Single-Molecule Magnets (SMMs): A Molecular (Bottom-up) Approach to Nanoscale Magnetic Materials

Lecture 1:
The Mn_{12} Family of Single-Molecule Magnets

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Types of Magnetic Materials

Magnetism

Traditional Magnets

3D arrays of metal atoms or ions
(metals, metal alloys, metal oxides
e.g. magnetite - Fe_3O_4)

Molecular Magnets

3D arrays of linked, interacting molecules

Single-Molecule Magnets (SMMs)

Molecular Nanomagnets

magnetism intrinsic to the molecule;
each molecule is a separate, nanoscale
magnetic particle

Single-Chain Magnets (SCMs)

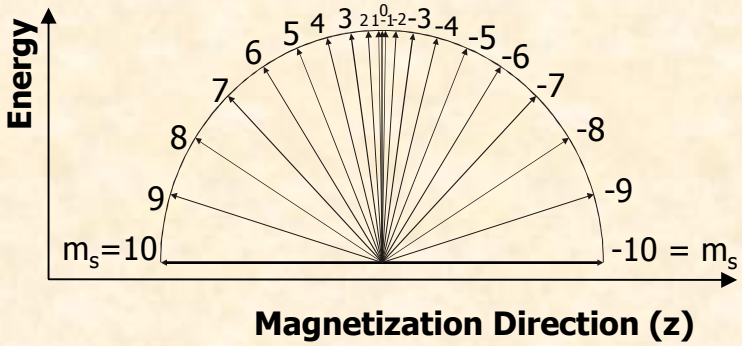
magnetism due to 1-D chains

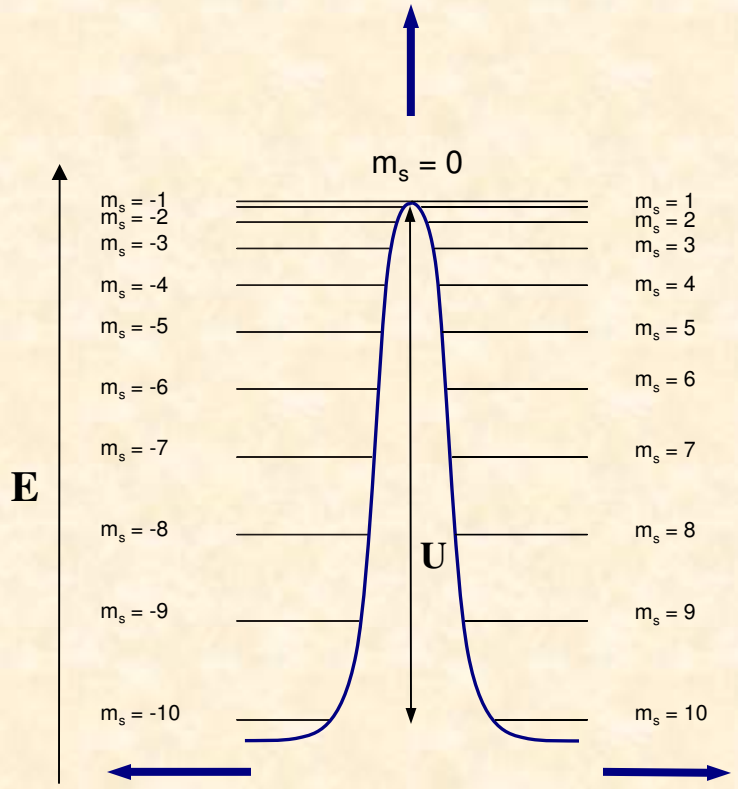
Single-Molecule Magnets (SMMs)

The barrier to magnetization relaxation in SMMs is not due to intermolecular interactions (as in traditional magnets) but to zero-field splitting (ZFS).

Requirements for SMMs:

1. **Large ground state spin (S)**
2. **Negative ZFS parameter (D)**





Spin Hamiltonian:

$$\mathrm{H} = \text{axial term} + \text{rhombic term} + \text{Zeeman term}$$

$$D\hat{S}_z^2 + B_4^0\hat{O}_4^0 \qquad E\left(\hat{S}_x^2 - \hat{S}_y^2\right) + B_4^4\hat{O}_4^4 \qquad g\mu_B\hat{S}\cdot H$$

$$\mathrm{H} = D\hat{S}_Z^2 + E(\hat{S}_X^2 - \hat{S}_Y^2) + g\mu_B\hat{S}\cdot H$$

Anisotropy barrier (U) = $S^2|D|$ Integer spin

or $(S^2-1/4)|D|$ Half- integer spin

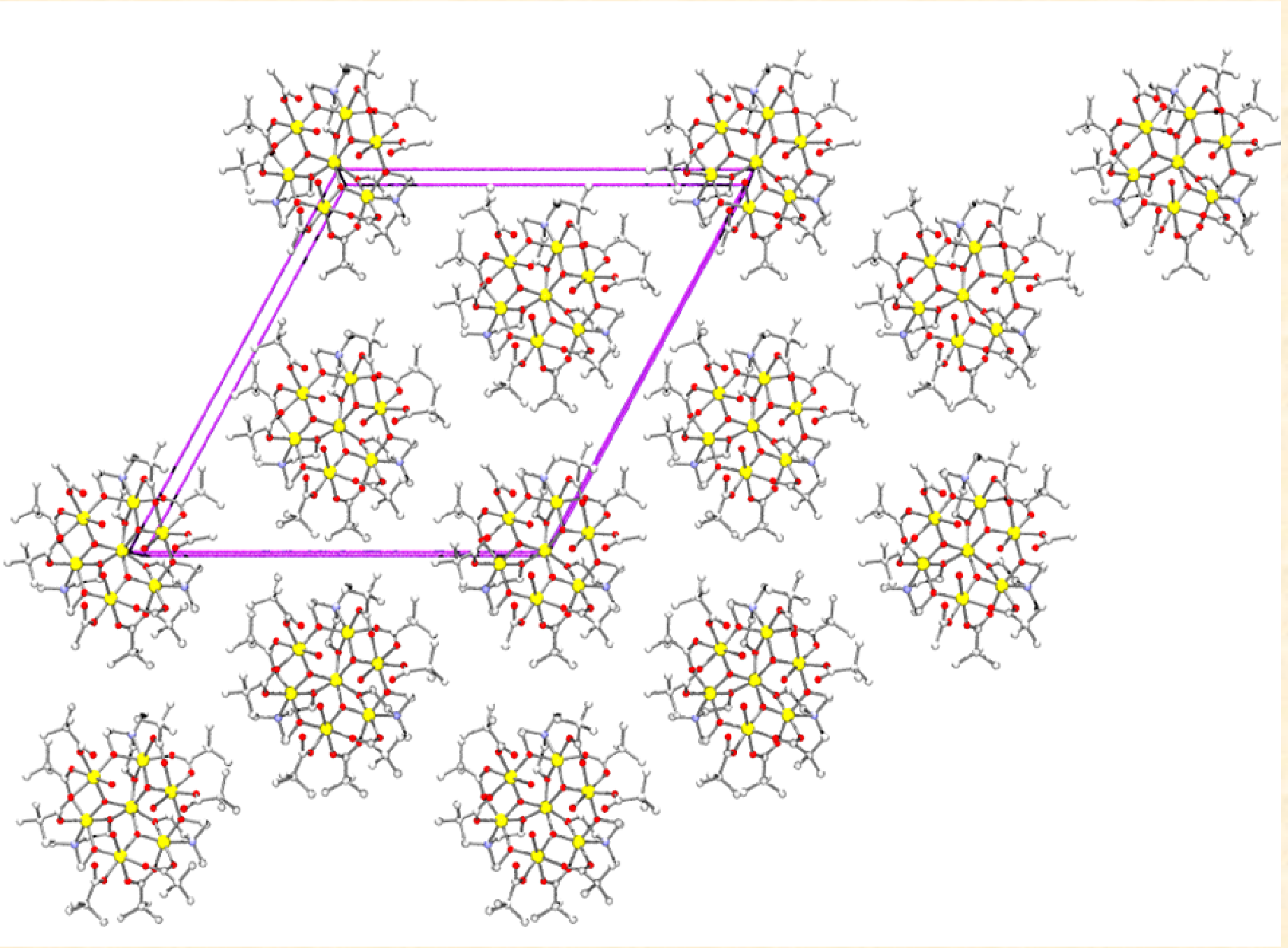
Advantages of SMMs over Traditional Nanoscale Magnetic Particles

Properties

- truly monodisperse particles of nanoscale dimensions
- crystalline, therefore contain highly ordered assemblies
- well-defined ground state spin, S
- truly quantum spin systems

Synthesis

- synthesized by room temperature, solution methods
- enveloped in a protective shell of organic groups (ligands)
- truly soluble (rather than colloidal suspensions) in organic solvents
- the organic shell (ligands) around the magnetic core can be easily modified, providing control of separations between molecules, coupling with the environment, etc.



Major Potential Applications of SMMs

Digital Information Storage

- the storage of information at the molecular level as the orientation direction of the magnetization vector.
- each molecule stores one bit of information.
- estimated 10^4 increase in storage density over present devices.
- requires ordered arrays of SMMs, either 2-D surfaces (present technology) or 3-D crystals (future technology).

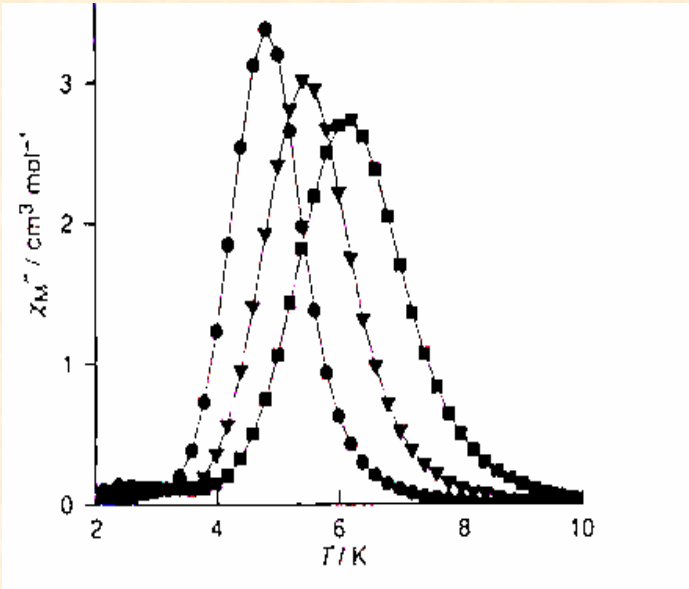
Quantum Computing

- the use of quantum bits (qubits) rather than classical bits as in present computation methods.
- requires SMMs capable of existing in quantum superpositions of two (or more) states i.e. 1 and 0 instead of classical 1 or 0.
- requires SMM to show appropriate quantum properties.

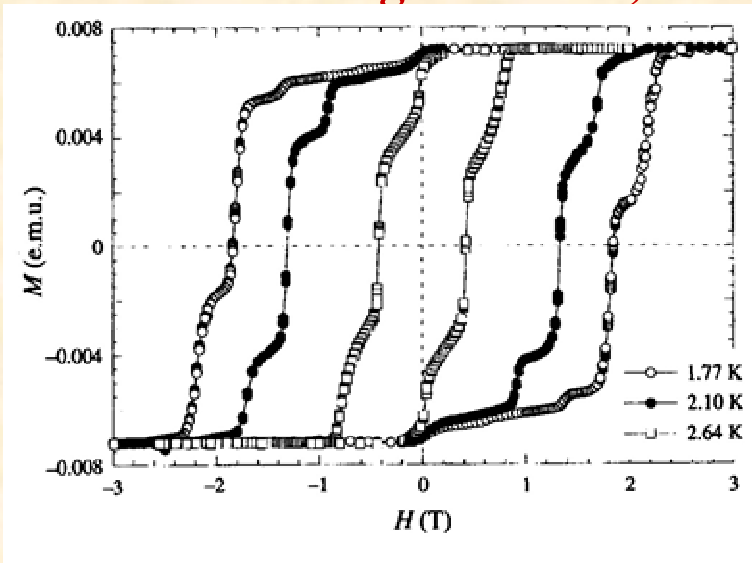
Experimental Identification of SMMs

They display the slow magnetization relaxation (reorientation) rates of single-domain superparamagnets, even though they are <u>much</u> smaller and the properties arise from a different origin (not long-range co-operativity)

Frequency-dependent out-of-phase AC susceptibility signals (χ_M'')

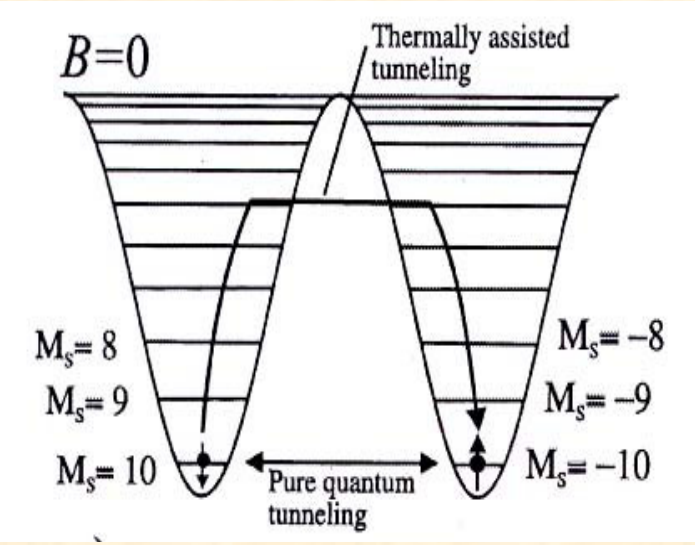


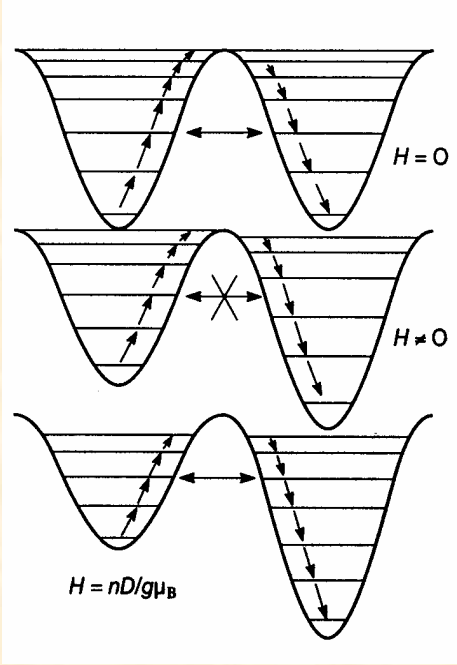
Hysteresis loops (with steps due to quantum tunneling of the magnetization)



Quantum Tunneling of the Magnetization (QTM)

SMM's are true mesoscale particles. They exhibit the macroscale property of hysteresis, and the microscale property of QTM through the anisotropy barrier

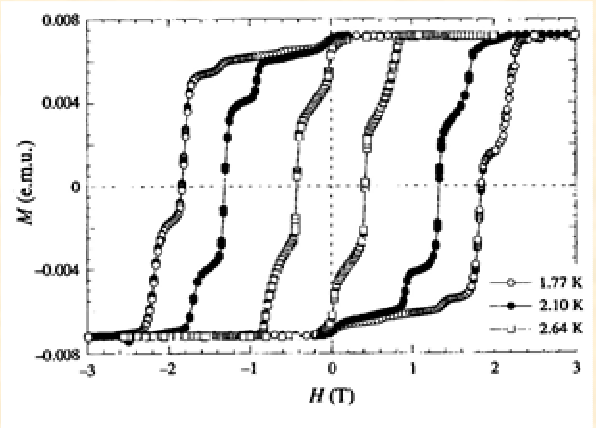




Barrier (U) = $S^2|D|$ for integer S

= $(S^2-1/4)|D|$ for half-integer S

Therefore, $U < U_{eff}$



Topics for this presentation:

- **Crystalline arrays of Mn_{12} SMMs, and their controlled modification.**
- **Faster-Relaxing Mn_{12} SMMs: Jahn-Teller Isomerism**
- **Electron addition onto Mn_{12} SMMs, and its effect on the properties**
- **New high-quality Mn_{12} SMMs: the picture comes into focus.**

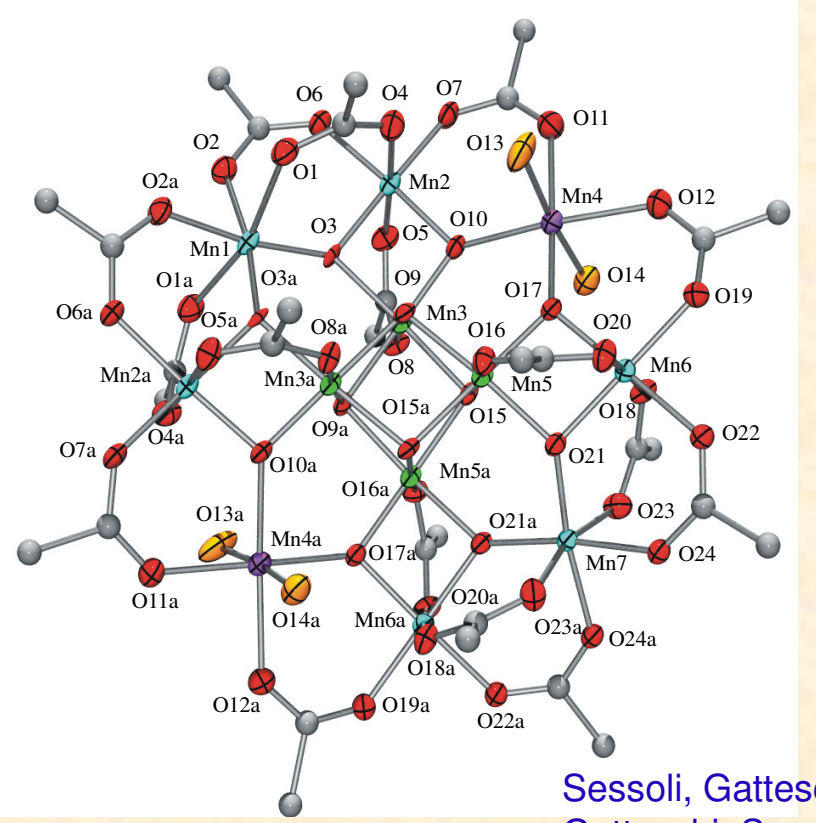
The Mn_{12} Family of Single-Molecule Magnets (SMMs)

$Mn(O_2CMe)_2$ + MnO_4^- in 60% acetic acid/H_2O ⟶

$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2AcOH\cdot 4H_2O$

(Lis, Acta Cryst. B,1980) **$[Mn_{12}Ac]$**

Identified as a SMM in 1993. $Mn_{12}Ac$ has axial symmetry (tetragonal space group *I*4(bar)), and has therefore been considered the best to study in detail.



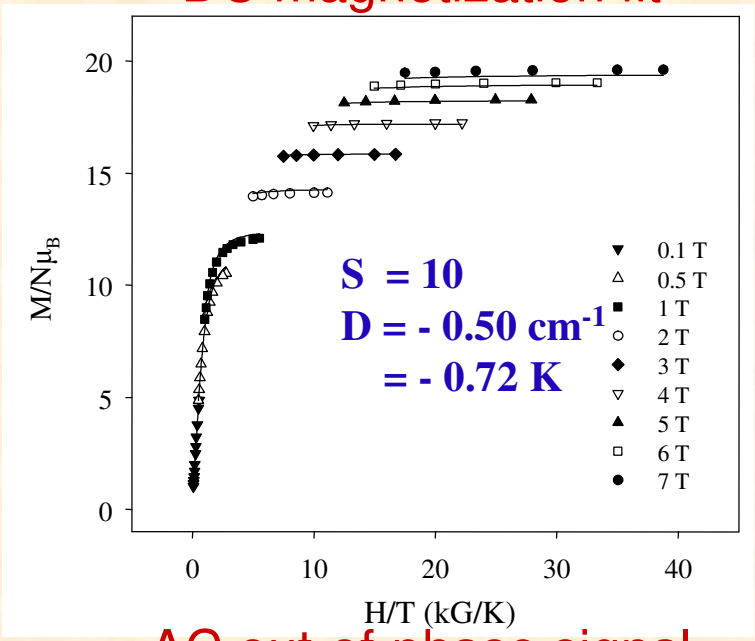
$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (Mn_{12}) complexes:

- **S = 10**
- **D = -0.40 to -0.50 cm^{-1} (-0.58 to -0.72 K)**
- **Magnets below 3K**

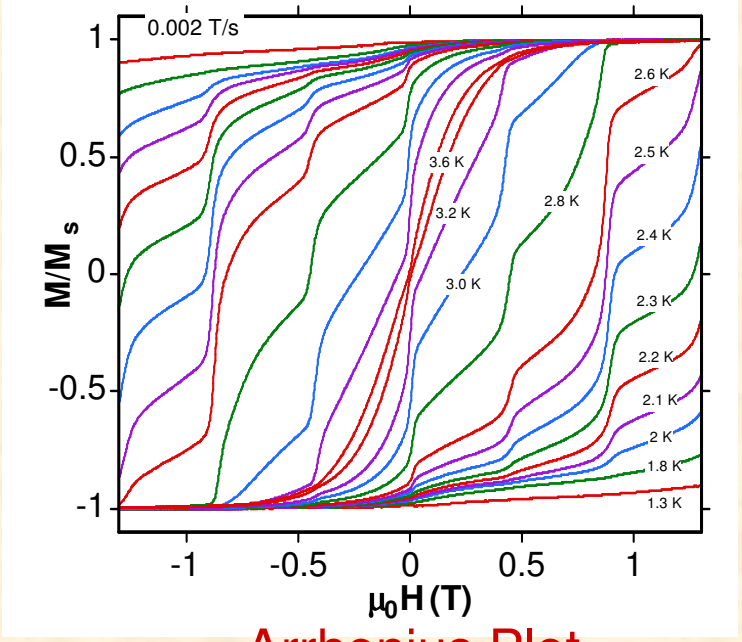
Volume of the $Mn_{12}O_{12}$ magnetic core ~ 0.1 nm^3

Sessoli, Gatteschi, Caneschi, Novak, Nature 1993, 365, 141
Gatteschi, Sessoli, Christou, Hendrickson, et al. JACS, 1993,115, 1804

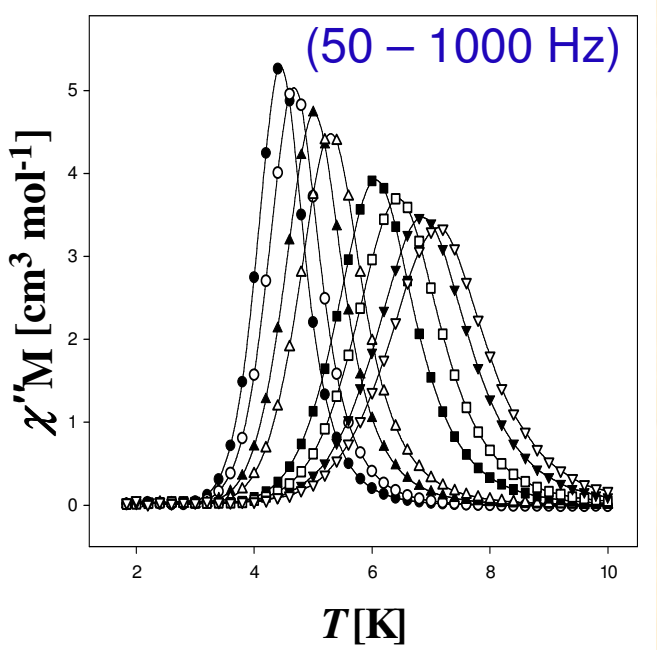
DC magnetization fit



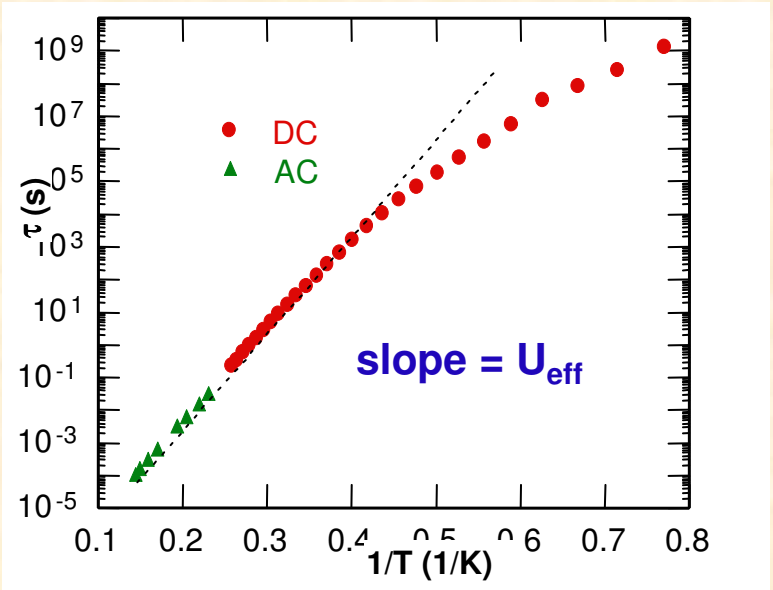
DC magnetization hysteresis loops



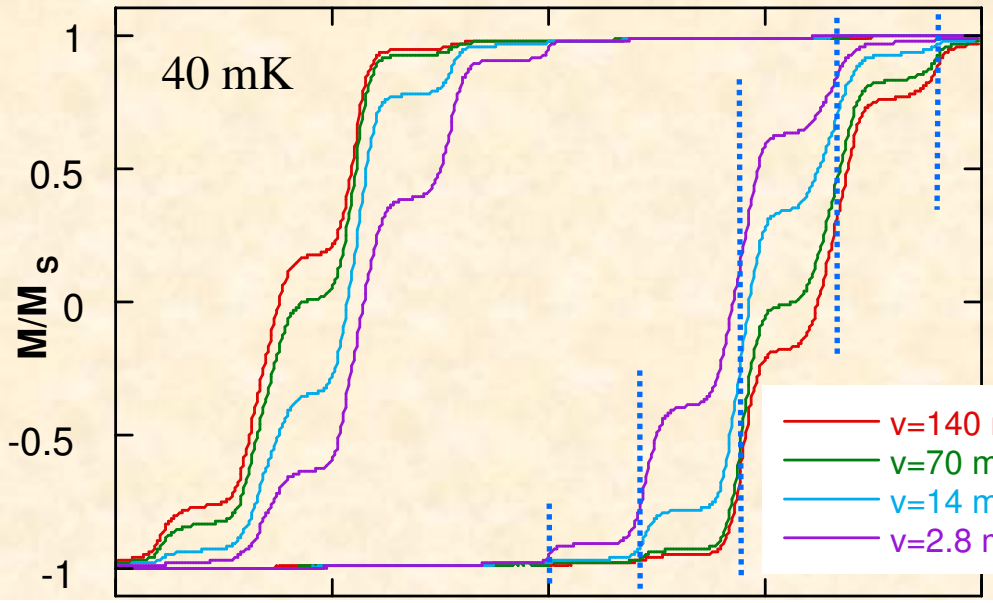
AC out-of-phase signal

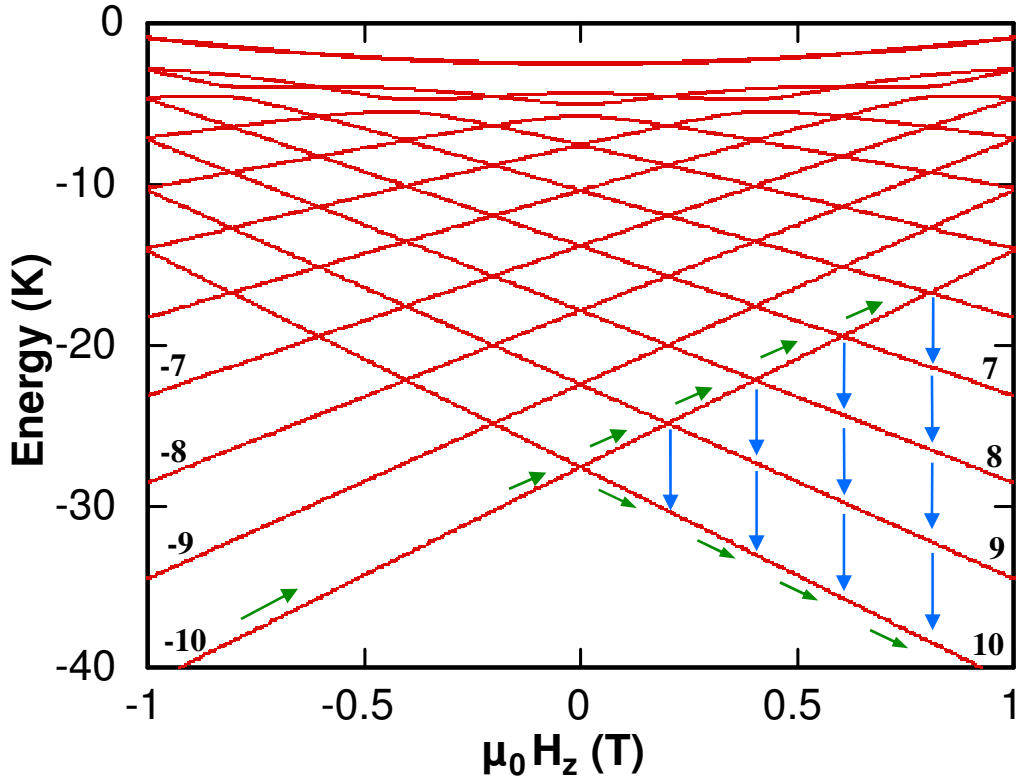


Arrhenius Plot



Tunneling Steps in a S = 10 Single-Molecule Magnet





Field is swept from –1 Tesla to + 1 Tesla.
Tunneling transitions are seen as steps, which correspond to a surge in the relaxation rate.

As expected from the Landau-Zener equation, the step size is inversely proportional to the sweep rate.

Modification of the Mn_{12} Family of SMMs

1) Carboxylate Substitution

-- replacement of acetate with other carboxylate groups.
-- add RCO_2H to Mn_{12}-Ac

$$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4] + 16\ RCO_2H \longrightarrow [Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + 16\ MeCO_2H$$

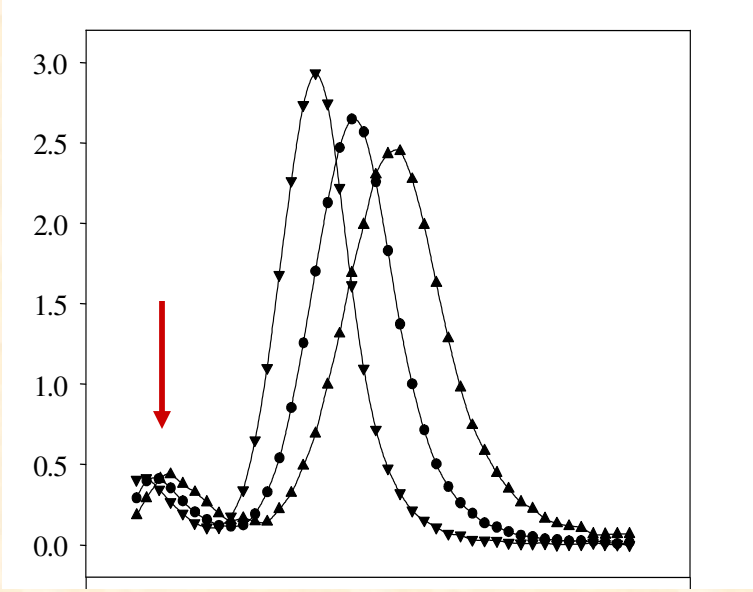
(*J. Am. Chem. Soc.* 1993, *115*, 1804, and *J. Am. Chem. Soc.* 1995, *117*, 301)

- The substitution is an equilibrium that is driven to 100% reaction by removing the generated acetic acid ($MeCO_2H$) as its toluene azeotrope under vacuum
- Many, many different carboxylate R groups have been used (big vs small, polar vs non-polar, isotopically-labelled, element-labelled (e.g. C_6F_5), etc
- Allows control of Mn_{12} solubility, crystallinity, redox potentials, etc

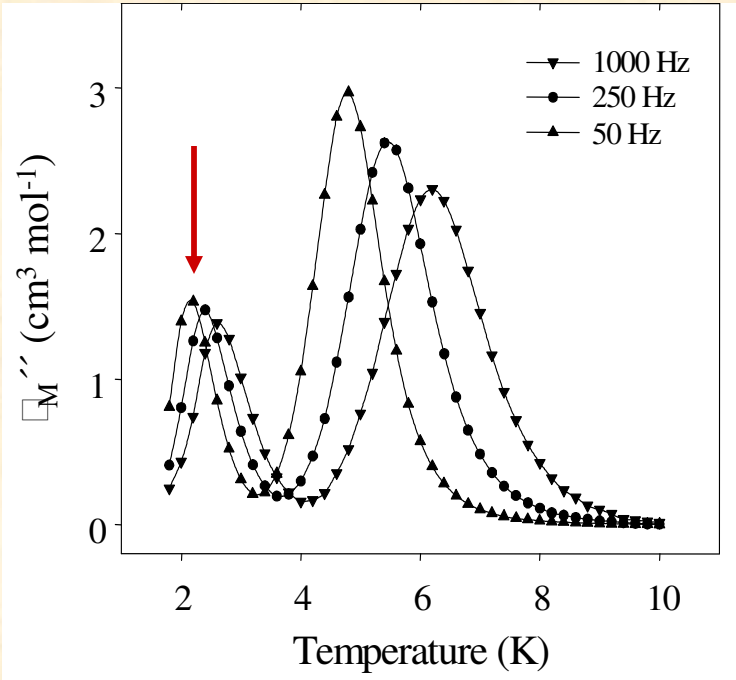
The Faster-Relaxing Variants of Mn_{12} SMMs

-- even in pure Mn_{12} crystals, additional signals from a faster-relaxing (LT) species are almost always seen
-- in Mn_{12}-Ac, the LT species is ~ 5%. In others, it can be much higher, and in some it is the majority species.

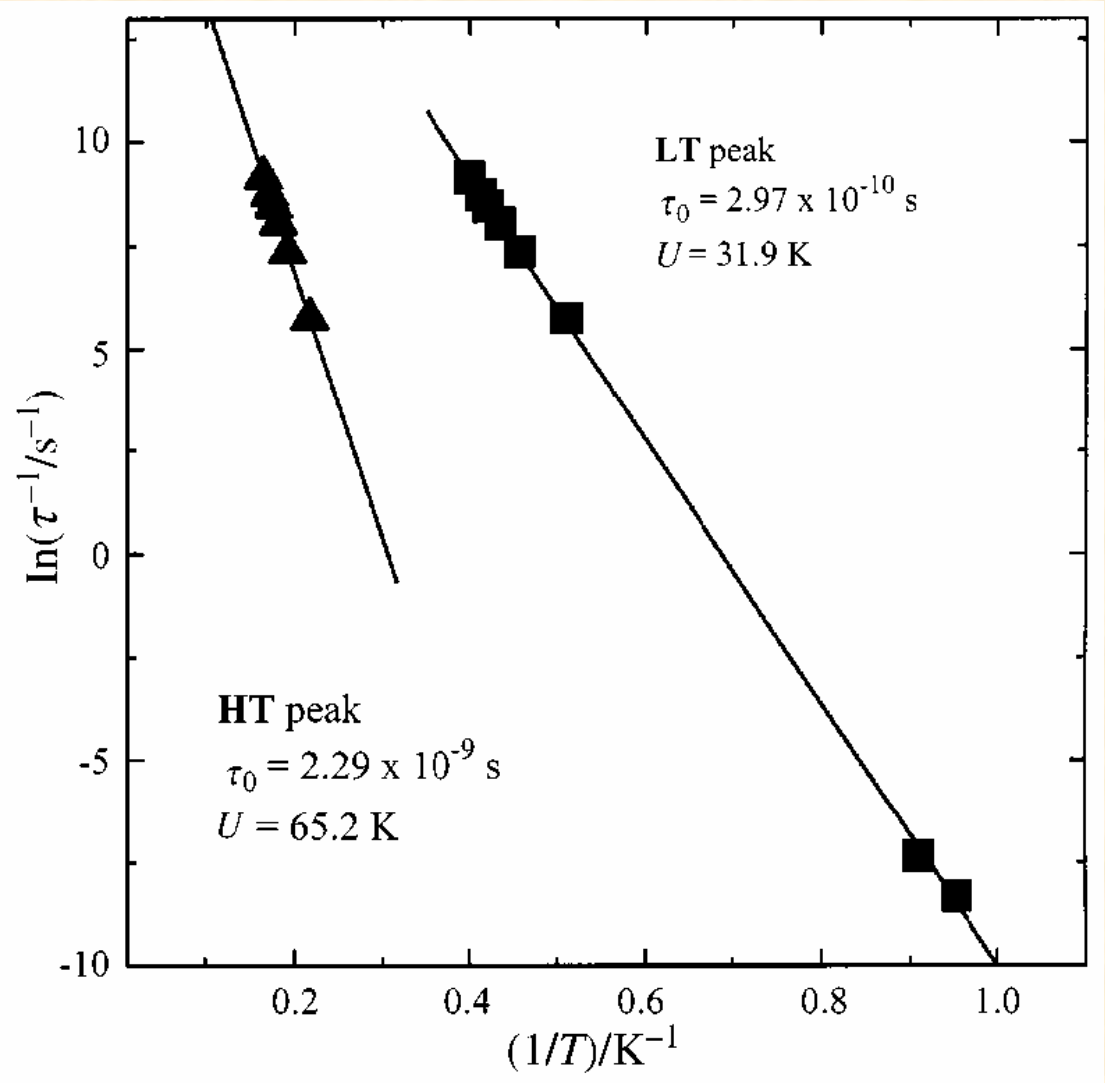
R = Me



R = C_6F_5

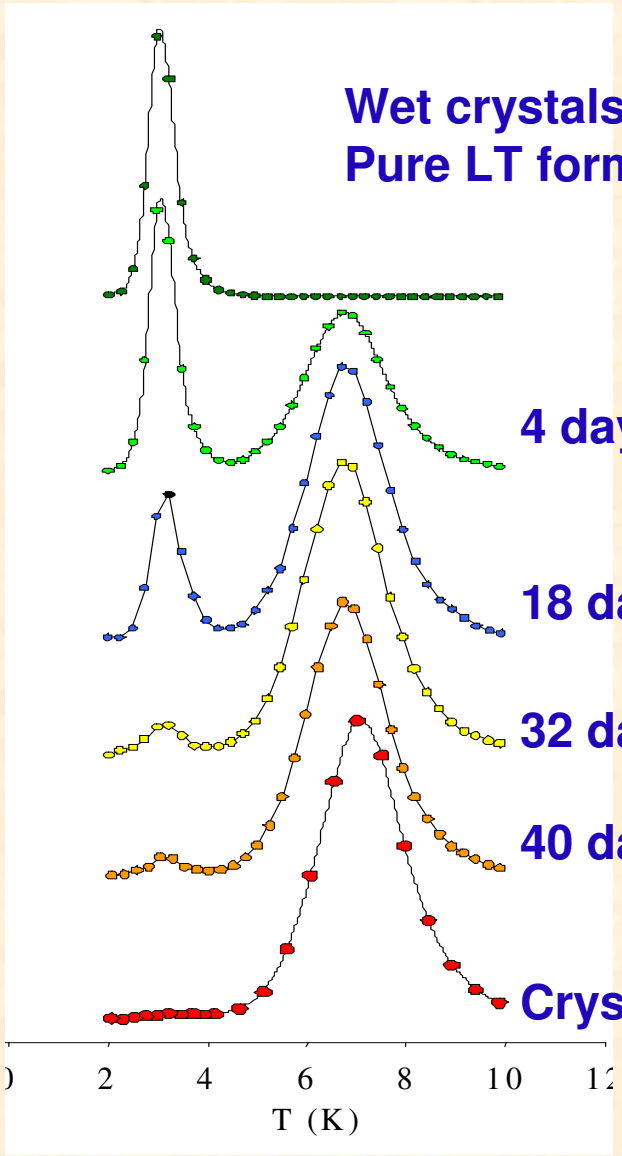


The U_{eff} typically differ by a factor of two



"Single-molecule magnets: control by a single solvent molecule of Jahn-Teller isomerism in $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(H_2O)_4]$"

Soler et al. *Chem. Commun.* 2003, 2672



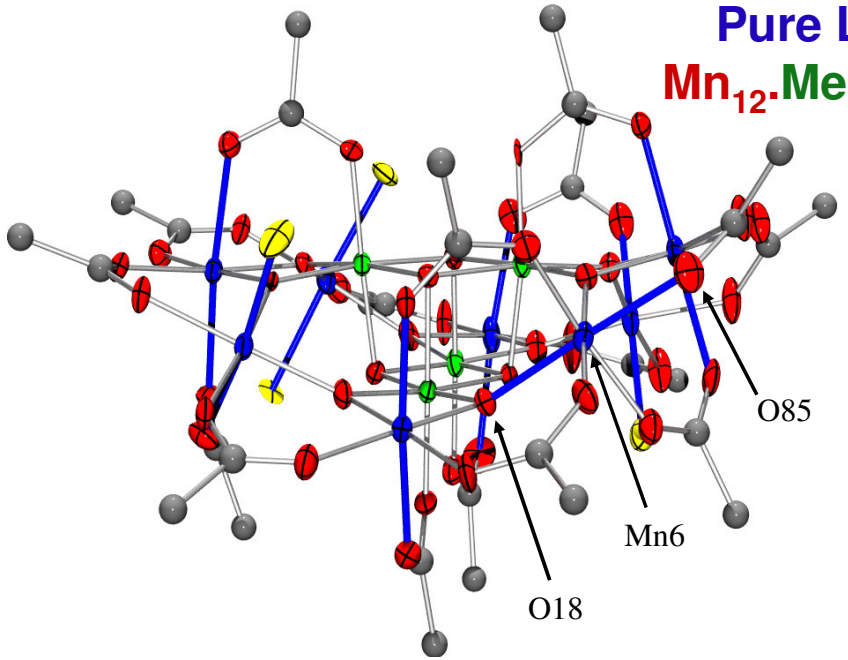
The compound crystallizes from a $MeNO_2/CH_2Cl_2$ solvent mixture as $Mn_{12}.MeNO_2.CH_2Cl_2$

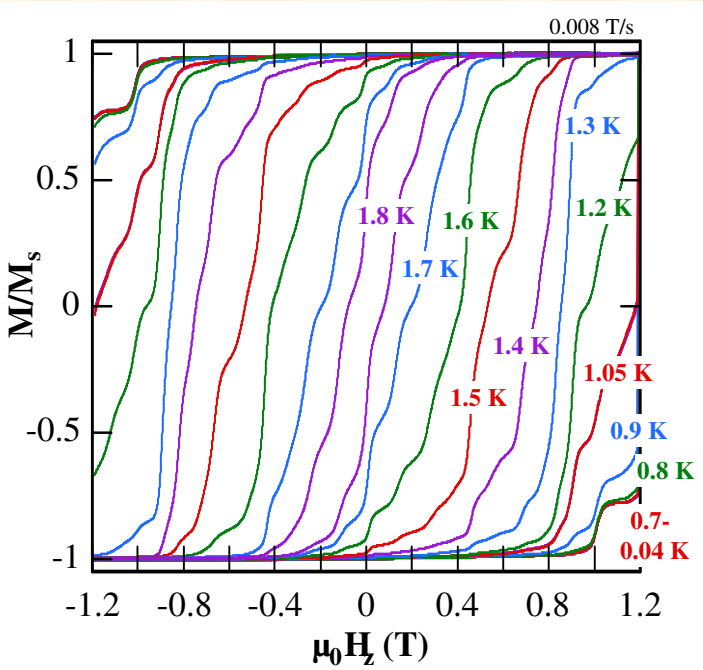
triclinic, *P*$\bar{1}$
a = 15.814(2), *b* = 16.42(2), *c* = 27.434(3) Å
α = 76.900(1), β = 78.220(1), γ = 78.210(1)º,
Z = 2, *V* = 6699.08 Å^3

The compound crystallizes from a $MeCN/CH_2Cl_2$ solvent mixture as $Mn_{12}.MeCN.CH_2Cl_2$

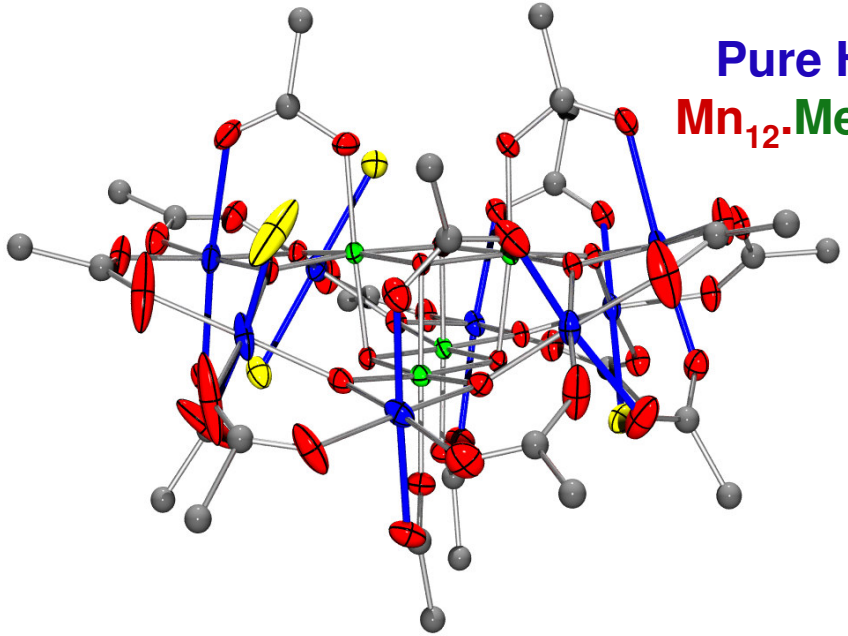
triclinic, *P*$\bar{1}$
a = 15.757(1), *b* = 16.763(1), *c* = 27.183(1) Å,
α = 77.444(1), β = 77.490(1), γ = 78.315(1)º,
Z = 2, *V* = 6750.17 Å^3

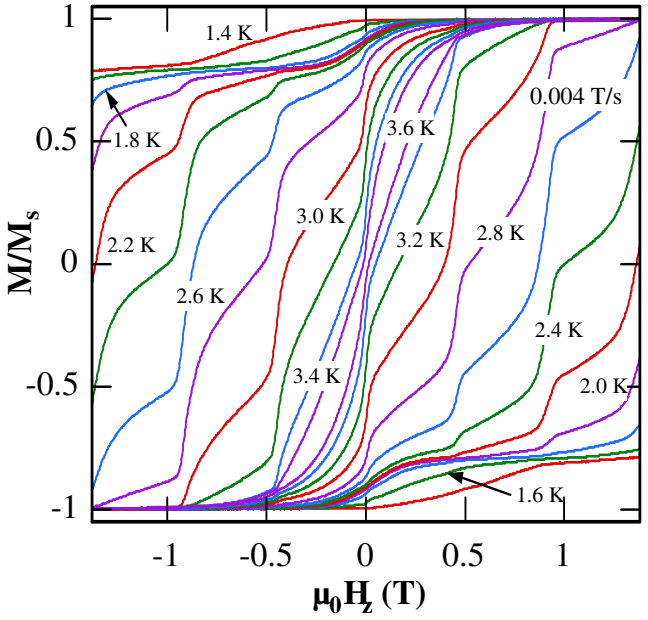
Pure LT form
$Mn_{12}.MeNO_2.CH_2Cl_2$





Pure HT form
$Mn_{12}.MeCN.CH_2Cl_2$





2. Site-Selective, Partial Carboxylate Substitution

$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ + x HL ⟶ $[Mn_{12}O_{12}(O_2CR)_{16-x}(L)_x(H_2O)_4]$

Examples:

$[Mn_{12}O_{12}(O_2CR)_{12}(NO_3)_4(H_2O)_4]$

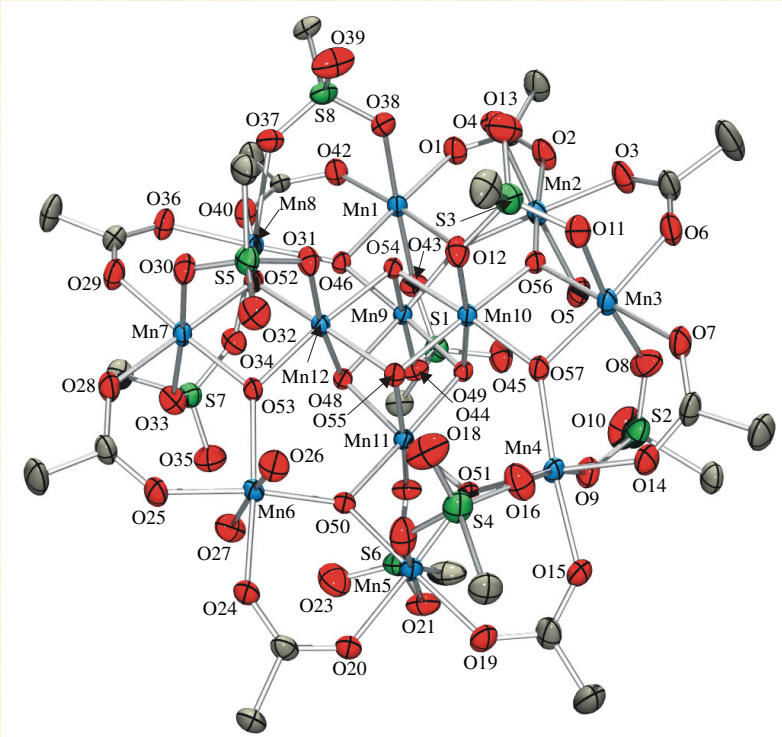
$[Mn_{12}O_{12}(O_2CR)_8(O_2CR')_8(H_2O)_4]$

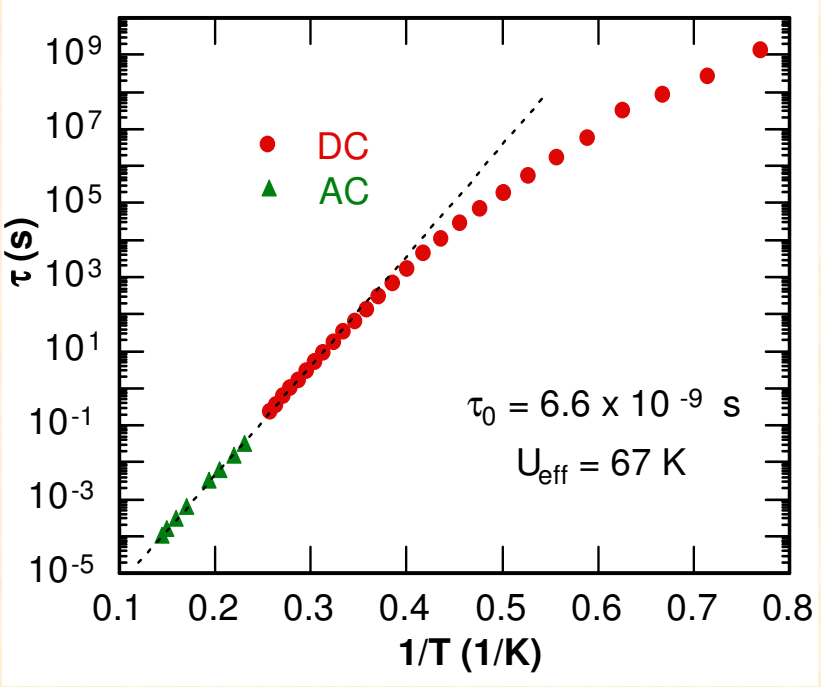
$[Mn_{12}O_{12}(O_2CR)_8(O_3SPh)_8(H_2O)_4]$

$[Mn_{12}O_{12}(O_2CR)_8(O_2PPh_2)_8(H_2O)_4]$

Inorg. Chem. **2001, *40*, 4199**

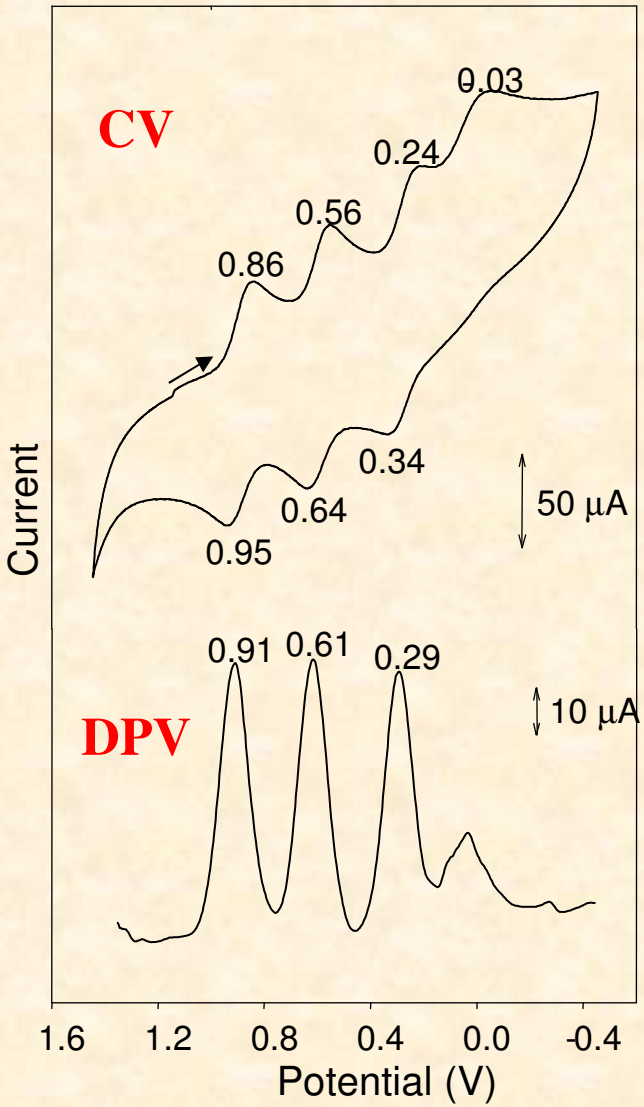
Dalton Trans. **2003, 2243-2248**





3. Electron Addition (Spin Injection)

Carboxylate variation alters the Mn_{12} redox potentials (E),
(related to the thermodynamic Gibbs free energy by $\Delta G^{o} = -nFE^{o}$
i.e. ease of addition (or removal) of electrons)
-- determined by electrochemistry



Electrochemical data for $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$

R	E_1 (V)[a]	E_2(V)[b]
$CHCl_2$	0.91	0.61
$C_6H_3(NO_2)_2$-2,4	0.74	0.45
C_6F_5	0.64	0.46
CH_2Cl	0.60	0.30
CH_2CH_3	0.02	-0.50

a. First e^- addition
b. Second e^- addition

in CH_2Cl_2 solution vs. ferrocene

Electron Addition to Mn_{12} : Bulk Isolation of Products

-- using iodide (I^-) as a one-electron donor

$$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + I^- \longrightarrow [Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^- + \tfrac{1}{2} I_2$$

$[Mn_{12}]^-$

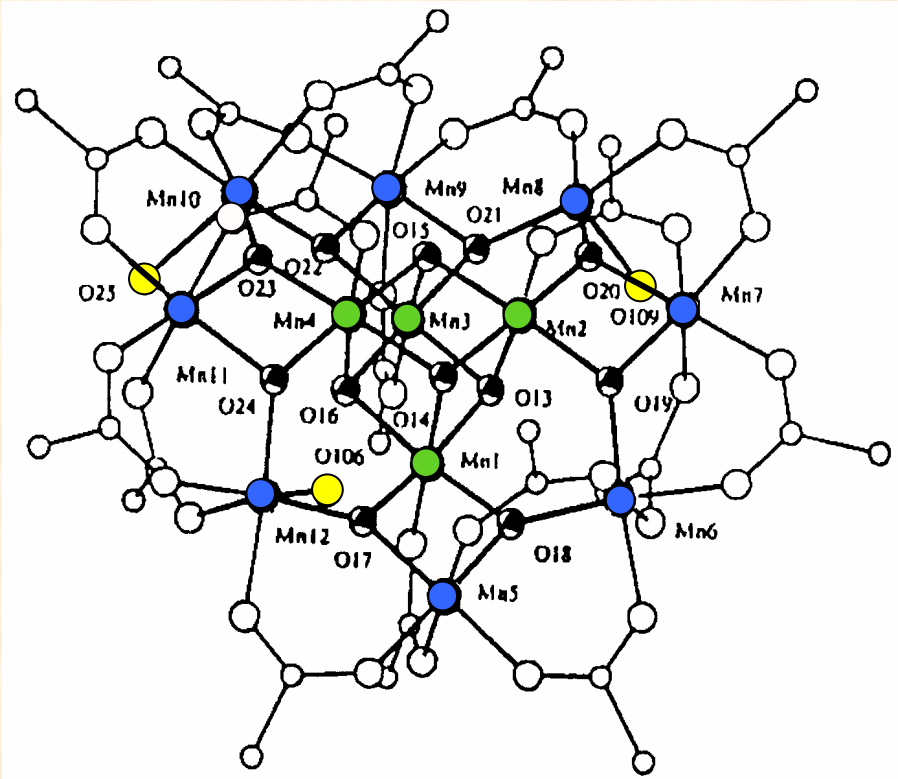
$$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + 2\ I^- \longrightarrow [Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^{2-} + I_2$$

$[Mn_{12}]^{2-}$

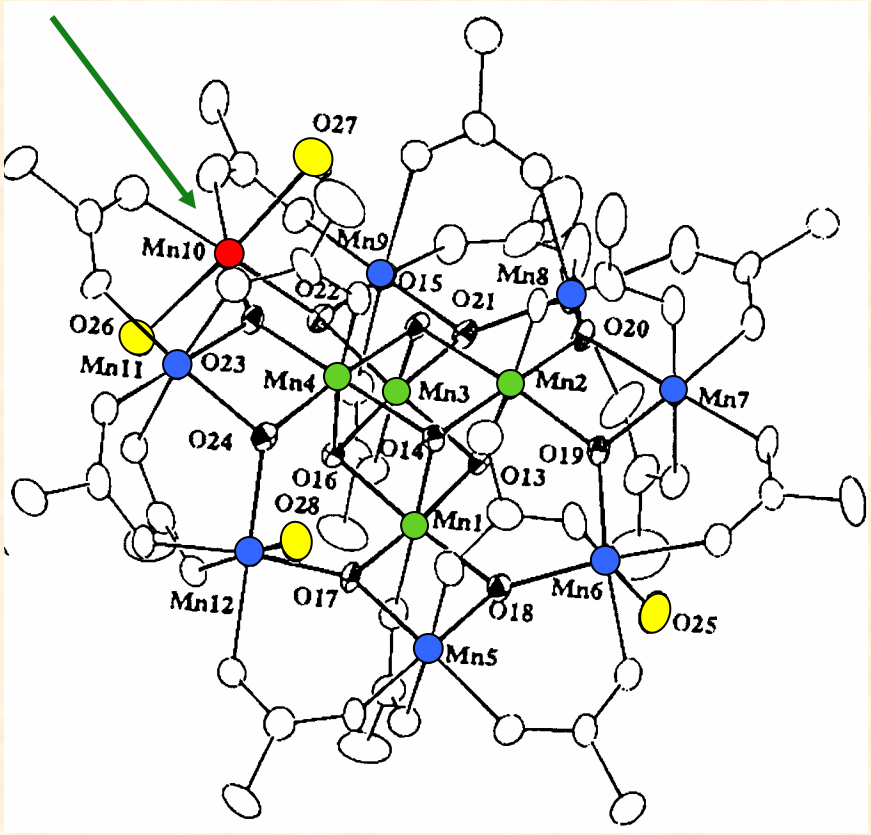
-- products can be made in multi-gram amounts, and isolated as pure, crystalline solids.

JACS 1995, *117*, 301, and *JACS*, 2003, *135*, 3576

Crystal Structures of Mn_{12} and $[Mn_{12}]^-$



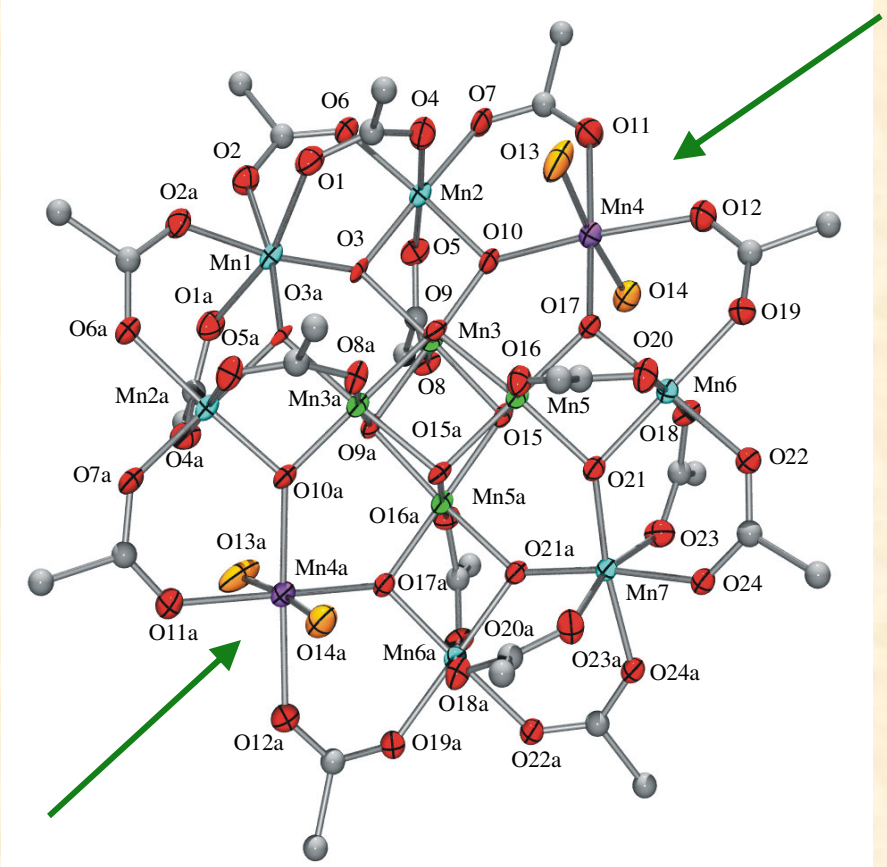
8 Mn^{III}(●), 4 Mn^{IV}(●) H_2O (●)



Mn^{II}(●), 7 Mn^{III}(●)
4 Mn^{IV}(●) H_2O (●)

Eppley et al. *JACS*, 1995, *117*, 301

Crystal Structure of $[Mn_{12}]^{2-}$

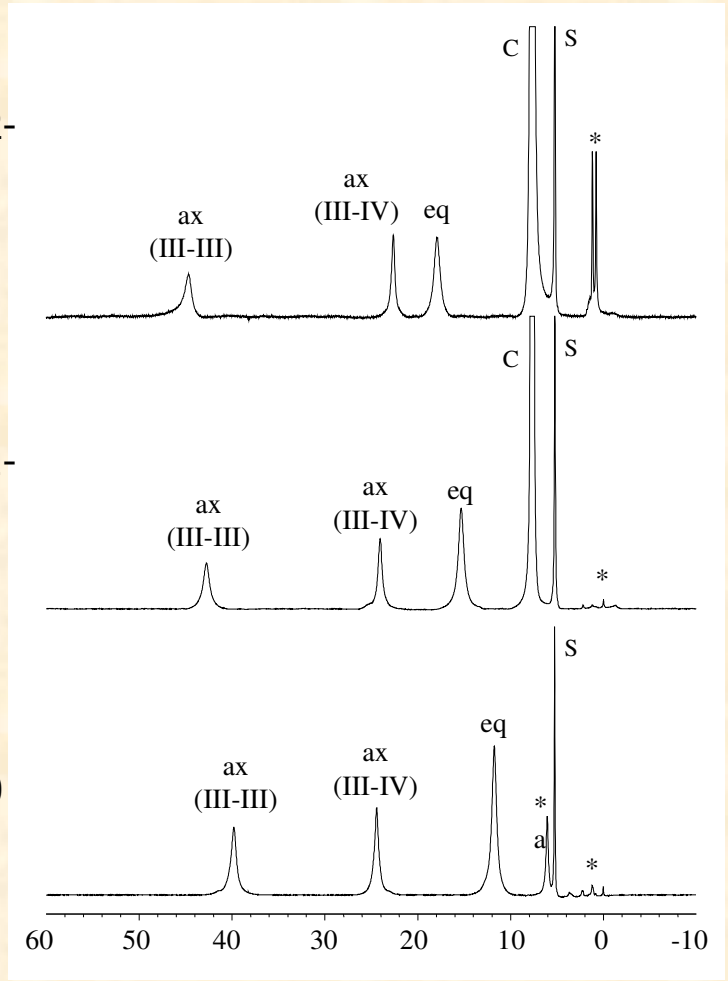


--- added electrons are localized on opposite sides of the Mn_{12} molecule

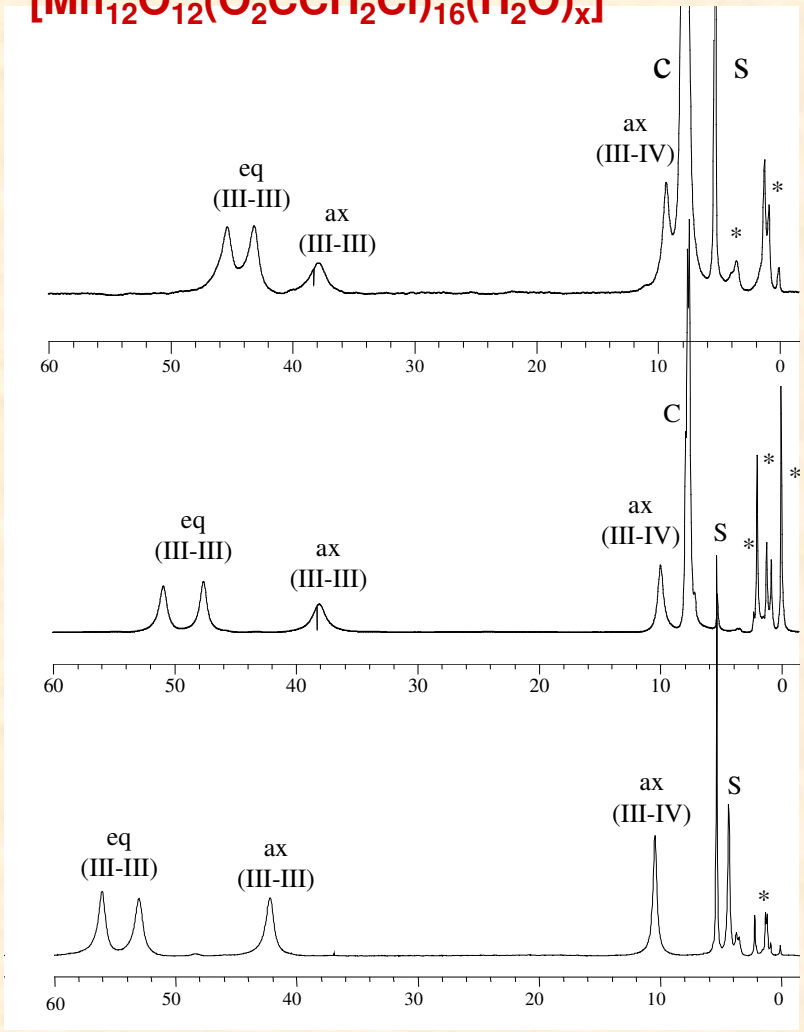
--- the neutral H_2O ligands bind preferentially to the Mn^{II} atoms

^{1}H NMR Spectra of $[Mn_{12}]^{2-}$ in CD_3CN Solution

$[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]^z$



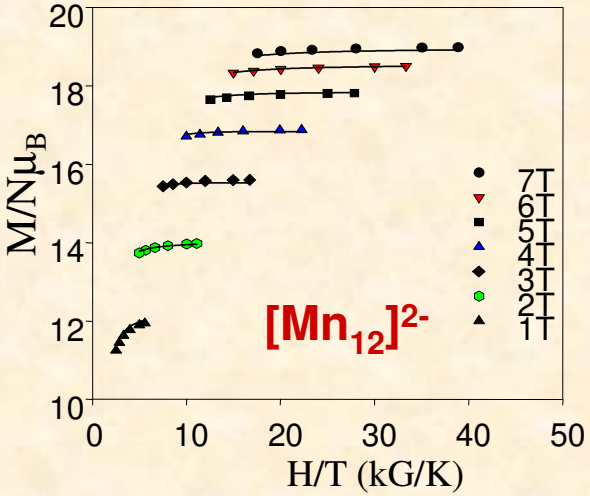
$[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_x]^z$



Effective solution symmetry D_{2d}

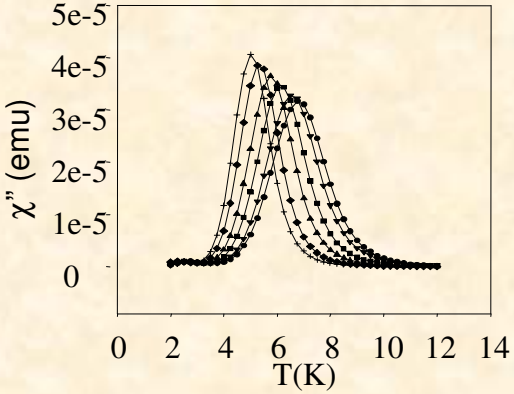
Magnetic Properties of $[Mn_{12}]^{1-,2-}$

DC Reduced Magnetization

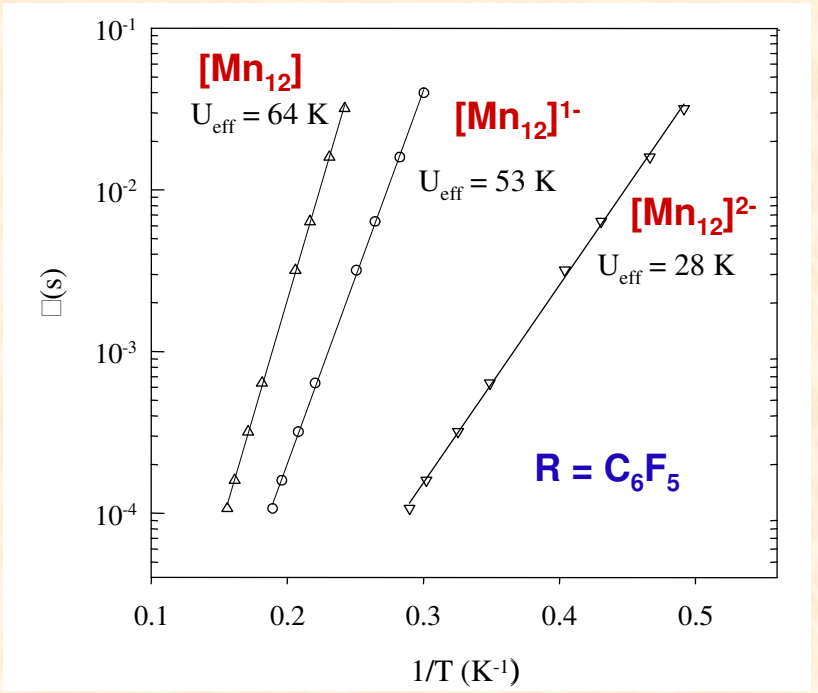


S = 10
D = - 0.27 cm^{-1}
= - 0.39 K

AC Susceptibility

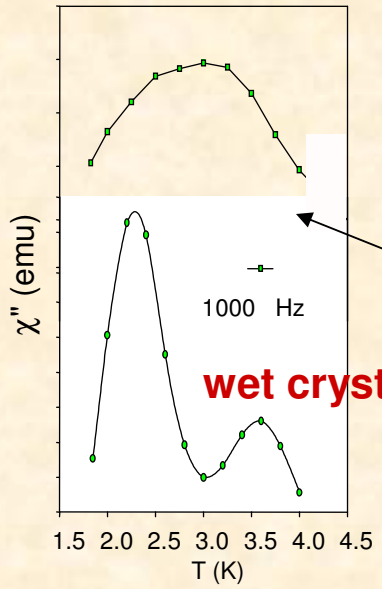


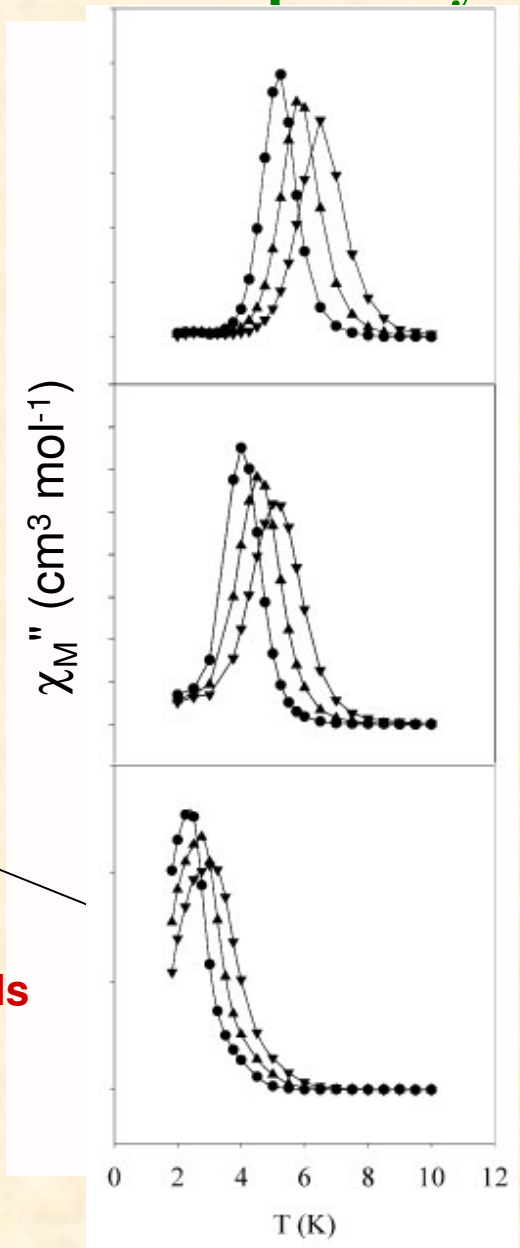
R = $CHCl_2$	$[Mn_{12}]$	$[Mn_{12}]^{1-}$	$[Mn_{12}]^{2-}$
S	10	19/2	10
D (K)	-0.65	-0.49	-0.39
U_{eff} (K)	66	57	32



Out-of-Phase AC Susceptibility for Mn_{12}, $[Mn_{12}]^-$ and $[Mn_{12}]^{2-}$

- dried solids





Mn_{12}

χ_M" peak at 6 - 8 K

$[Mn_{12}]^-$

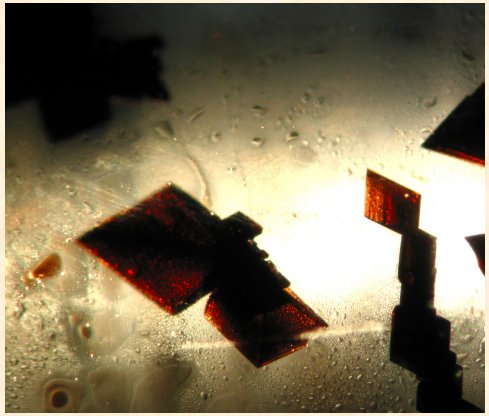
χ_M" peak at 4 - 6 K

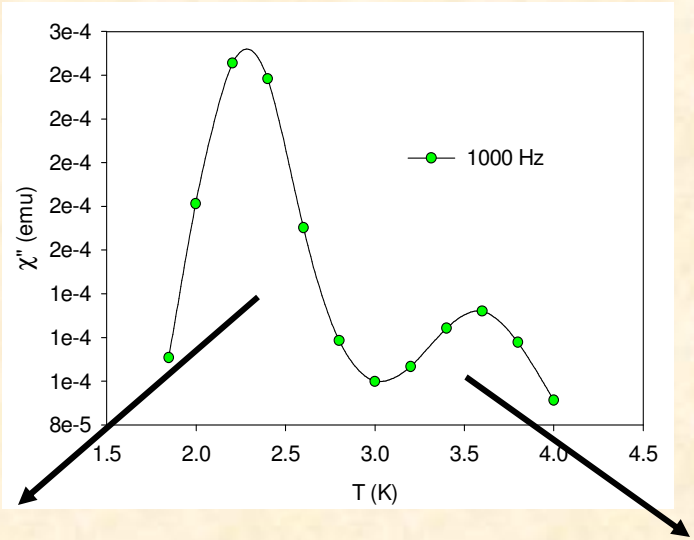
$[Mn_{12}]^{2-}$

χ_M" peak at 2 - 4 K

***Soler, et al., JACS*, 2003, *135*, 3576**

Out-of-phase AC Magnetic Susceptibility for $(PPh_4)_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$





Peak at 2.4 K

Arrhenius → U_{eff} = 18.5 K

$(PPh_4)_2[Mn_{12}]\cdot 4CH_2Cl_2\cdot H_2O$

triclinic P□
V = 6969.79 Å^3

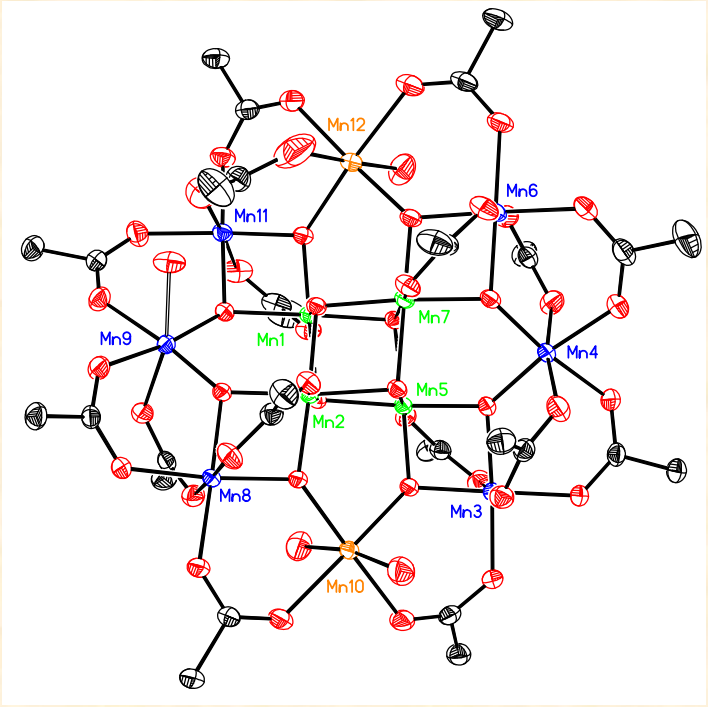
Peak at 3.6 K

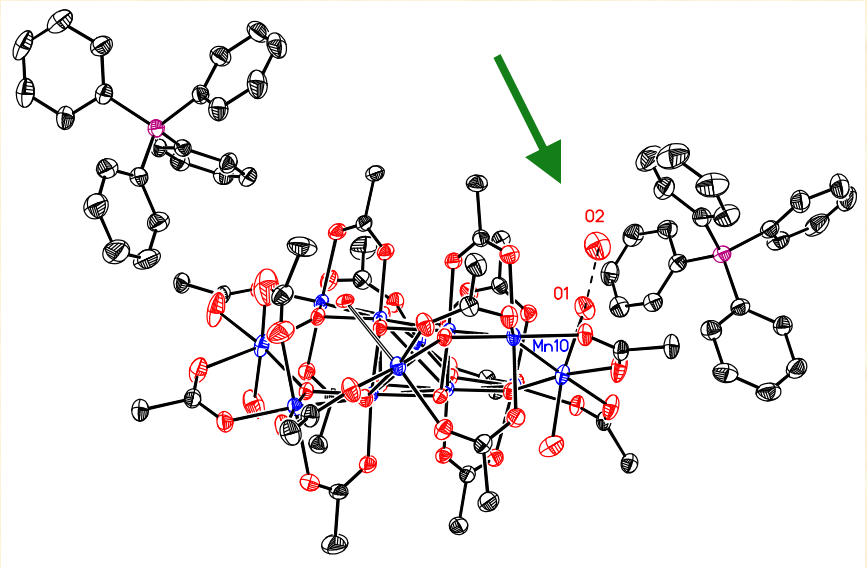
Arrhenius → U_{eff} = 30.2 K

$(PPh_4)_2[Mn_{12}]\cdot 6CH_2Cl_2$

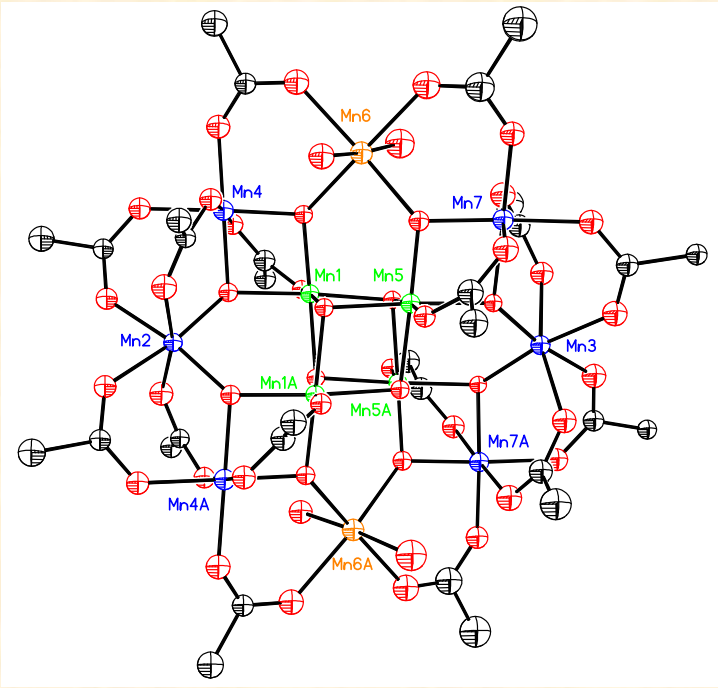
Monoclinic $P2_1/c$
V = 7468.51Å^3

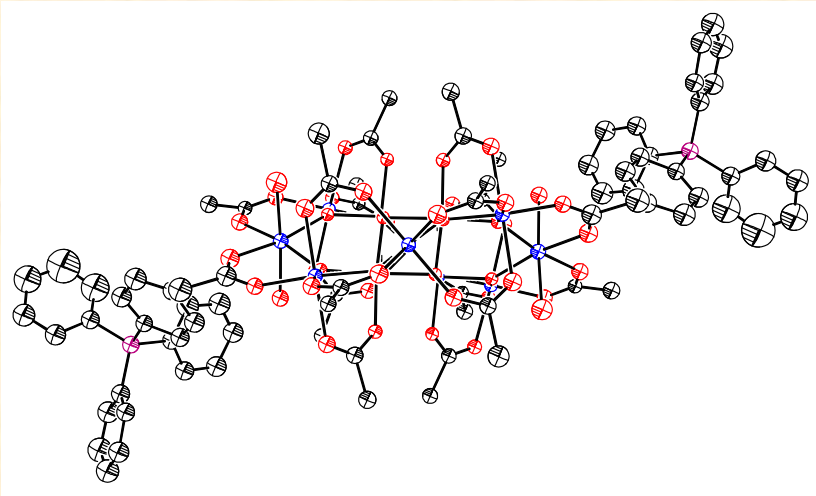
$(PPh_4)_2[Mn_{12}]\cdot 4CH_2Cl_2\cdot H_2O$





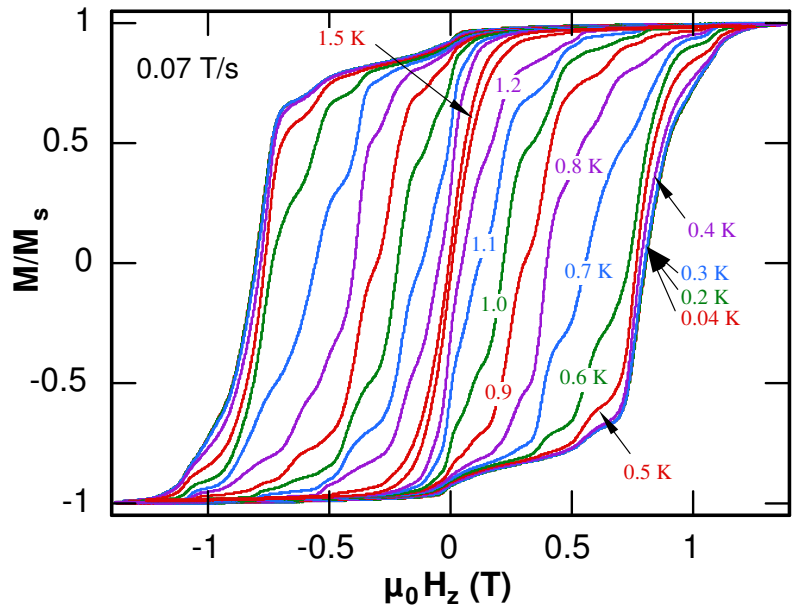
$(PPh_4)_2[Mn_{12}]\cdot 5CH_2Cl_2$





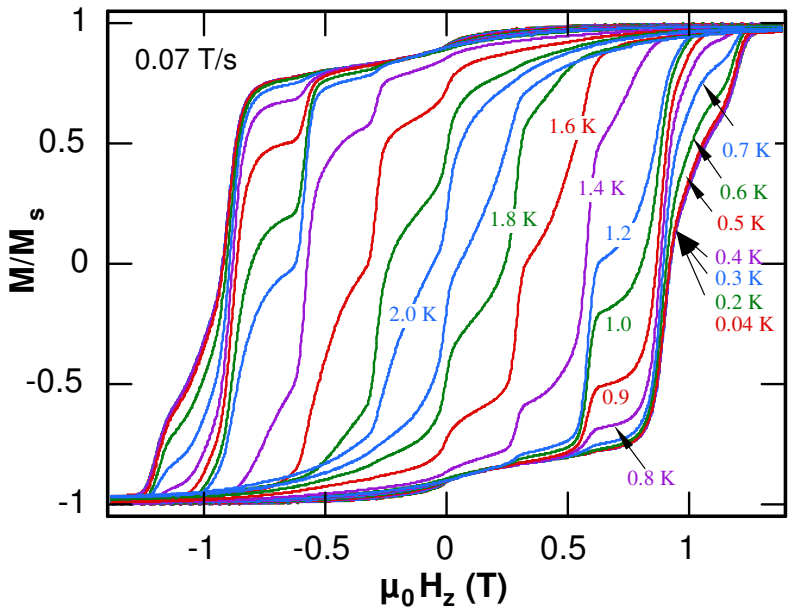
Hysteresis Loops for $(PPh_4)_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$

$(PPh_4)_2[Mn_{12}]\cdot 4CH_2Cl_2\cdot H_2O$ (plates)

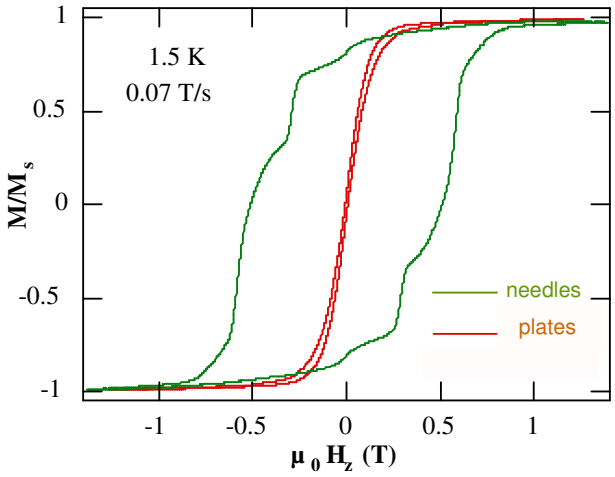


- SMM below T_B = 1.5 K
- Tunneling steps
- D = - 0.17 cm^{-1}
- U_{eff} = 12.9cm^{-1} = 18.5K

$(PPh_4)_2[Mn_{12}]\cdot 6CH_2Cl_2$ (needles)



- SMM below T_B =2.0 K
- Tunneling steps
- D = - 0.28 cm^{-1}
- U_{eff} = 21.0cm^{-1} = 30.2K

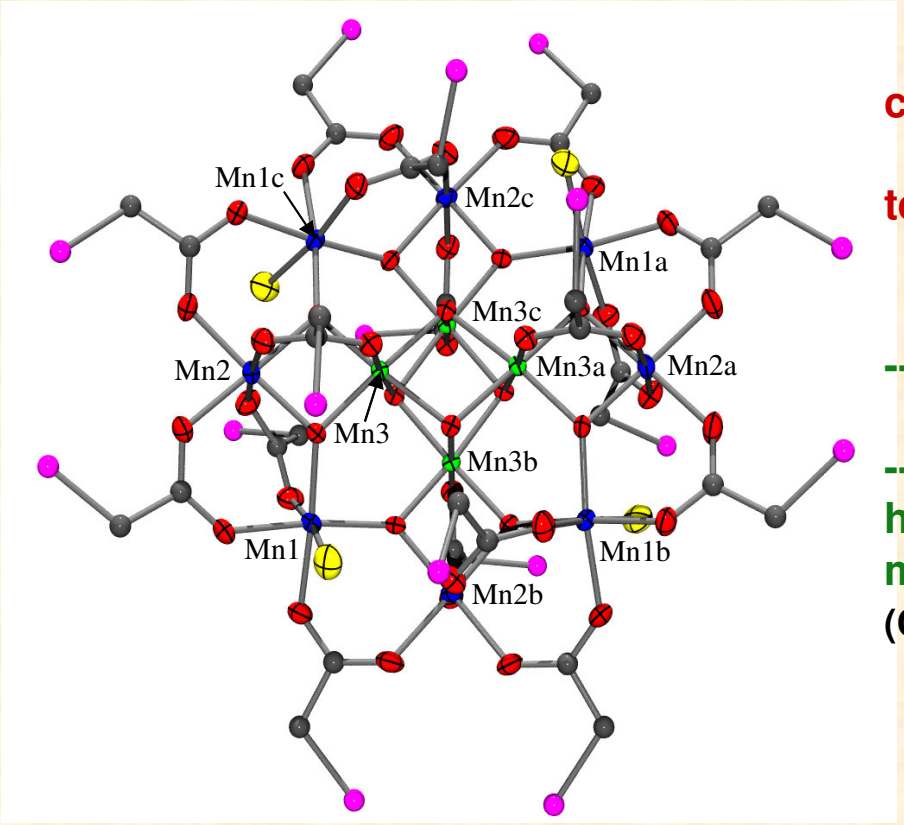


Topics for this presentation:

- **Crystalline arrays of Mn_{12} SMMs, and their controlled modification.**
- **Faster-Relaxing Mn_{12} SMMs: Jahn-Teller Isomerism**
- **Electron addition onto Mn_{12} SMMs, and its effect on the properties**
- **New high-quality Mn_{12} SMMs: the picture comes into focus.**

A Mn_{12} Complex with Tetragonal (Axial) Symmetry: $[Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4]$ (Mn_{12}-BrAc)

$$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4] + 16\ BrCH_2CO_2H \longrightarrow [Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4] + 16\ MeCO_2H$$



crystallizes as $[Mn_{12}BrAc]\cdot 4CH_2Cl_2$

tetragonal space group I42d

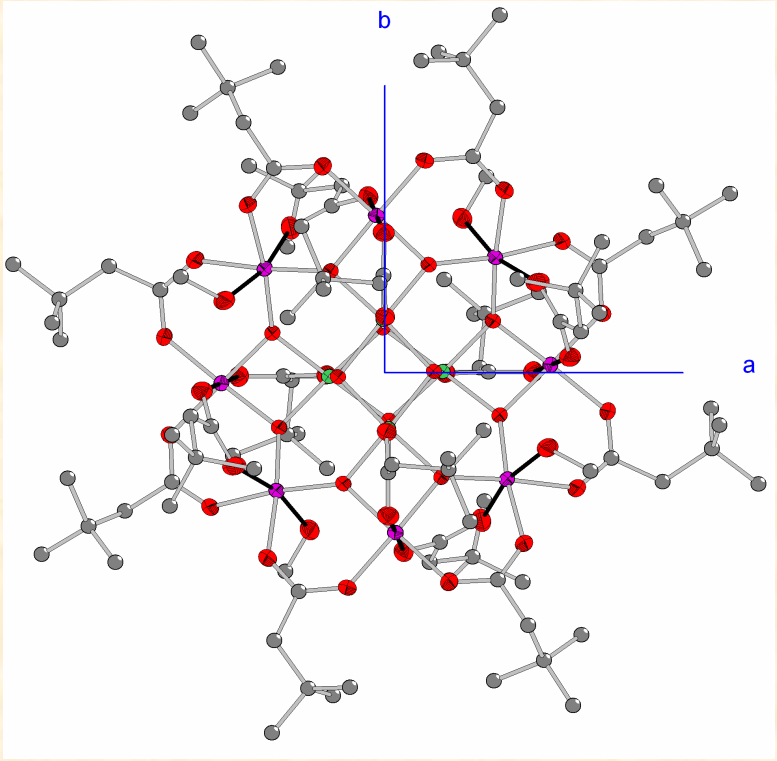
--- single type of molecule in the crystal.

--- in contrast to $Mn_{12}Ac$, where each molecule has strong H-bonding to 0,1, 2, 3 or 4 acetic acid molecules of crystallization

(Cornia et al., *Phys. Rev. Lett.* 2002, *89*, 257201)

Nicole Chakov

A New Mn_{12} Complex with Tetragonal (Axial) Symmetry: $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(MeOH)_4]$ (Mn_{12}-tBuAc)



Mn_{12}Ac	Mn_{12}BrAc	$Mn_{12}Bu^tAc$
*I*4(bar)	*I*42d	*I*4(bar)

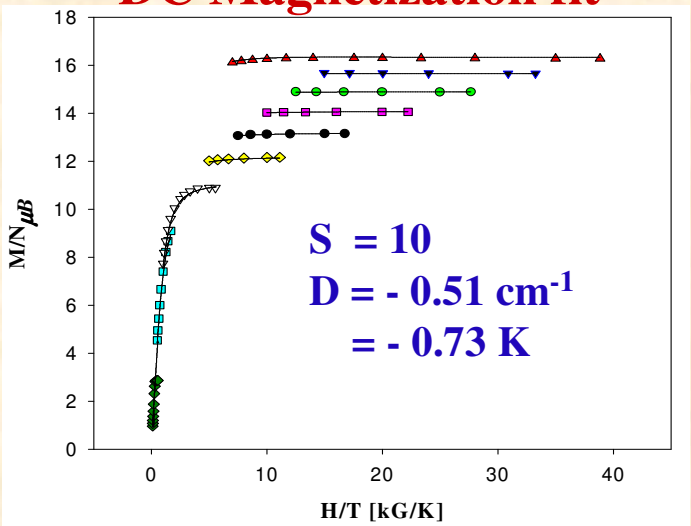
- Better even than Mn_{12}BrAc
- Less solvent of crystallization
- Bulky R group : well separated molecules
- Well aligned with cell axes

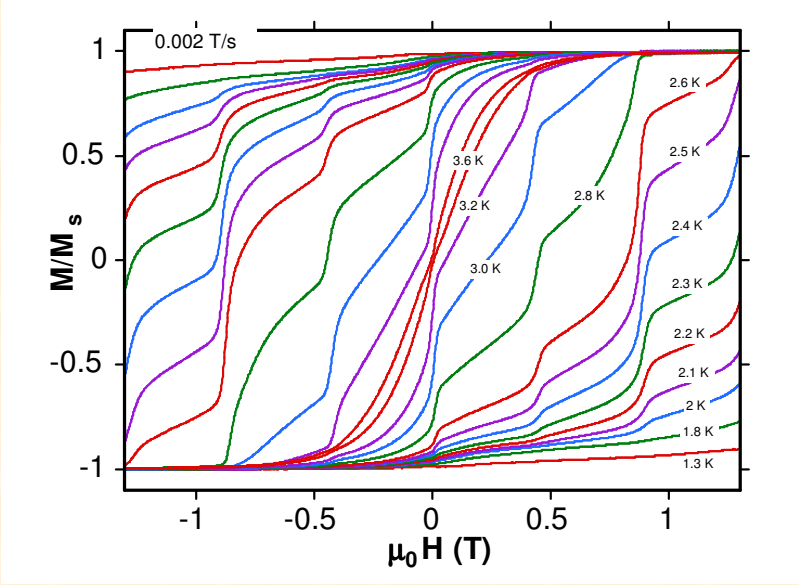
Muralee Murugesu

Magnetic Properties of $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(MeOH)_4]$ ($Mn_{12}Bu^tAc$)

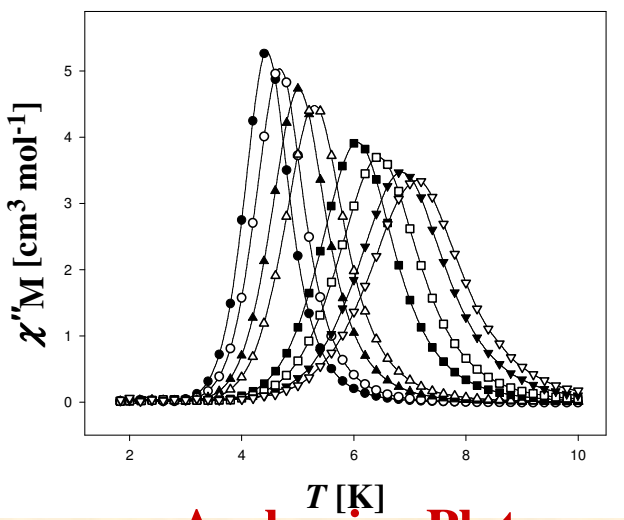
Dr. Muralee Murugesu

DC Magnetization fit

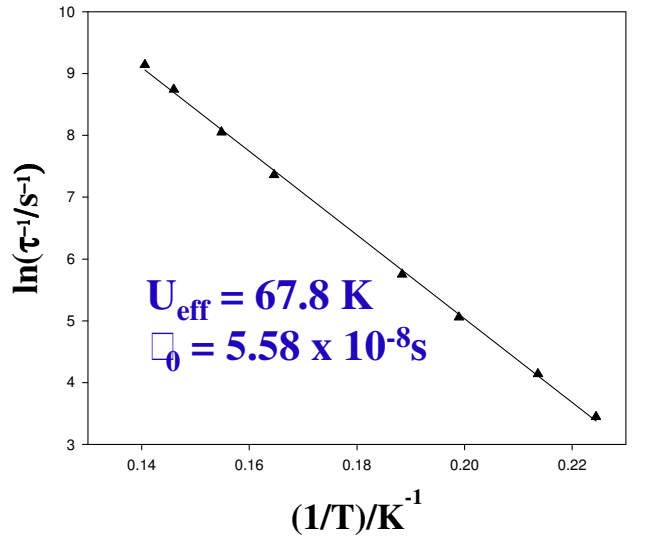




AC Susceptibility

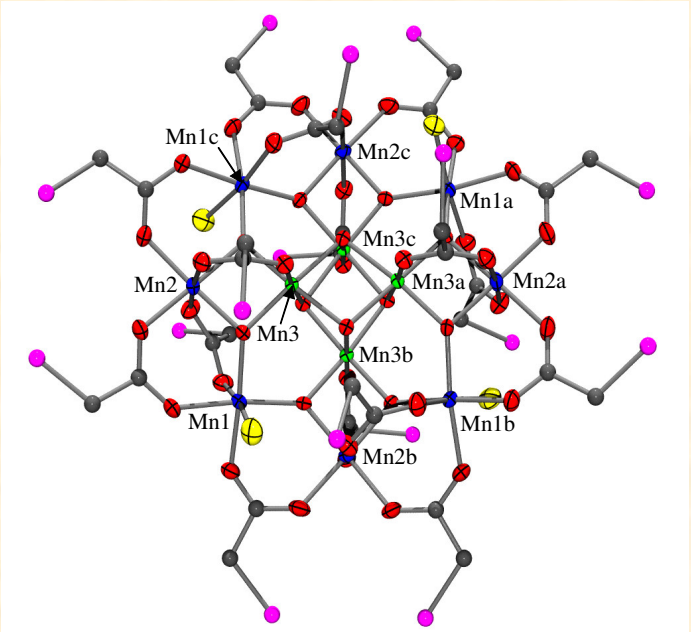


Arrhenius Plot



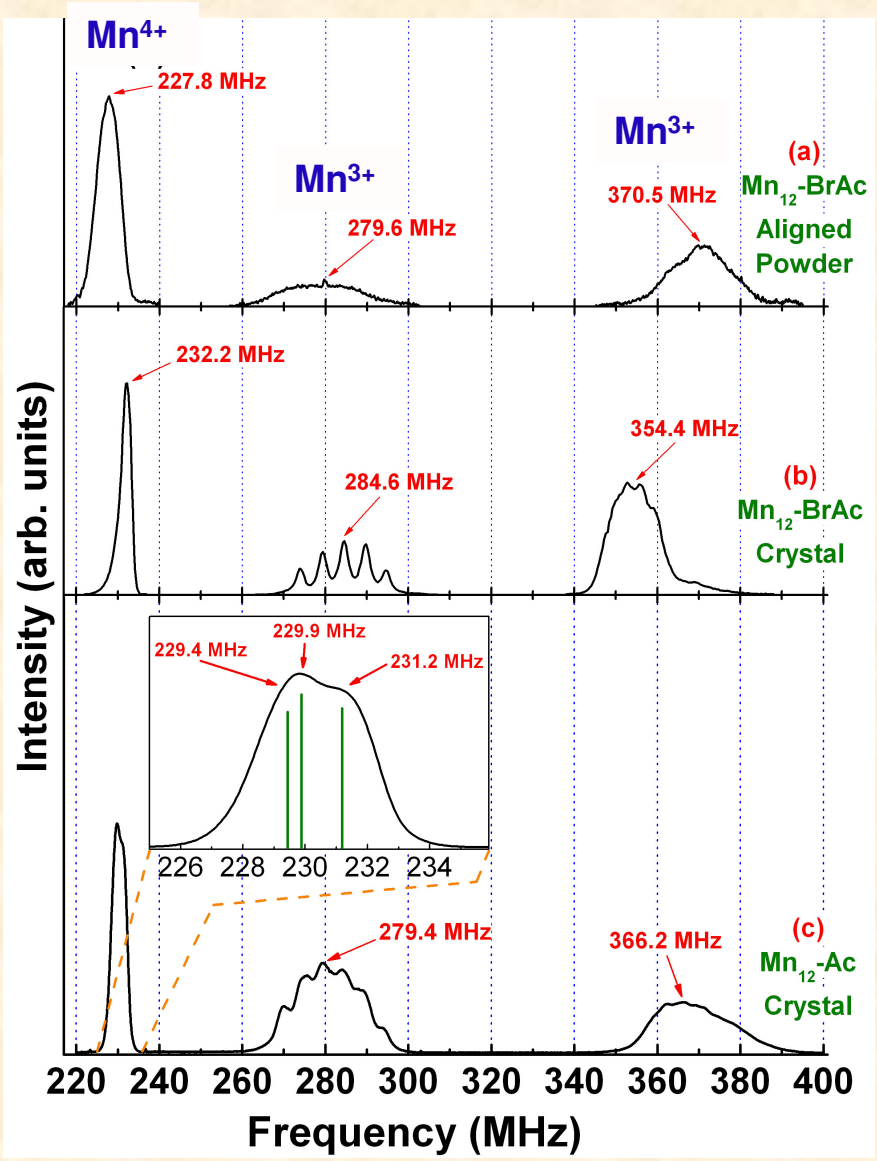
Single-Crystal ^{55}Mn NMR Spectra of Mn_{12}Ac vs Mn_{12}BrAc with S_4 (Axial) Symmetry

Mn_{12}BrAc



Mn_{12}-Ac: tetragonal space group I4(bar)
Mn_{12}-BrAc: tetragonal space group I42d

N. S. Dalal, S. O. Hill, G. Christou, *et al.*
Inorg. Chem. 2005, *44*, 2122.
JACS, 2006, *128*, 6975

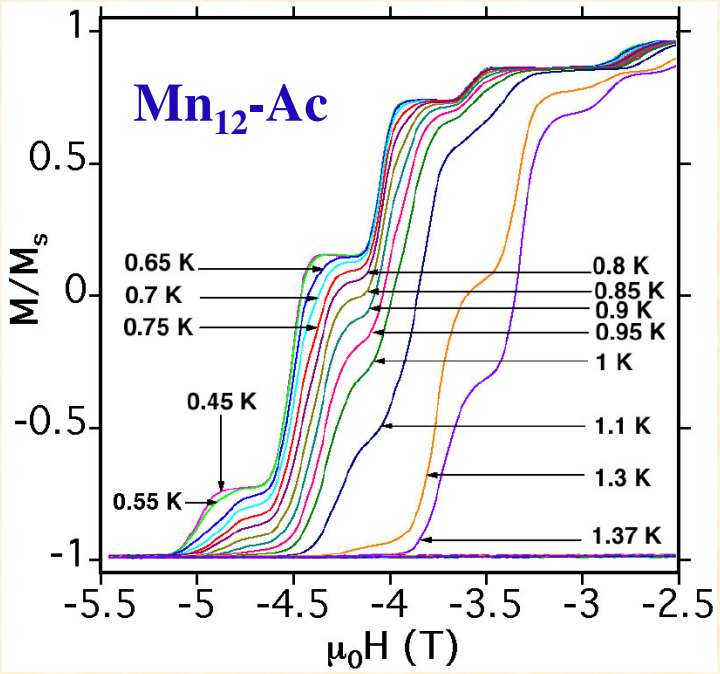


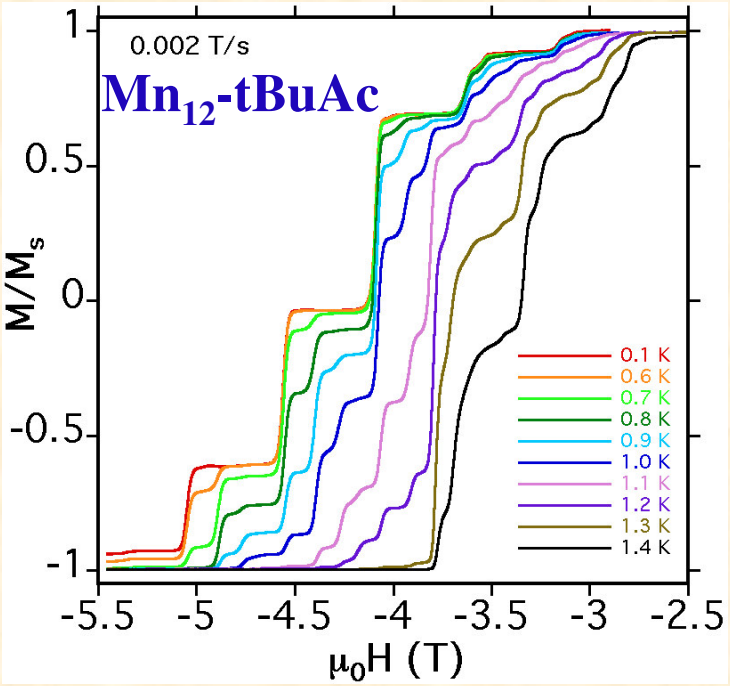
A New Mn_{12} Complex with Tetragonal (Axial) Symmetry: $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(MeOH)_4]\cdot MeOH$ (Mn_{12}-tBuAc)

Mn_{12}-Ac	Mn_{12}-tBuAc
*I*4(bar)	*I*4(bar)

--- no symmetry-lowering contacts with the solvent molecules in the crystal

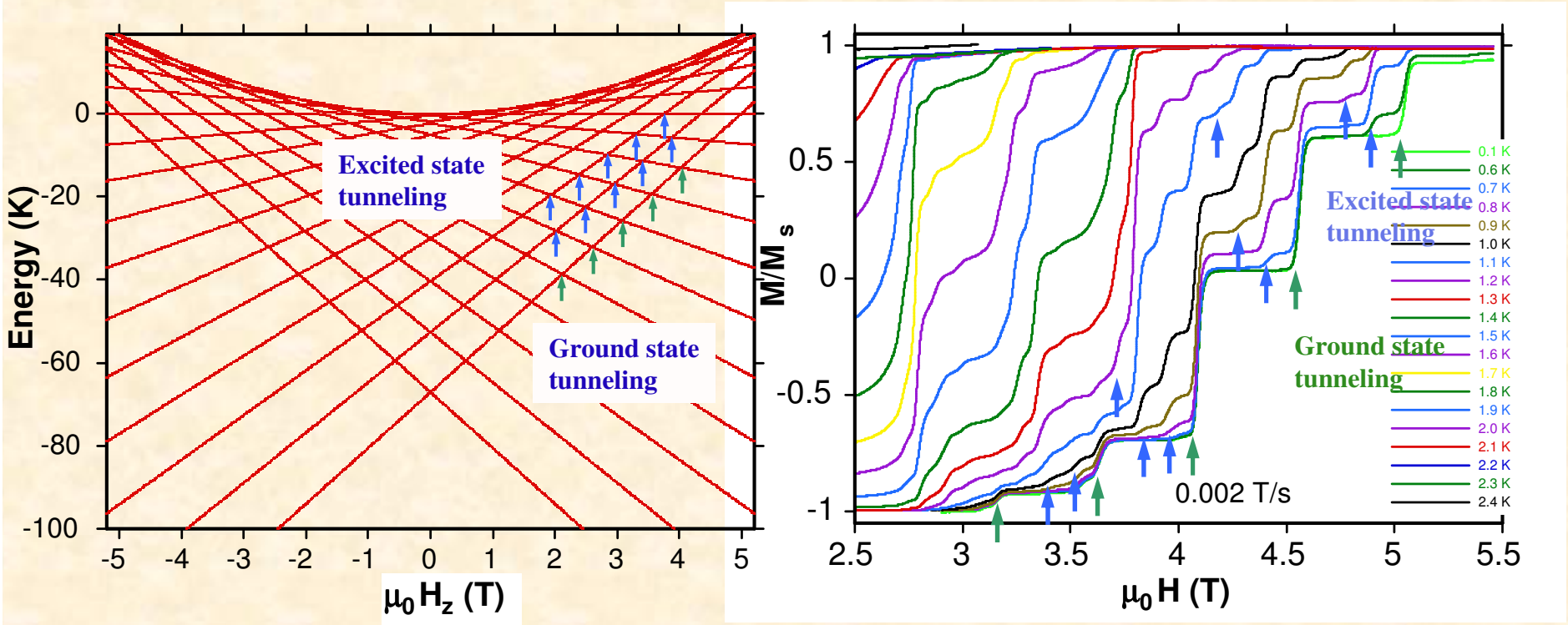
--- bulky R group : well separated molecules





Wernsdorfer, Murugesu, and Christou, *P. R. L.*, 2006, 96, 057208

The Sharpness of the Hysteresis Loops in Mn_{12}-tBuAc allows Steps due to Excited State Tunneling to be seen



Wernsdorfer, Murugesu and Christou, *Phys. Rev. Lett.*, 2006, 96, 057208

<u>Summary</u>: Researchers have thought for over 13 years that axial Mn_{12}-Ac is the best one to study, but it is not. More interesting physics is now being discovered with cleaner, truly axial Mn_{12} SMMs