Single-Molecule Magnets: Insights from High-Field EPR

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Outline

Part I
• Overview of the Magnet Lab
• Why high-fields/frequency EPR, with brief examples
• Overview of instrumentation and personnel at lab

Part II
• Introduction to single-molecule magnets (SMMs)
• The best known SMM, Mn$_{12}$acetate
• Simpler examples and important insights from EPR

Summary
National High Magnetic Field Laboratory

Multi-site Facilities: Tallahassee FL, Gainesville FL, Los Alamos NM
Multi-disciplinary and Inter-disciplinary Scientific Research
Annual User Program: ~1000 Scientists

www.magnet.fsu.edu

Florida State University

Los Alamos National Laboratory

University of Florida

Advanced Magnetic Resonance Imaging and Spectroscopy Facility

11.1T MRI Magnet
400mm warm bore

45T Hybrid DC Magnet

900MHz 105mm bore NMR Magnet

University of Florida

65T Pulse Magnet
15mm bore

1.4 GVA Motor-Generator

High B/T Facility
17T, 6wks at 1mK

Los Alamos National Laboratory

11.1T MRI Magnet
400mm warm bore
Some Statistics:

- Supercon. outsert – 11.5 T
- Resistive insert – 33.5 T (up to 74kA @ ~450V)
- Magnet rated at 33 MW
- 0.5 m³/s de-ionized H₂O
- Lab rated at 56 MW
- $7.2M/yr in electricity ~30% of lab’s NSF budget
  ~7% Tallahassee usage
  Lot more @ peak loads
  $4,600/hour at peak
- Fully compatible with several EPR instruments + many other techniques
Why high-fields and high-frequencies?

Increased resolution in terms of g-factor anisotropy

\[ g_i = 2.00 \]  
\[ g_j = 1.80 \]
#1 — Why high-fields and high-frequencies?
Increased resolution in terms of g-factor anisotropy

Organic radical DPPH (Diphenyl-Picryl-Hydrazyl) in frozen toluene

**Simulation A**

\[ g_x = 2.0050, \quad g_y = 2.0043, \quad g_z = 2.0032 \]

\[ A_x = A_y \approx 0, \quad A_z = 20.35 \text{ G} \]

A. Ozarowski (unpublished)

**Simulation B**

\[ g_x = g_y = 2.0045, \quad g_z = 2.0032 \]

\[ A_x = A_y \approx 0, \quad A_z = 20.35 \text{ G} \]
#2 — Why high-fields and high-frequencies?
Tetrahedral $\text{Co}^{2+}$, $3d^7$ with spin $S = \frac{3}{2}$: the ‘Florida map’
#2 — Why high-fields and high-frequencies?

Tetrahedral Co$^{2+}$, 3$d^7$ with spin $S = 3/2$: the ‘Florida map’

Highest frequency commercial spectrometer

Why high-fields and high-frequencies?

Tetrahedral Co$^{2+}$, 3$d^7$ with spin $S = \frac{3}{2}$: the ‘Florida map’

Nearly all EPR performed Here at X-band (9 GHz)
Why high-fields and high-frequencies?

New (emergent) physics at high magnetic fields

Example: BaCuSi$_2$O$_6$ spin $s = \frac{1}{2}$ dimer system with isotropic (?) zero-field Hamiltonian

*BEC

*Han Dynasty et al., Early Chinese J. Chem 1, 1 (~0000).
Sebastian et al., PRB 74, 180401(R) (2006).
#4 — Why high-fields and high-frequencies?
Other: sensitivity, temporal resolution, etc..

A. Higher fields/frequencies
   → shorter wavelengths + higher ratio of $B/T$
   → Better sample filling factors
   → Increased absolute spin sensitivity

B. CW spectra recorded at higher $f$ are sensitive to faster motions

C. Optical signal processing becomes possible for $f \sim 100$ GHz
   → Faster time-domain EPR (spin-echo, FID)*

D. Greater orientational ($g$) selectivity in 2D pulsed EPR

E. Dynamic Nuclear Polarization
   → Advantages of NMR increase with increasing field

*Most significant obstacle is the availability of high-power sources
working at $f > 100$GHz, and subsequent signal processing
Technological Challenges: Microwave Sources

Multiplier chain

Molecular gas laser
Gunns (pulsed)
BWO
MVNA
Homodyne
Bruker

X QW

BWO
VNA

0 100 200 300 400 500 600 700 800 900 1000
Frequency (GHz)
114 – 336 GHz, Super-heterodyne
Also pulsed

FIR laser, 800-2500 GHz, 45 T hybrid

Homodyne (190-660 GHz)
Transmission (23-660)

BWO – Keck magnet
(150-900 GHz)
# EMR Systems at the Magnet Lab in Tallahassee

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>Frequency (GHz)</th>
<th>Field range (T)</th>
<th>C.W. - EPR</th>
<th>Pulsed</th>
<th>Time Resolved</th>
<th>ENDOR</th>
<th>Rotation</th>
<th>Absolute Sensitivity at 290 K (spins/mT)</th>
<th>Concentration Sensitivity at 290 K (spin/cm³·mT)</th>
<th>Max. sample size (µl)</th>
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<tbody>
<tr>
<td>Transmission</td>
<td>23-660</td>
<td>0-17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10^{13}</td>
<td>5×10^{13}</td>
<td>200</td>
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<tr>
<td>Homodyne QO</td>
<td>190-670</td>
<td>0-17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5×10^{11}</td>
<td>2×10^{13}</td>
<td>10</td>
</tr>
<tr>
<td>Heterodyne QO &amp; Transmission</td>
<td>120, 240, 336</td>
<td>0-12.5</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>10^9 (in cavity)</td>
<td>5×10^{13}</td>
<td>0.1</td>
</tr>
<tr>
<td>DC-field QO &amp; Transmission</td>
<td>50-900</td>
<td>0-45</td>
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<td></td>
<td>10^9 (in cavity)</td>
<td>2×10^{11}</td>
<td>2×10^{12}</td>
</tr>
<tr>
<td>Bruker X-band</td>
<td>9.7</td>
<td>0-1.5</td>
<td></td>
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<td></td>
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<td>10^{11}</td>
<td>10^{13}</td>
<td>70</td>
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<td>Bruker W-band</td>
<td>95</td>
<td>0-6</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>5×10^{8}</td>
<td>10^{12}</td>
<td>0.4</td>
</tr>
</tbody>
</table>

1. The absolute sensitivity is the minimum number of detectable spins per mT linewidth and a 1 Hz bandwidth at room temperature.
2. In combination with a far-infrared laser, selected frequencies up to 2500 GHz are available.

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**Hans van Tol**  **Andrew Ozarowski**  **Jurek Krzystek**
Research Funding Opportunities

The Magnet Lab strives to further magnet-related science and engineering by offering the First-Time User Support Program and the Visiting Scientist Program. In addition, Magnet Lab personnel are eligible to apply for funding from the User Collaboration Grants Program. All requests for support are carefully reviewed and, in some instances, highly competitive.

First-Time User Support

The Mag Lab is charged by the National Science Foundation with developing and maintaining facilities for magnet-related research that are open to all qualified scientists and engineers through a peer-reviewed proposal process. Facilities are generally available to users without cost. In an effort to encourage new research activities, first-time users may request modest support for travel expenses. Support for this funding is provided by the State of Florida and is available for Tallahassee facilities only.

Support: About $500.

Application Info: Discuss your request with the applicable facility director. There is no deadline.

Contact: Applicable facility director or Eric Palm, director of the DC Field Facility.

Visiting Scientist Program

The Mag Lab offers researchers from academia, industry and national laboratories the opportunity to use the unique, world-class facilities of the Mag Lab to conduct magnet-related research. The Visiting Scientist Program (VSP) provides financial support for these research projects on a competitive basis.

The primary intent of this program is to provide greater access to our facilities and to seed research programs that help advance the laboratory. Funding is principally intended to support travel and local expenses. Requests for stipends are considered but given a lower priority.
Part II
Single-Molecule Magnets
The king of single-molecule magnets – \( \text{Mn}_{12} \)

**Crystals (3D arrays)**
- High symmetry - \( S_4 \)
- Monodisperse

**Organic ligands** (insulation)

**Axial anisotropy from Jahn-Teller elongation on \( \text{Mn}^{\text{III}}-\text{O} \) bridges**

\( S = (8 \times 2) - (4 \times 3/2) \)
\( S = 10 \)

\( \text{Mn}_{12}\)-acetate (Lis - 1980); \( \text{Mn}_{12}\)-tBuAc (Murugesu – 2005, unpublished)
The king of single-molecule magnets – Mn\textsubscript{12}

Magnetic anisotropy $\rightarrow$ bistability, hysteresis

[Mn\textsubscript{12}O\textsubscript{12}(O_2CCH_2Bu^t)_\textsubscript{16}(MeOH)_\textsubscript{4}]\cdot\text{MeOH}

- Ensemble average (Avogadro number)
- Hysteresis, $T < 4K$
- Steps evidence for quantum tunneling of $M$

Wernsdorfer, PRL 96, 057208 (2006)
Christou group (U. of FL)

Mn₄, Mn₁₂, Mn₃₀, Mn₈₄

Quantum world
Molecular (bottom-up) approach

Classical world
Classical (top-down) approach
Not only manganese

\[ \text{[Fe}_8\text{O}_2\text{(OH)}_{12}\text{(tacn)}_6\text{]Br}_8 \]

**Biaxial system**

\[ S = 10 \]

\[ \text{[Ni(hmp)(dmb)Cl]}_4 \]

\[ S = 4, \text{ } S_4 \text{ symmetry} \]

Also: Co, Cr, etc.

1. Large spin ground state

2. Axial magnetoanisotropy

\[ \hat{\mathcal{H}}_{zfs} = D \hat{S}_z^2 \quad (D < 0) \]
The giant spin approximation

\[ S = (8 \times 2) - (4 \times 3/2) \]

\[ S = 10 \]

Magnetic anisotropy \(\rightarrow\) bistability, hysteresis
The giant spin approximation

Simplest effective model: uniaxial anisotropy

\[ \mathcal{E}(m_s) = -|D|m_s^2 \]

Magnetic anisotropy \(\rightarrow\) bistability, hysteresis
Quantum effects at the nanoscale ($S = 10$)

Simplest effective model: uniaxial anisotropy

$$\mathcal{E}(m_s) = -|D| m_s^2$$

- Small barrier - $DS^2$
- Superparamagnetic at most temperatures

Thermal activation

$|D| \sim 0.1 - 1\ K$ for a typical single molecule magnet

Spin projection - $m_s$

Energy

$E_{m_s}$

-10 -8 -6 -4 -2 0 2 4 6 8 10

$E_{-10} E_{-9} E_{-8} E_{-7} E_{-6} E_{-5} E_{-4} E_4 E_5 E_6 E_7 E_8 E_9 E_{10}$
Quantum effects at the nanoscale ($S = 10$)

Break axial symmetry:

$$\hat{H} = D\hat{S}_z^2 + \hat{H}_T$$

$$[\hat{H}_T, \hat{S}_z] \neq 0$$

Contains $\hat{S}_x$ and $\hat{S}_y$.

- $m_s$ not good quantum #
- Mixing of $m_s$ states
  \[\Rightarrow\] resonant tunneling
  (of $m_s$) through barrier
Quantum effects at the nanoscale ($S = 10$)

- **Spin projection** - $m_s$
  - $E_{m_s}$
  - $-10, -8, -6, -4, -2, 0, 2, 4, 6, 8, 10$

**Break axial symmetry:**

\[ \hat{H} = D\hat{S}_z^2 + \hat{H}_T \]

- **Energy**
- **Ground state degeneracy** lifted by $\hat{H}_T$:
  \[ \Delta_0 \propto \left( \frac{\hat{H}_T}{D} \right)^{S/n} \quad [n = 1, 2, \ldots] \]

- **Temperature-independent quantum relaxation** as $T \rightarrow 0$

- **Ground states** a mixture of pure "up" and pure "down".

- **Tunnel splitting** a measure of tunneling rate
Application of a longitudinal magnetic field

Spin projection - $m_s$

Application of a longitudinal magnetic field

\[ \hat{H} = D\hat{S}^2_z + \hat{H}_T + g\mu_B\vec{B} \cdot \vec{S} \]

\[ \vec{B} \cdot \vec{S} \equiv B_x\hat{S}_x + B_y\hat{S}_y + B_z\hat{S}_z \]

Consider only $B//z$:

(also neglect transverse interactions)

\[ \mathcal{E}(m_s) = -|D|m_s^2 + g\mu_B Bm_s \]

- System off resonance
- Magnetic quantum tunneling is suppressed
- Metastable magnetization is blocked ("down" spins)
Application of a longitudinal magnetic field

Spin projection - $m_s$

$\hat{H} = D\hat{S}_z^2 + \hat{H}_T + g\mu_B\vec{B} \cdot \hat{S}$

$\vec{B} \cdot \hat{S} \equiv B_x\hat{S}_x + B_y\hat{S}_y + B_z\hat{S}_z$

Consider only $B//z$:
(also neglect transverse interactions)

$E(m_s) = -|D|m_s^2 + g\mu_B B m_s$

- Resonant magnetic quantum tunneling resumes
- Metastable magnetization can relax from "down" to "up"
Hysteresis and magnetization steps

This hysteresis loop represents an ensemble average of the response of ~$10^{23}$ molecules.

**Mn$_{12}$-tBuAc**

First observed: Wernsdorfer, PRL 96, 057208 (2006)
(Mn$_{12}$-acetate) Thomas et al., Nature (1996)

Tunneling "on"
Step height a measure of tunnel splitting ($\Delta_o$), or MQT probability

Tunneling "off"
Transverse field: quantum interference

Biaxial $S = 10$ system: Fe$_8$

\[ \hat{H} = DS_z^2 + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) + g\mu_B B_x \hat{S}_x \]

Measure relaxation of $M$

\[ \Delta B = \frac{2k_B}{g\mu_B} \sqrt{2E (E + D)} \]

Wernsdorfer, Sessoli, Science 284, 133 (1999)
What can we learn from single-crystal HFPEPR?

How on earth are we going to measure transverse terms ($\Delta_0 \sim \text{Hz}$)?

What can we learn from single-crystal HFPEPR?

How on earth are we going to measure transverse terms ($\Delta_0 \sim \text{Hz}$)?

Obtain the axial terms in the z.f.s.

Hamiltonian:

$$\hat{H} = \left( \frac{D}{S^2} \right) \hat{S}_z^2 + \left( \frac{B}{S^4} \right) \hat{S}_z^4 + \left( \frac{C}{S^4} \right) \left( \hat{S}_+^4 + \hat{S}_-^4 \right)$$

$D = 55 \text{K}$; $B = 13 \text{K}$; $C = 0.3 \text{K}$
What can we learn from single-crystal HF EPR?

Rotate field in $xy$-plane and look for symmetry effects.

$$\mathcal{E}(m_s) \approx \left\{-\frac{1}{2} D \pm |\hat{\mathcal{H}}_T|\right\} m_s^2 + g\mu_B B m_s$$

In high-field limit ($g\mu_B B > DS$), $m_s$ represents spin-projection along the applied field-axis.
Direct/systematic determination of spin Hamiltonian

\[ \text{Mn}_{12}\text{-Acetate} - [\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]\cdot2\text{MeCO}_2\text{H}\cdot4\text{H}_2\text{O} \]

Hard-plane (xy-plane) rotations

- Four-fold line shifts due to a quartic transverse interaction in \( \mathcal{H}_T \)
- \( B_4^4 \) is the only free parameter in our fit

S. Hill et al., PRL 90, 217204 (2003)

\[ B_4^4 \left( \hat{S}_+^4 + \hat{S}_-^4 \right) \]

\[ B_4^4 = 46(1) \mu\text{K} \]
Direct/systematic determination of spin Hamiltonian

\[ \text{Mn}_{12}\text{-Acetate} - [\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]\cdot2\text{MeCO}_2\text{H}\cdot4\text{H}_2\text{O} \]

- Two-fold line shifts associated with the high- and low-field shoulders due to a quadratic transverse interaction in \( \mathcal{H}_T \)
- S. Hill et al., PRL 90, 217204 (2003)

\[
\frac{1}{2} B_4^4 \left( \hat{S}_+^4 + \hat{S}_-^4 \right) E \left( \hat{S}_x^2 - \hat{S}_y^2 \right) \quad B_4^4 = 46(1) \mu\text{K} \\
E \approx 20 \text{mK}
\]

Incompatible with the crystallographic symmetry!
Discrete disorder lowers symmetry of the molecules

\[ E \left( S_x^2 - S_y^2 \right) \]

Solvate molecules (acetic acid)


\[ -E(S_x^2 - S_y^2) + +E(S_x^2 - S_y^2) \]

Mn12 =

\[ n = 0 (S_4) \quad n = 1 (C_1) \quad n = 2 \text{ "cis" (C}_4 \text{)} \quad n = 2 \text{ "trans" (C}_2 \text{)} \quad n = 3 (C_1) \quad n = 4 (S_4) \]

E. del Barco et al., JLTP 140, 119 (2005)

S. Hill et al., PRL 90, 217204 (2003)
Truly high-symmetry Mn$_{12}$

Experimental spectra

[Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu$^t$)$_{16}$(MeOH)$_4$]·MeOH

- Less solvent of crystallization
- Bulky R group: well separated molecules
- Well aligned

Mn$_{12}$-tBuAc

Phys. Rev. B 80, 094408 (2009)

Mn$_{12}$-BrAc


Mn$_{12}$-Ac

51.5 GHz

Normalized cavity transmission (arb. units)

Magnetic field (tesla - normalized to $\alpha_8$)
Why use a giant spin approximation?

Matrix dimension 21 × 21

$J^s$ irrelevant (apparently)!!

Ignores (10^8 - 21) higher-lying states

But what is the physical origin of parameters obtained from EPR and other experiments - particularly those that cause MQT?
To answer this... study simpler molecules

\[
\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[ d_i \hat{s}_{zi}^2 + e_i \left( \hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + g \mu_B \vec{B} \cdot \hat{s}_i \right]
\]

\( \text{Ni}^{\text{II}}_4 \)  
\( S_4 \) symmetry

\( \text{Mn}^{\text{III}}_3 \)  
\( R\bar{3} \)

\( \text{Mn}^{\text{III}}_6 \)  
Centrosymmetric

\((2S + 1)^4 = 81\)

\((2S + 1)^3 = 125\)

\((2S + 1)^6 = 15625\)

\text{Ni}_4: \ E.-C. Yang et al., Inorg. Chem. 44, 3836 (2005); A. Wilson et al., PRB 74, R140403 (2006).


\text{Others:} \ C. Ramsey et al., Nature Phys. 4, 277 (2008); del Barco et al., PRL 109, 059701 (2009).
To answer this.... study simpler molecules

\[ \hat{H} = \sum_{i} \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_{i} \left[ d_i \hat{s}_{zi}^2 + e_i \left( \hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + g \mu_B \vec{B} \cdot \hat{s}_i \right] \]

\( S = 4 \)

Ni\( ^{\text{II}} \)\( _4 \)\( ^{\text{S}} \) symmetry

Can also study the Zn analog doped with Ni\( ^{\text{II}} \) to obtain single-ion parameters

En-Che Yang et al., Inorg. Chem. 44, 3836 (2005)

- Angle-dependent single-crystal HFEPR of 2% Ni-doped Zn complex
- Obtain 3×3 matrices and orientations for \( S = 1 \) Ni\( ^{\text{II}} \)
- Only 2\( ^{\text{nd}} \) order anisotropy for \( S = 1 \)

Wilson et al., PRB 74, R140403 (2006); Datta et al., PRB 76, 052407 (2007); Lawrence et al., Inorg. Chem. 47, 1965 (2008); Cao et al., PRL 100, 167206 (2008).
To answer this... study simpler molecules

\[ \hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[ d_i \hat{s}_{z_i}^2 + e_i \left( \hat{s}_{x_i}^2 - \hat{s}_{y_i}^2 \right) + g \mu_B \vec{B} \cdot \hat{s}_i \right] \]

\( S = 4 \)

\( \text{Ni}_4^{\text{II}} \)

\( S_4 \) symmetry

Matrix = \((2S + 1)^4 = 81 \times 81\)

- Interplay between isotropic (exchange) and anisotropic (single-ion spin-orbit) admixes \( S = 3, 2, \) etc.. to the \( S = 4 \) state
- Causes \( S \)-mixing \( \rightarrow \) corrections to zfs \( \sim (\hat{S}_z^2)^n \), i.e. 4th, 6th order....

Wilson et al., PRB 74, R140403 (2006); Datta et al., PRB 76, 052407 (2007); Lawrence et al., Inorg. Chem. 47, 1965 (2008); Cao et al., PRL 100, 167206 (2008).
To answer this... study simpler molecules

This physics is responsible for the QTM in Ni$_4$

- Interplay between isotropic (exchange) and anisotropic (single-ion spin-orbit) admixes $S = 3, 2, \text{etc.}$ to the $S = 4$ state
- Causes $S$-mixing → corrections to zfs $\sim (\hat{S}_z^2)^n$, i.e. 4th, 6th order....

Wilson et al., PRB 74, R140403 (2006); Datta et al., PRB 76, 052407 (2007); Lawrence et al., Inorg. Chem. 47, 1965 (2008); Cao et al., PRL 100, 167206 (2008).
To answer this, study simpler molecules. This physics is responsible for the QTM in Ni$_4$.

\[ D = -0.600 \text{ cm}^{-1}, \quad B_4^0 = -0.00012 \text{ cm}^{-1}, \quad d = -4.72 \text{ cm}^{-1}, \quad e = \pm 1.19 \text{ cm}^{-1}, \quad J = -5.9 \text{ cm}^{-1}, \quad \text{Tilt} = 15^\circ \]

\[ B_4^0 \quad \text{and} \quad B_4^{\perp} \propto \frac{1}{J} \]

Wilson et al., PRB 74, R140403 (2006); Datta et al., PRB 76, 052407 (2007); Lawrence et al., Inorg. Chem. 47, 1965 (2008); Cao et al., PRL 100, 167206 (2008).
Spin control: targeted ligand-imposed distortion

\[ \text{Mn}^{\text{III}}_3 \]

S = 6

or

S = 2

\[ \text{S} = 12 \]

or

\[ \text{S} = 4 \]

\[ \text{Mn}^{\text{III}}_6 \]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Molecule} & \text{Torsion angle } \alpha / ^\circ & \text{J/cm}^{-1} & \text{S} & \Delta_{\text{eff}} / \text{K} & \Delta_{\text{EPR}} / \text{K} \\
\hline
[\text{Mn}_6\text{O}_2(\text{Me-sao})_6(\text{O}_2\text{CCPH}_3)_2(\text{EtOH})_4] & 25.5, 29.7, 42.4 & 1.2/-1.95 & 4 & 31.7 & 29.2 \\
[\text{Mn}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CCMe}_3)_2(\text{EtOH})_4(\text{H}_2\text{O})_2] & 23.3, 36.9, 42.1 & -1.9/+1.4 & 7 & 30 & \\
[\text{Mn}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh})_2(\text{EtOH})_4(\text{H}_2\text{O})_2] & 31.3, 38.2, 39.9 & +0.93 & 12 & 53 & \\
[\text{Mn}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPhMe}_2)_2(\text{EtOH})_4(\text{H}_2\text{O})_2] & 34.9, 39.1, 43.1 & +1.6 & 12 & 86 & 75 \\
\hline
\end{array}
\]

\text{Mn}_3: \text{P. Feng et al., Inorg. Chem. 48, 3480 (2009); R. Inglis et al., Dalton Tran., in press (2009).}

\text{Mn}_6: \text{C. Milios et al., JACS 129, 12505 (2007); S. Datta et al., Polyhedron 28, 1911 (2009).}
Spin control: raising the magnetic barrier

\[ DS_{\text{S=4}} = -1.27(2) \text{ cm}^{-1} \]
\[ B_4^0 = +1.3(3) \times 10^{-6} \text{ cm}^{-1} \]

\[ DS_{\text{S=12}} = -0.360(5) \text{ cm}^{-1} \]
\[ B_4^0 = -5.7(5) \times 10^{-6} \text{ cm}^{-1} \]

\[ DS_{\text{S=12}}/DS_{\text{S=4}} = 0.28; \quad \Delta_{12}/\Delta_4 = 2.6 \]
Spin control: raising the magnetic barrier

Spin projection calculations:

\[ D_{S=12}/D_{S=4} = 0.16 - 0.19; \quad \Delta_{12}/\Delta_{4} = 1.44 - 1.71 \]

\[ D_{S=12}/D_{S=4} = 0.28; \quad \Delta_{12}/\Delta_{4} = 2.6 \]
Mn₃, R̅3, S = 6, no solvent → spectacular SMM

\[
\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[ d_i \hat{s}_{zi}^2 + e_i \left( \hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + \mu_B \vec{B} \cdot \vec{g}_i \cdot \hat{s}_i \right]
\]

Chiral SMM: [NEt₄]₃[Mn₃Zn₂(salox)₃O(N₃)X₂] with X = Cl/Br

Clear observation of spin-selection rules; Likely due to lack of disorder

Mn₃, R₃, $S = 6$, no solvent → spectacular SMM

\[ \hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[ d_i \hat{s}_{zi}^2 + e_i \left( \hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + \mu_B \vec{B} \cdot \vec{g}_i \cdot \hat{s}_i \right] \]

\[ \Delta m_S = 6,3 \]

\[ \Delta m_S \neq 6,3 \]

\[ \phi_1 = 0^\circ \]
\[ \phi_2 = 120^\circ \]
\[ \phi_3 = 240^\circ \]

\( s = 2 \)
\( d = 4.2 \text{ K} \)
\( J = 4.88 \text{ K} \)
\( g = 2 \)
\( e = 0.9 \text{ K} \)
\( \theta = 8.5^\circ \)

Tilting JT axes + dipolar fields explains all behavior

→ Chirality → $B_{4^3} = S_z(S_{+3} + S_{-3})$
Summary and conclusions

Simple is better

- Simple low-nuclearity clusters provide remarkable insights into the physics of SMMs
- The breakdown of the giant-spin phenomenology and the resultant interplay between exchange and anisotropy is behind much of the low-temperature anisotropy is behind much of the low-temperature quantum dynamics in SMMs
- High-field EPR provides crucial insights into the physics and chemistry of polynuclear transition metal complexes
Many Collaborators....

**University of Florida Physics:** Saiti Datta, Jon Lawrence, Changhyun Koo, Susumu Takahashi, Tony Wilson, John Lee, Erica Bolin, Rachel Edwards. 
Also: Hai-Ping Cheng and Chao Cao

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