. Molecules, with their extensive chemical tunability, are a perfect platform for directed fundamental studies to understand how structure relates to spin coherence. In this talk, I will talk about our two major efforts to understand and control spin coherence in molecules using nuclear spins as the main design principle.

In the first effort from my lab, I will talk about how nuclear spins on ligand shells and counterions are among the most important in dictating electronic spin coherence [1,2]. Nuclear spins in the environment create a local magnetic noise, which destabilizes coherence. In this section of the talk, I will show how to modulate this magnetic noise through detailed fundamental studies of the canonical vanadium complex  $[V(\text{cat})_3]^{2-}$  (where cat = catecholate). Here specifically, I will delineate how the identity and specific substitutional patterning of nuclear spins in a complex and counterion impact the coherence stability.

In the second part of the presentation, I will discuss our efforts to harness the coherence of Cobalt-59 nuclear spin qubits via molecular design [3]. Nuclear spins display notably robust spin coherence (relative to electronic spins), yet are relatively less explored owing to, in part, the lack of environmental sensitivity. In this section of the talk, I will cover some of our efforts learn how to manipulate the sensitivity of the coherence in Cobalt-59 nuclear spin qubits. In the long term, both of the efforts covered in this presentation will contribute to the advancement of molecular qubit species.



**Figure.** This presentation will cover our efforts to manipulate molecular spin coherence via nuclear spin engineering.

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## **Coupled magnetic, electric and structural orders in metal-organic complexes including spin crossovers**

Vivien Zapf

We explore metal-organic complexes that show unconventional routes to magnetoelectric behavior. Traditionally, magnetoelectric behavior has been most commonly studied in inorganic oxides, where ferro or antiferromagnetism couples to dielectric or ferroelectric properties. Such coupling allows an electric field to control and switch e.g. a quantum magnetic state or vice versa. This field contains a wealth of intriguing fundamental science, as well as applications being targeted in ultra-low power sensing, qubits, memories, tunable antennas, and other devices. In this talk I will discuss our recent efforts to extend this field of magnetoelectrics to metal-organic complexes, which contain transition metal ions and organic ligands. These compounds tend to have soft lattices that mediate magnetoelectric coupling, and a broad array of intriguing forms of magnetism going beyond (anti) ferromagnetism. I will show results on spin crossovers where the spin state of a transition metal ion changes with applied magnetic fields, thereby modifying the electric polarization. We studied several Mn-based spin crossovers where magnetic fields toggle the spin state and thereby induce structural phase transitions or Jahn Teller effects. These structural changes result in very strong magnetoelectric coupling as well as complex phase diagrams. I will also discuss metal-organic frameworks that are effectively intrinsic heterostructures where magnetic and electric properties can be combined with flexible architectures. I will review the state of this nascent field and potential new directions.

# **Boost all-electron full-potential DFT calculation with the domain specific SIRIUS library**

Long Zhang, Samuel Trickey, Hai-Ping Cheng  
Department of Physics and Center for Molecular Magnetic Quantum Materials,  
University of Florida

We introduce the domain specific SIRIUS library for full potential linearized augmented plane wave (FP-LAPW) and pseudo-potential plane wave (PP-PW) DFT calculations. SIRIUS is a collection of common calculation elements within the family of plane wave DFT. By abstracting and encapsulating the common objects like: lattice vectors, atomic configuration, plane wave G vectors, G+k vectors, FFT grid, charge density, effective potential, local orbitals and wavefunctions etc., SIRIUS can be interfaced with FP-LAPW codes like ELK, EXCITING Berlin and EXCITING Plus, and PP-PW codes like Quantum Espresso. The library includes both direct eigen system solver like LAPACK and ScaLAPACK and iterative type eigen system solver of the Davidson type, so that it can extend the ability of host code to deal with larger systems. The library also implements multi-level MPI parallelization so that the host code can benefit from distributed k-point parallelization and band parallelization within one k-point, and thread level shared memory parallelization within one rank. We demonstrate the accuracy and efficiency of SIRIUS library by interfacing it to the EXCITING Plus FP-LAPW code. The interface specifically improved the host code with the band parallelization within one k-point and the Davidson eigen solver. We tested small crystalline materials and got good accuracy in total energy and magnetic moment. We also tested isolated molecules up to 100-200 atoms and got almost ideal scaling. The overall benchmark results show that SIRIUS is a powerful computational tool for all-electron DFT calculation.

# Many-body localization from random magnetic anisotropy

Xiaoguang Zhang

One of the main difficulties of observing many-body localization in natural solid-state materials is creating strong enough disorder. A strong random local magnetic field is difficult to achieve in a solid state material. We propose exploiting large random magnetic anisotropy, either in magnitude or direction, which can be realized in organo-metallic quantum magnets. We present the phase diagram of an  $S = 1$  Heisenberg chain in terms of both a random magnetic anisotropy and a random magnetic field. The many-body localization phase emerges with sufficiently large anisotropy under very small random fields. We propose candidate materials of doped single-chain organo-metallic quantum magnets for realizing many-body localization, where either orientation disorder or substitution of metal ions can create large random magnetic anisotropy required in our prediction.