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

Lecture 3: What next?

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What is the current status of the field?

1. **Single-molecule magnetism has been identified**

    -- it was not predicted, it was discovered -----

    -- Mn_{12} (S = 10) showed this new magnetic phenomenon to be possible.

    -- Fe_8 (S = 10) and Mn_4 (S = 9/2) came 3 years later and showed:

    (a) Mn_{12} was not a freak;

    and (b) that half-integer spin SMMs are also possible.

    -- the operating ("blocking") temperatures are very low (the highest are still between 3 and 4 K for the Mn_{12} SMMs).

    -- the importance of Mn_{12} was to show this new magnetic phenomenon is possible, even though it itself will probably never be used in devices (like Hg in superconductivity)

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

What is the current status of the field? (cont)

2. SMMs have brought all the advantages of molecular chemistry to nanomagnetism. ---

   -- e.g. modification of the Mn_{12} acetate by

   (i) carboxylate (RCO_2^-) substitution

   (ii) site-selective introduction of other types of ligands

   (iii) addition of one or two extra electrons

   These gave not just more of the same ("stamp collecting"), but instead revealed fundamentally important new knowledge and behavior (faster-relaxing variants, subtle environmental effects on relaxation barriers and anisotropies, modulation of quantum properties, etc)

   -- the field would soon have died if only the original Mn_{12} acetate was still available to study!

Advantages of SMMs over Traditional Nanoscale Magnetic Particles

Properties

- truly monodisperse (identical size) particles of nanoscale dimensions
- crystalline, therefore contain highly ordered ensembles
- well-defined ground state spin, S
- truly quantum spin systems

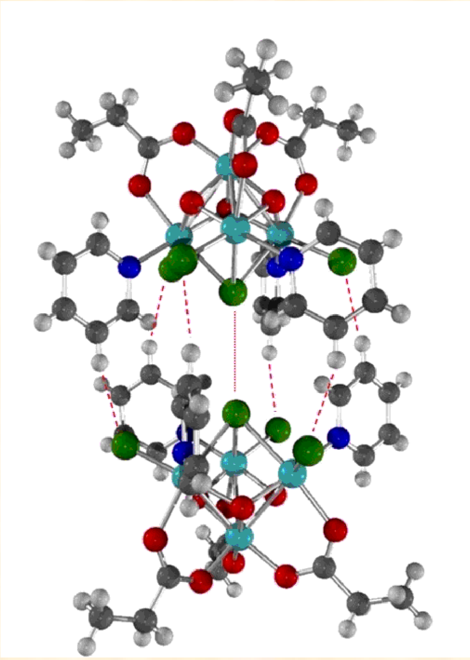
Synthesis

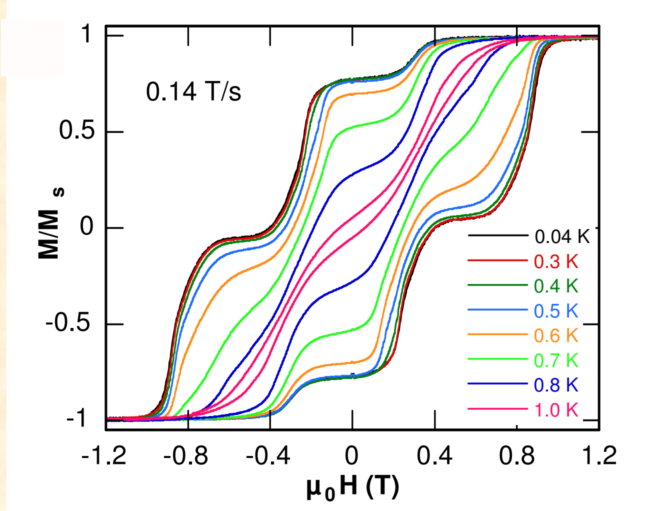
- synthesized by room temperature, solution methods
- enveloped in a protective shell of organic groups (ligands)
- truly soluble (rather than colloidal suspensions) in organic solvents
- the organic shell (ligands) around the magnetic core can be easily modified, providing control of separations between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

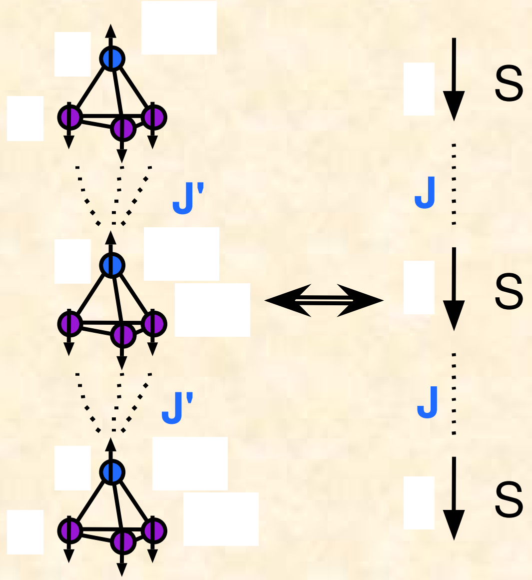
What is the current status of the field? (cont)

3. **Weakly-linking SMMs (through hydrogen-bonds) into dimers (pairs), chains, etc is a way to modulate the quantum tunneling.**

-- e.g. the exchange-biased dimers that are the only way so far found to shut down tunneling in zero field.







What is the current status of the field? (cont)

4. **Many, many new SMMs have been discovered around the world, most (>80%) in Mn chemistry, and a few each in Fe, Ni, Co and mixed 3d/4f chemistry.**

   -- new ones being discovered every month as more synthetic chemistry groups around the world join the search

What properties should we be trying to improve to make future applications more feasible?

1) Raise the blocking temperature (T_B)

-- the higher the better, of course, but even 20 K would be a major breakthrough in this regard

-- we are not trying to replace traditional magnets, but to develop materials for more specialized applications where small size, monodispersity, etc are an advantage.

2) Overcome the instability in water

-- potential applications in medicine-biochemistry-biotechnology (binding to specific amino-acids on proteins as markers, MRI agents, insertion into cells, etc) are hampered by hydrolysis to 3D metal oxides.

-- various ways to stabilize them are under investigation

3) Shut down quantum tunneling at zero field

-- for classical information storage, where each molecule would represent one bit, the tunneling at zero field is a major problem, since it would dissipate away the stored information as the magnetization equilibrates

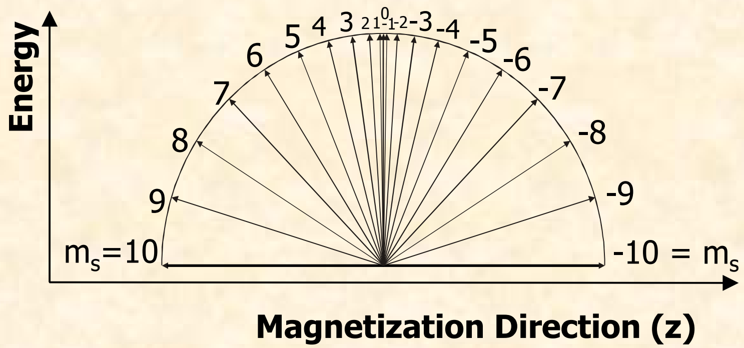
-- the $[Mn_4]_2$ dimer has shown one example of how it can be done.

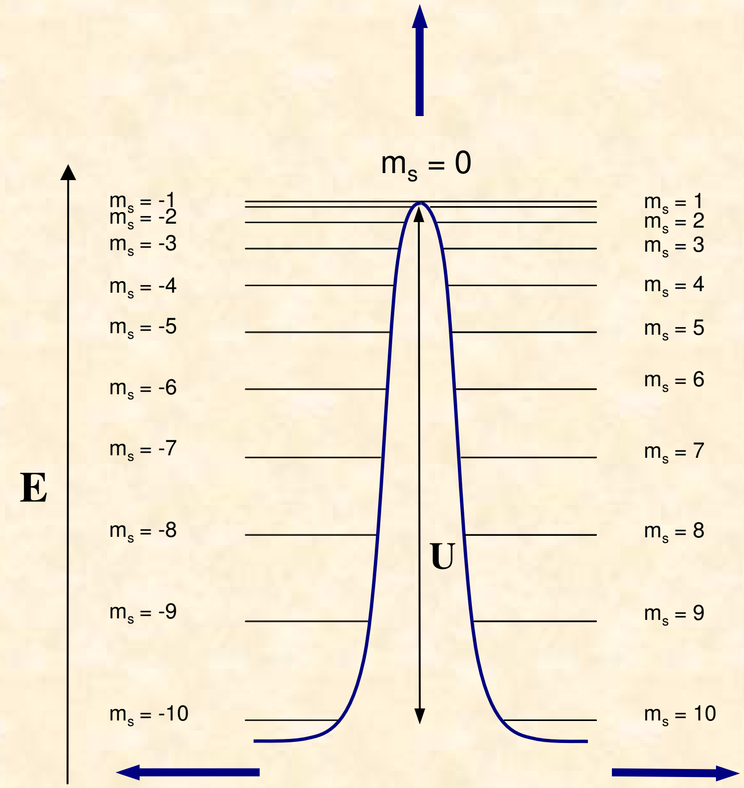
So, how are we going to raise T_B?

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)**





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

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

So, how are we going to raise T_B?

1) Increase S

and/or

2) Increase D

BUT: also A) Keep the molecular and crystal symmetry high to minimize tunneling through the barrier.

B) Ensure excited states are far above the ground state.

C) Control/eliminate those damn solvent molecules of crystallization!

We are trying….. but it's not easy

Still, interesting things are being found along the way:

Some recent results from our attempts to:

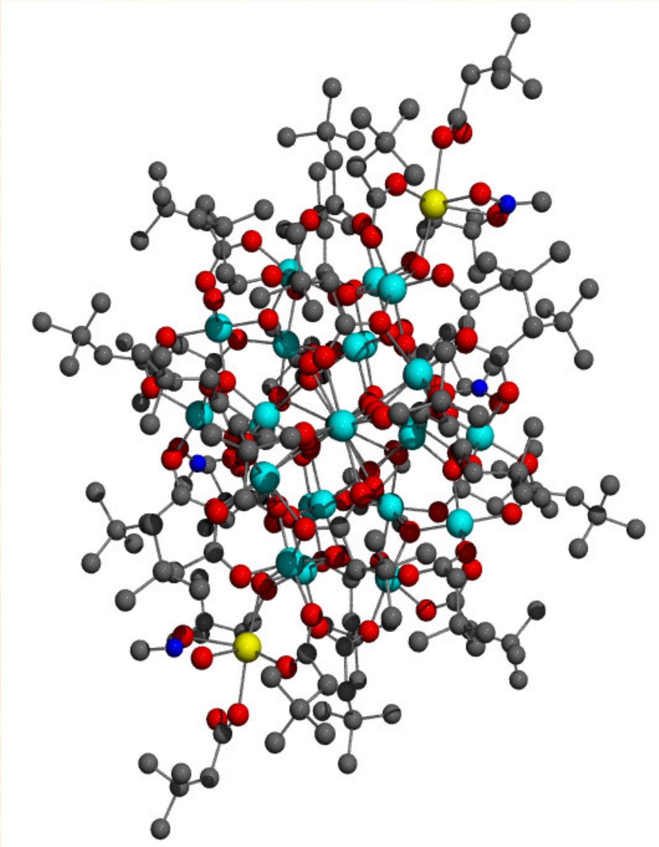
1) Increase S
   - -- increase the metal content (i.e. the molecular size)
   - -- ensure ferromagnetic coupling
2) Increase D
   - -- incorporate lanthanides

A Mn_{30} Single-Molecule Magnet with S = 5

$[Mn_{30}O_{24}(OH)_8(O_2CR)_{32}(MeNO_2)_4(H_2O)_2]$

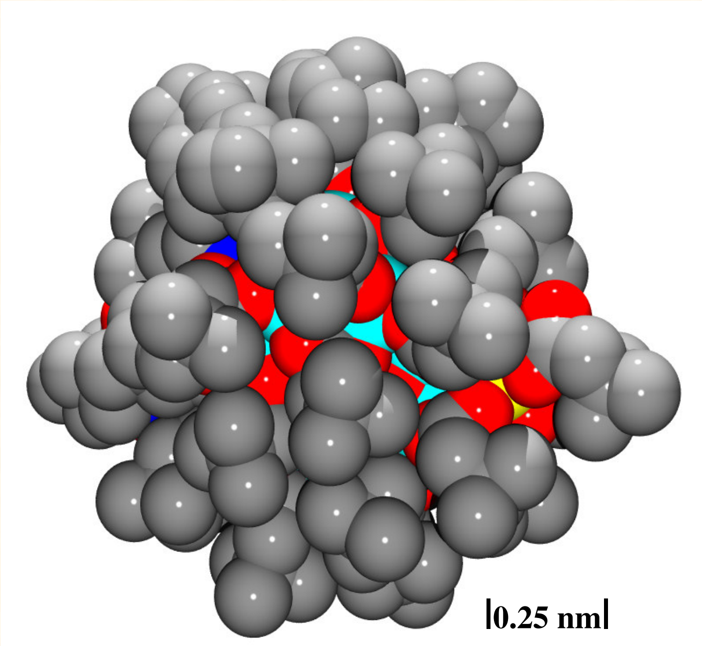
$3Mn^{2+}$, 26 Mn^{3+}, Mn^{4+}

Monoclinic C2/c



Ball-and-stick View

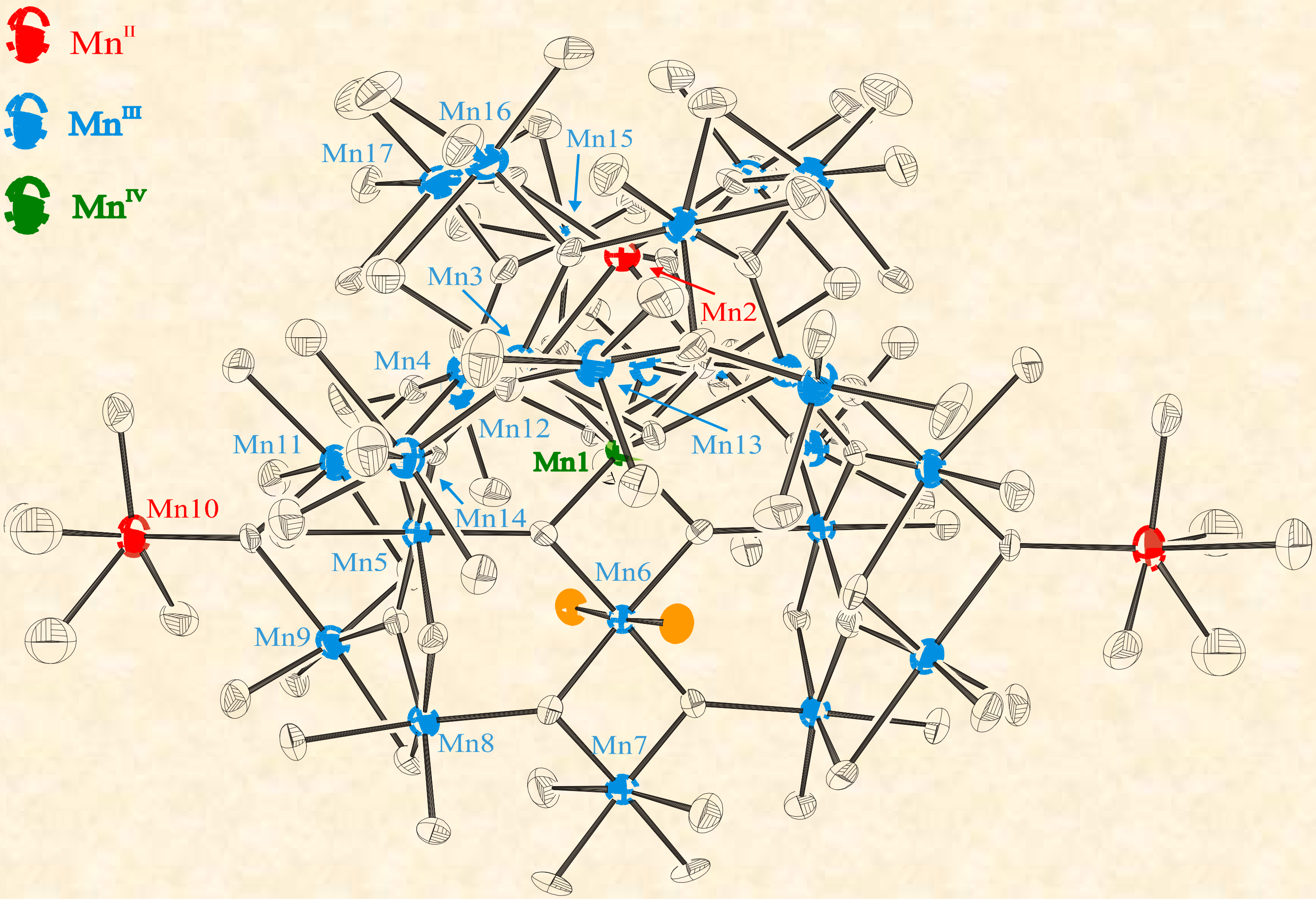
Mn^{2+}: sky-blue
Mn^{3+}: yellow
O : red
N : dark blue



Space-fillingView

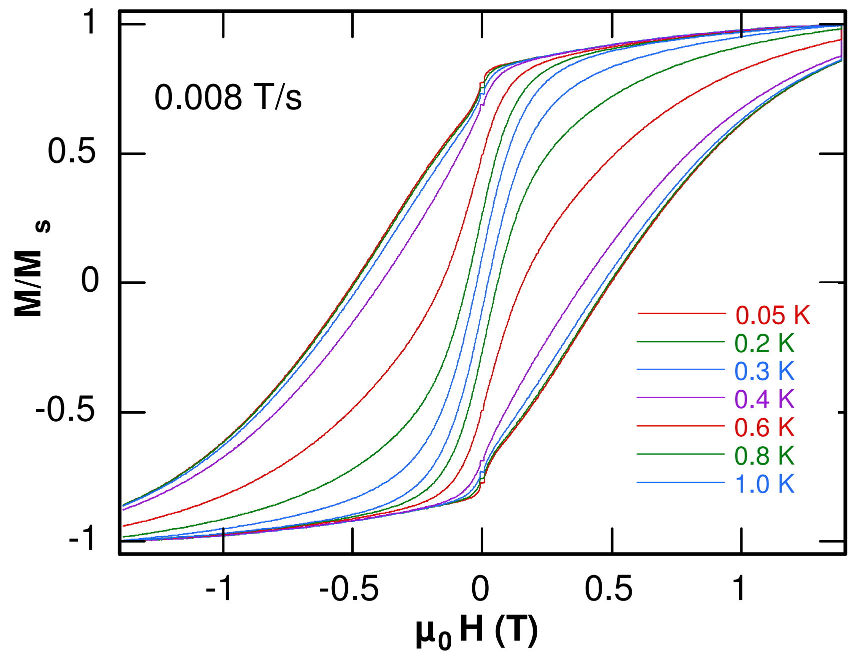
M. Soler, *et al. J. Am. Chem. Soc.*, 2004, *126*, 2156

$[Mn_{30}O_{24}(OH)_8(O_2CCH_2Bu^t)_{32}(H_2O)_2(CH_3NO_2)_4]\cdot$solvent

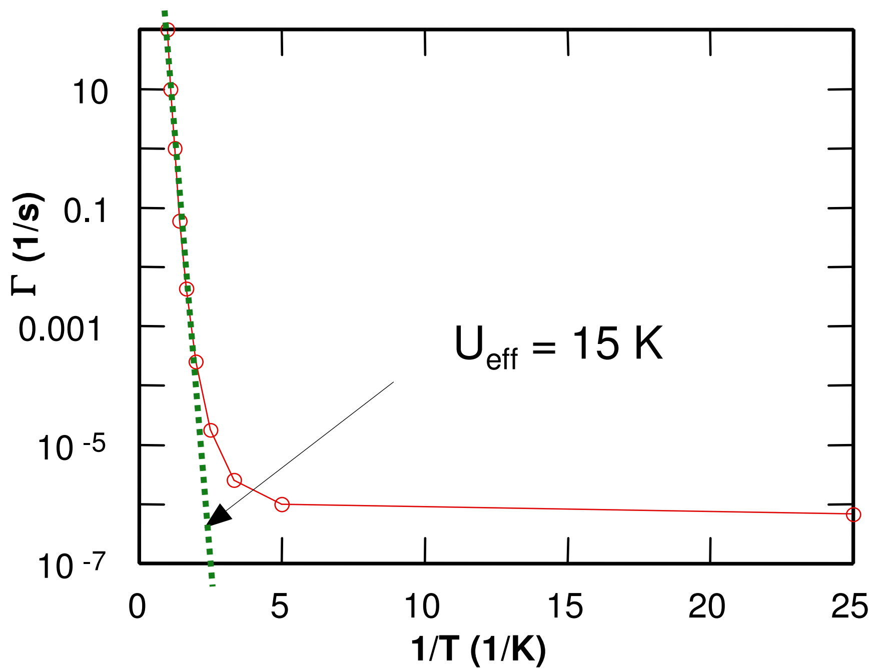


$[Mn_{30}O_{24}(OH)_8(O_2CCH_2Bu^t)_{32}(H_2O)_2(MeNO_2)_4]$•solvent

Hysteresis loops



Arrhenius plot



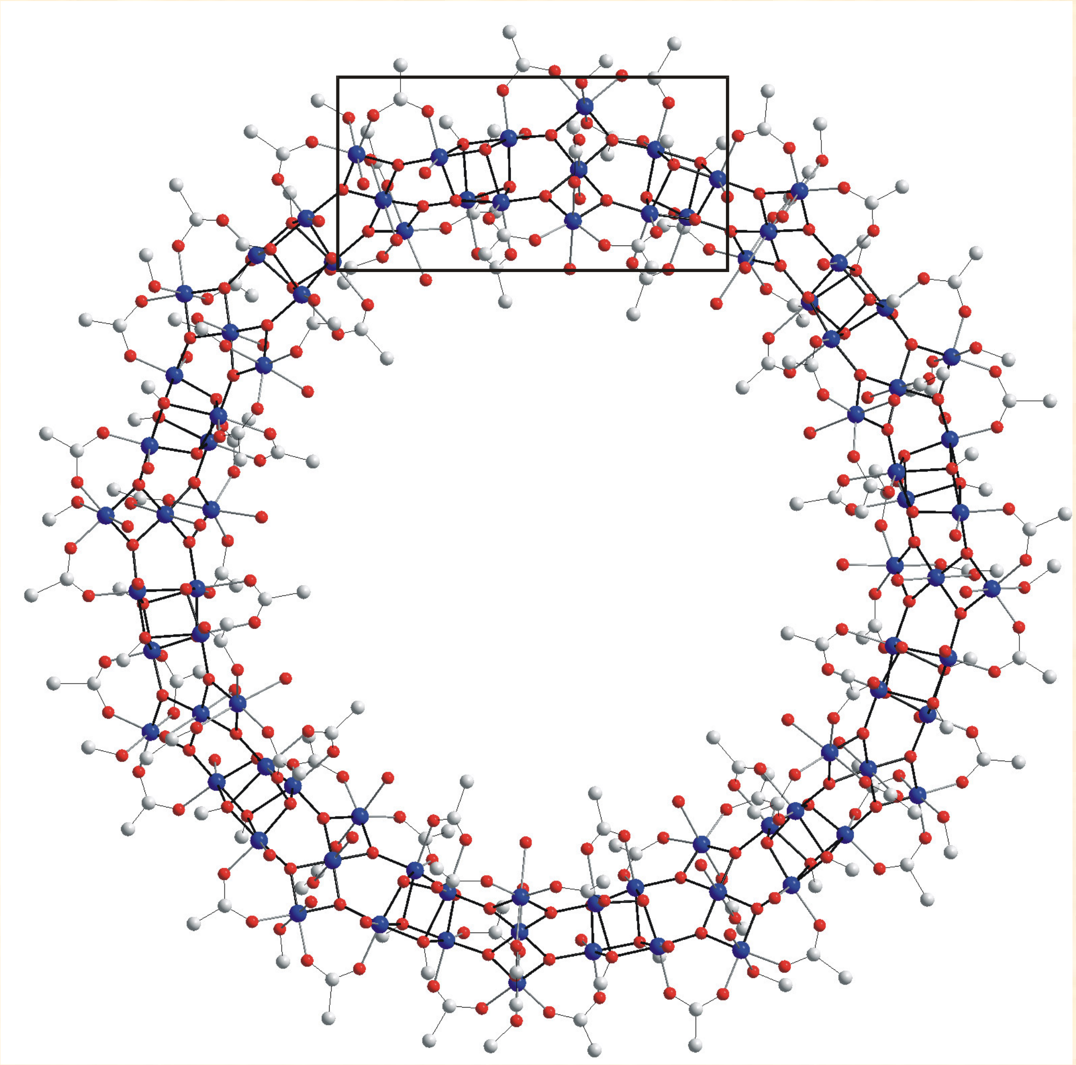
- Mn_{30} is a SMM with a T_B of ~ 1.2K
- Only step at H = 0 can be clearly seen
- Distribution of barriers/environments, due to ligand and solvent disorder

U_{eff} = 15 K

<0.2 K relaxation becomes T-independent

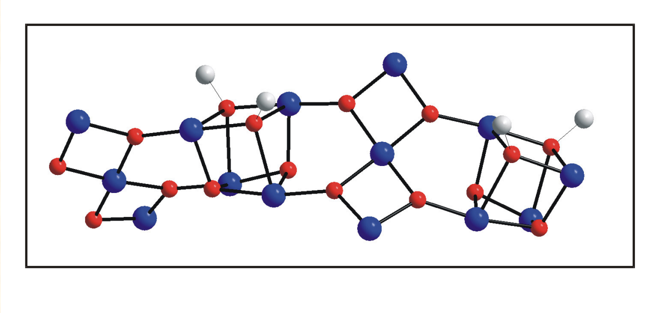
A New Generation of Mn Clusters: A Mn_{84} Torus

$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + MnO_4^-$ in $MeOH/MeCO_2H$

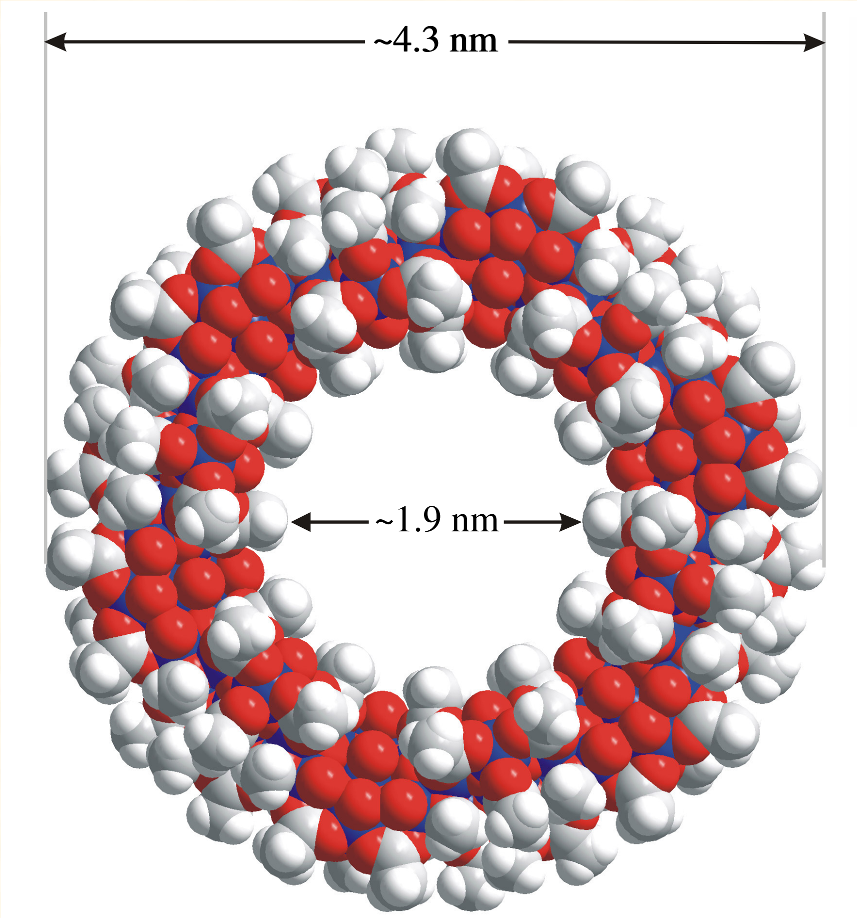


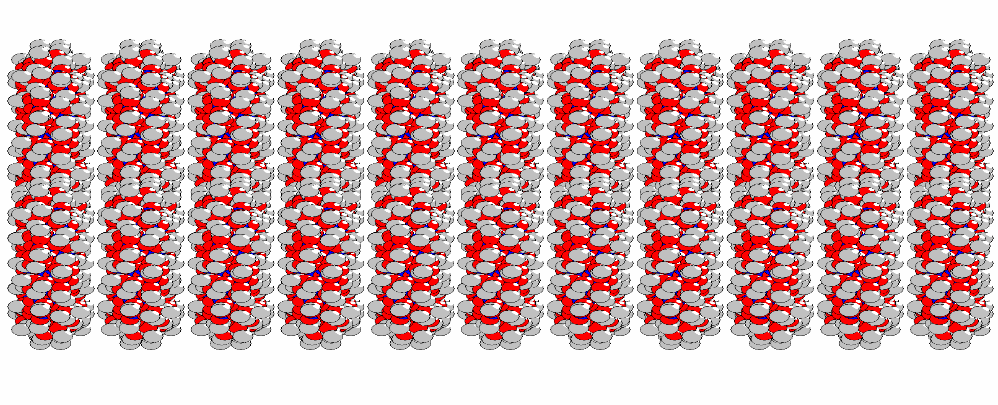
Space group *P6*

The structure consists of six Mn_{14} units i.e. $[Mn_{14}]_6$

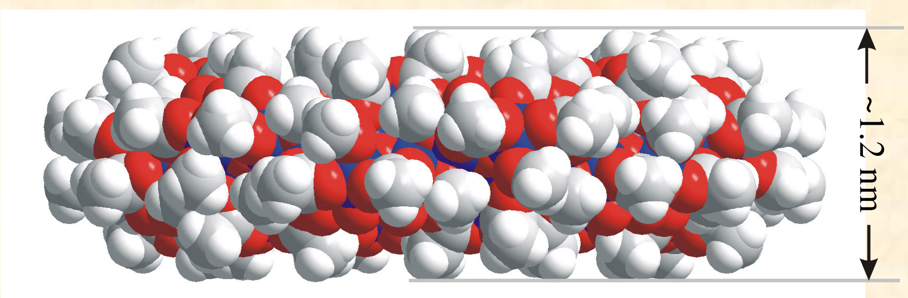


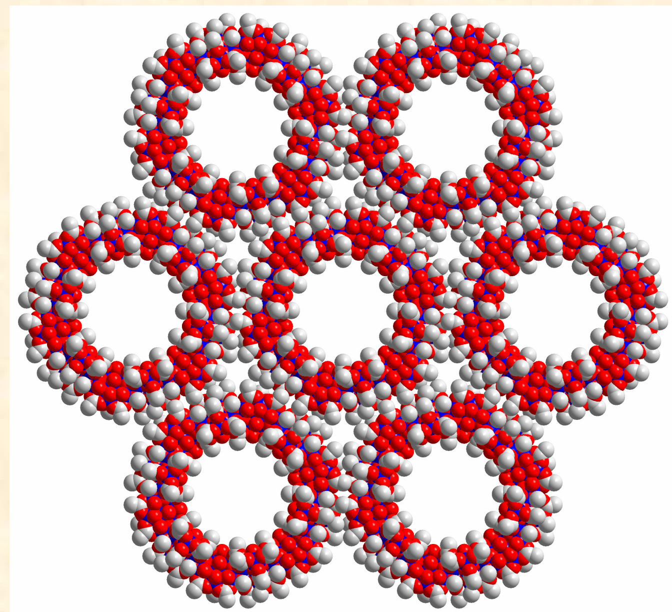
Tasiopoulos *et al*. *Angew. Chem. Int. Ed.* 2004, *43*, 2117



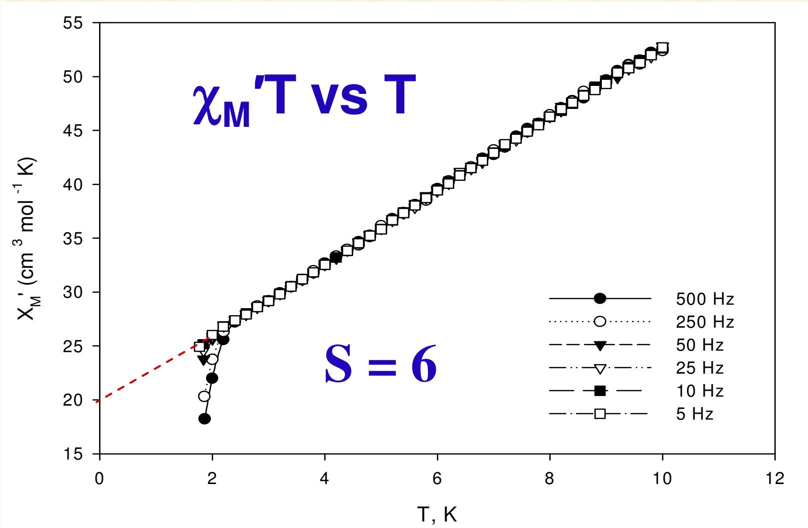


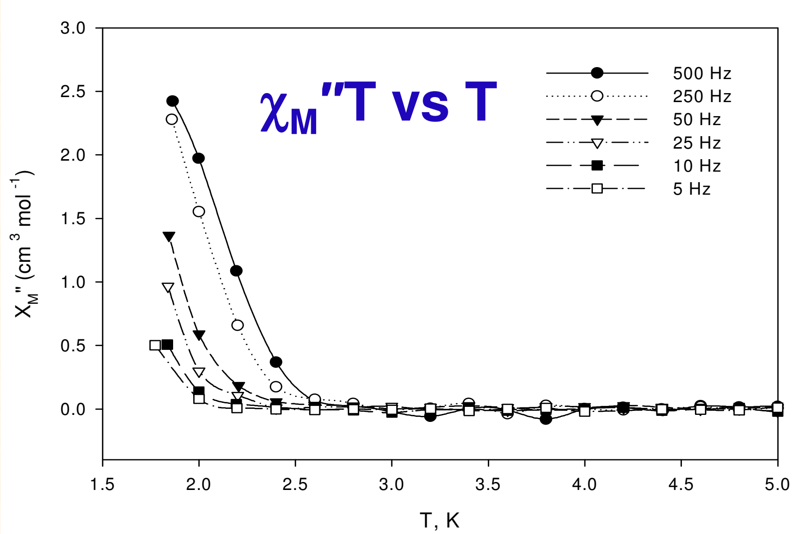
Side-view

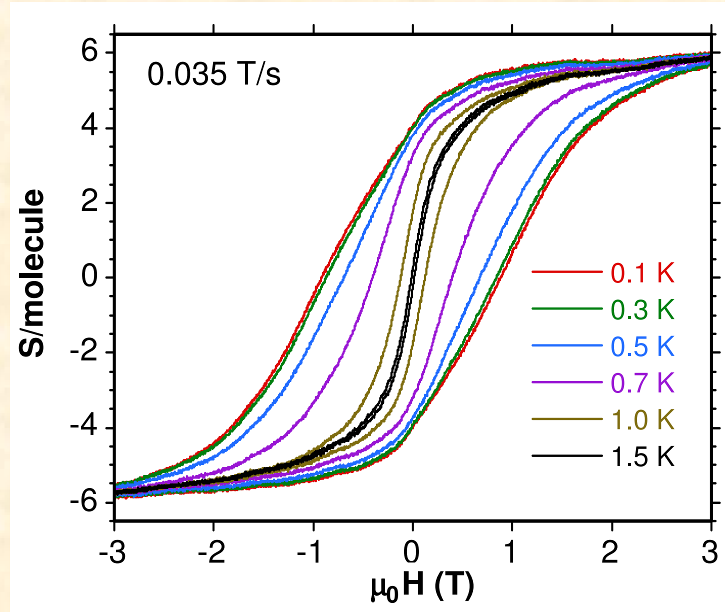


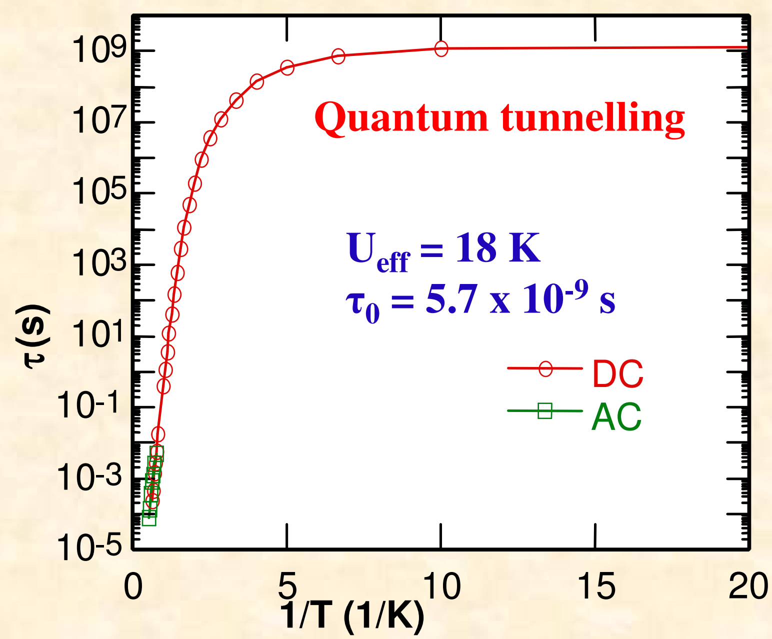


Front-view

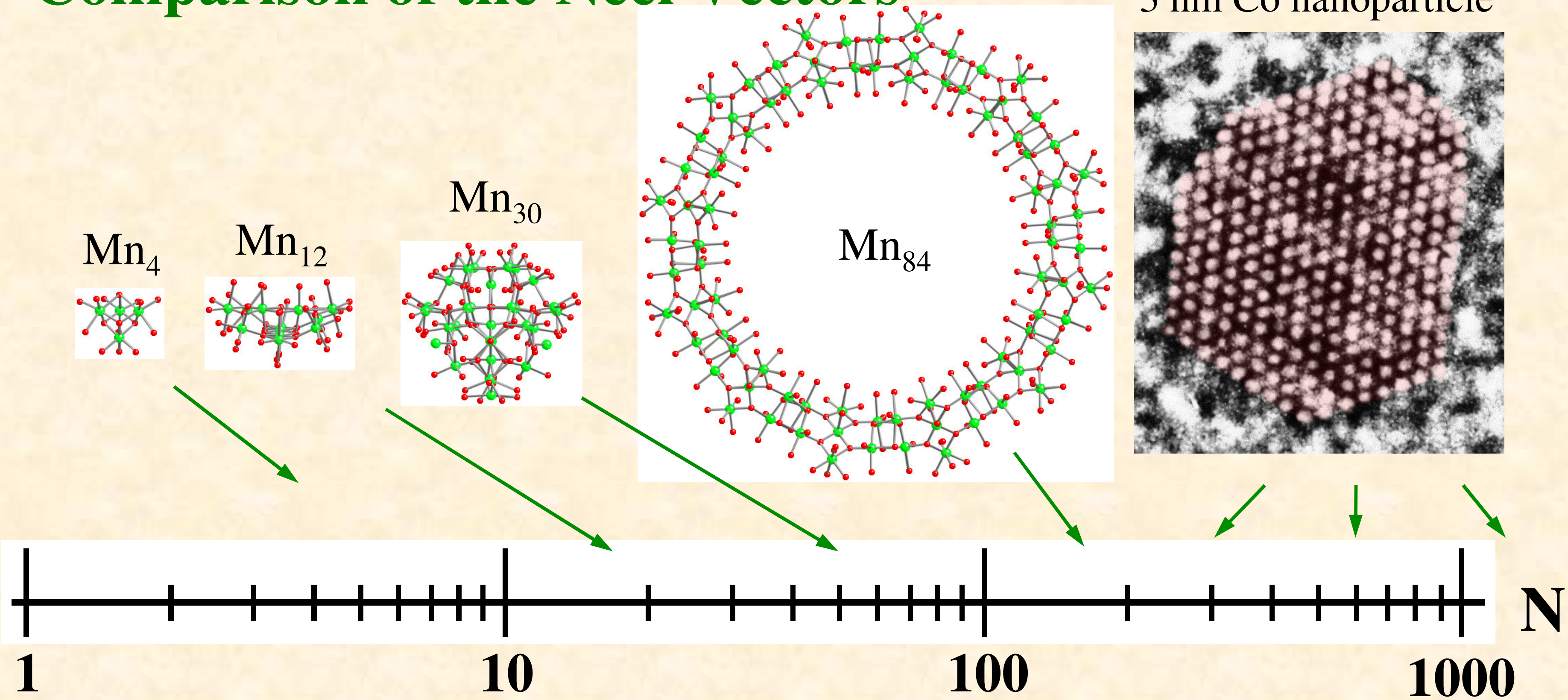

χM'T vs T
S = 6
500 Hz
250 Hz
50 Hz
25 Hz
10 Hz
5 Hz
XM' (cm 3 mol -1 K)
T, K


χM''T vs T
500 Hz
250 Hz
50 Hz
25 Hz
10 Hz
5 Hz
XM'' (cm 3 mol -1)
T, K


0.035 T/s
0.1 K
0.3 K
0.5 K
0.7 K
1.0 K
1.5 K
S/molecule
μ0H (T)


Quantum tunnelling
Ueff = 18 K
τ0 = 5.7 x 10-9 s
DC
AC
τ (s)
1/T (1/K)

Comparison of the Néel Vectors

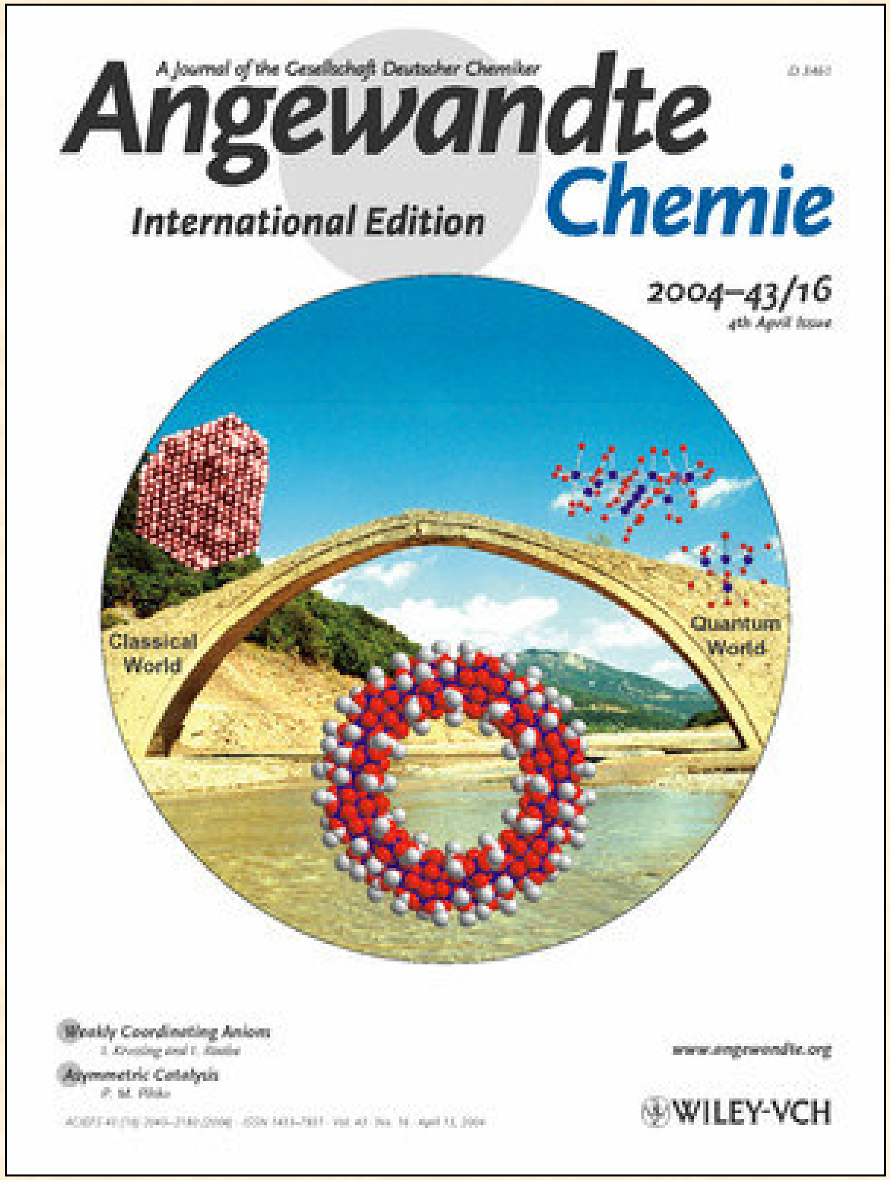


Quantum world ⟷ **Classical world**

Molecular (bottom-up) approach ⟷ **Classical (top-down) approach**

A meeting of the two worlds of nanomagnetism

Tasiopoulos *et al*. *Angew. Chem. Int. Ed.* 2004, *43*, 2117

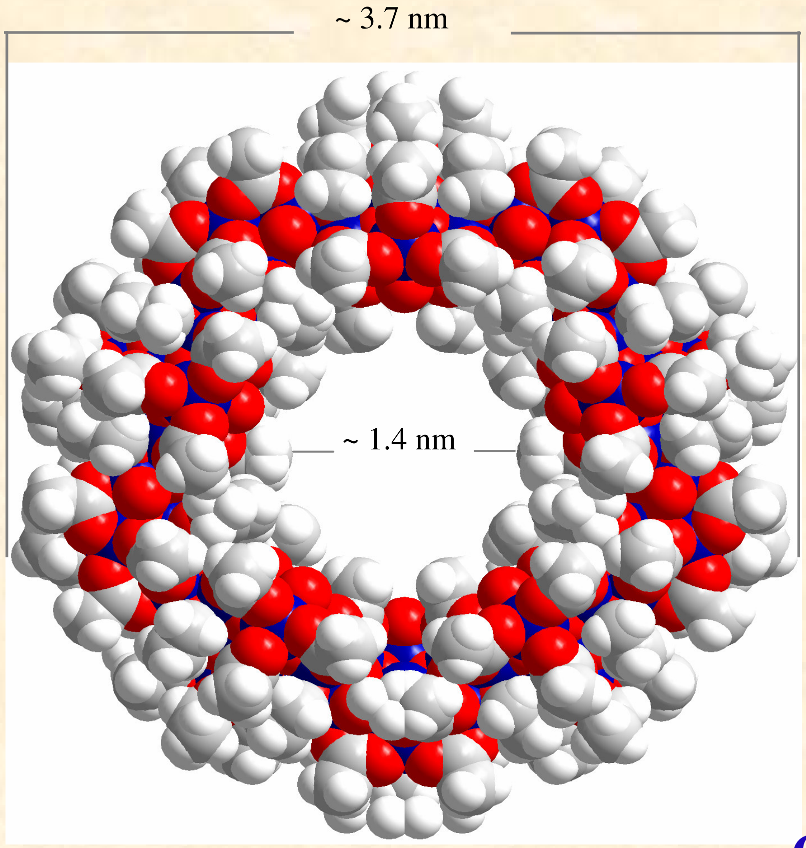


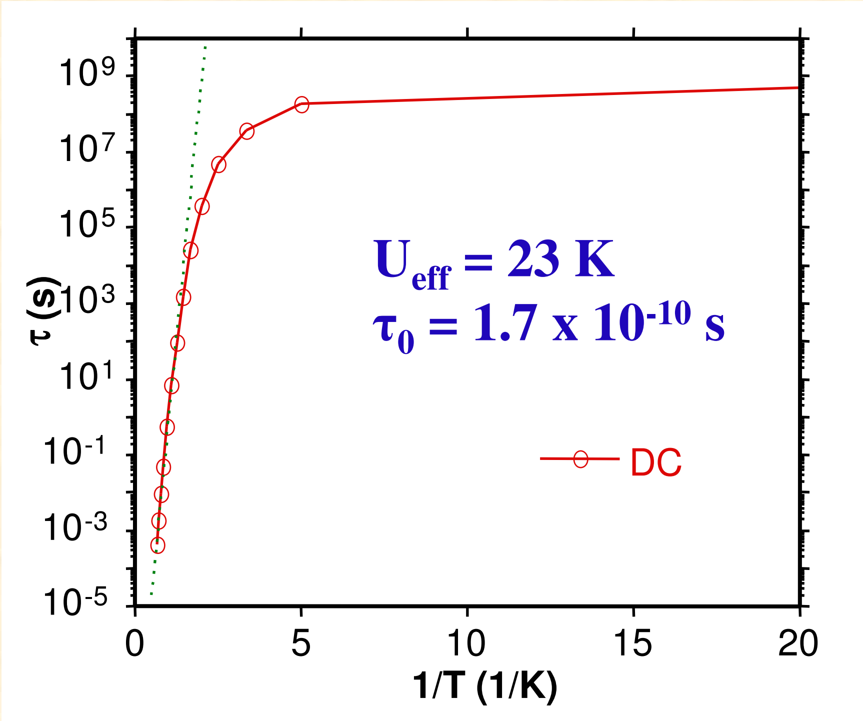
April 4, 2004 issue

Tasiopoulos *et al*. *Angew. Chem. Int. Ed.* 2004, *43*, 2117

A Mn_{70} Torus

EtOH yields a smaller torus of five units i.e. $[Mn_{14}]_5$



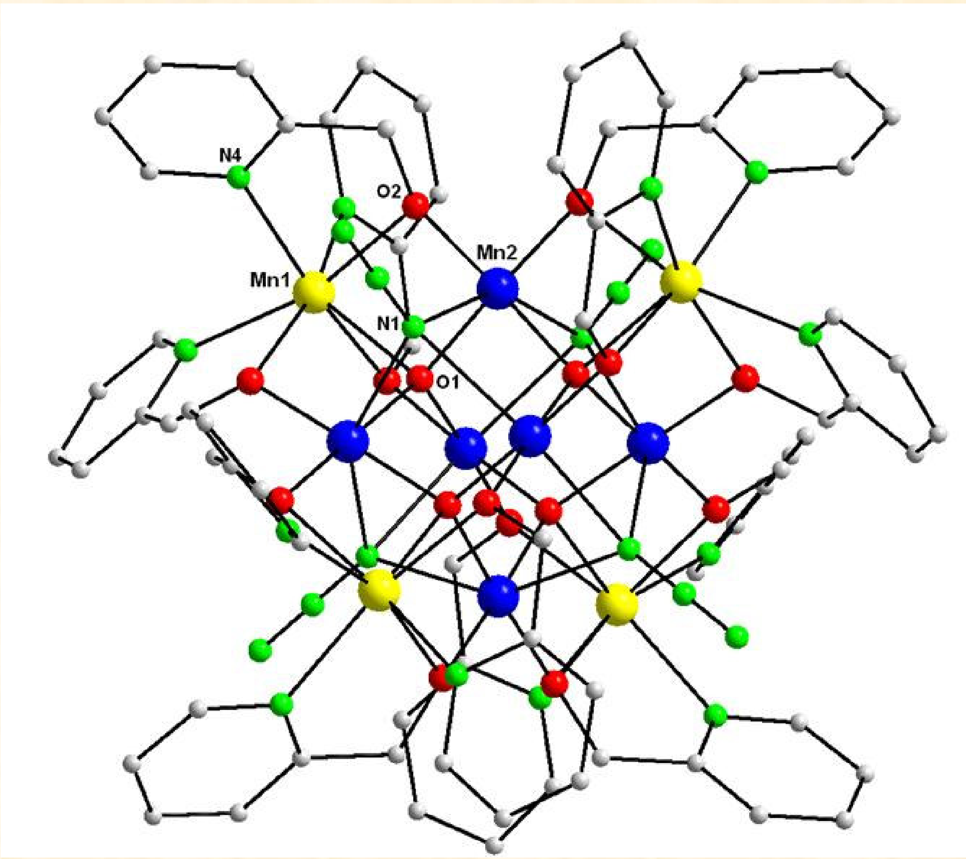


Compare Mn_{84}: U_{eff} = 18 K, $\tau_0 = 5.7 \times 10^{-9}$ s

A Targeted High-Spin Cluster: Mn_{10} with $S = 22$

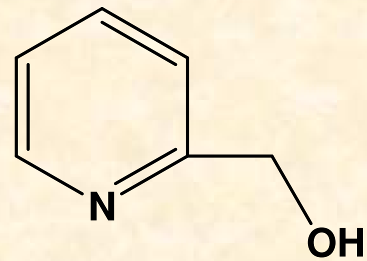
--- we use azide and hmp^- to maximize chances of ferromagnetic coupling

--- the product is indeed <u>completely</u> ferromagnetically coupled



Yellow Mn^{2+} Blue Mn^{3+}

S = 22 ground state – the maximum possible for 6 Mn^{III}, 4 Mn^{II}



hmpH

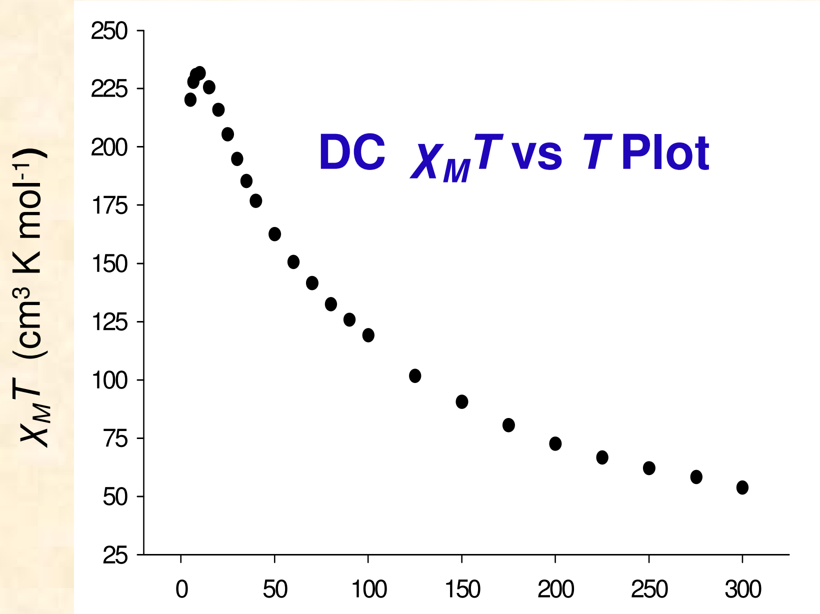
N-N-N^-

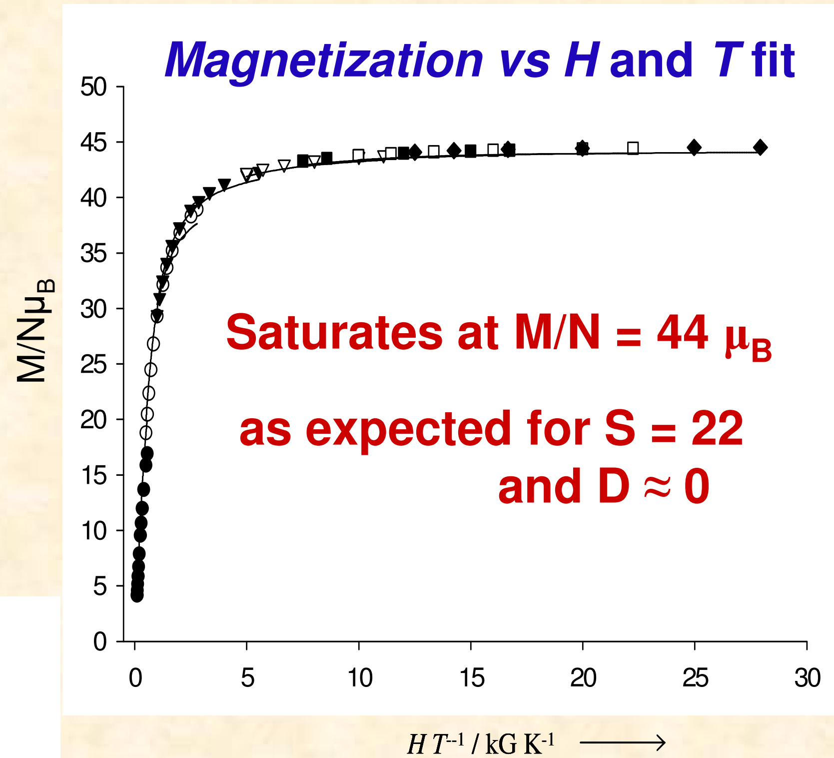
azide ion

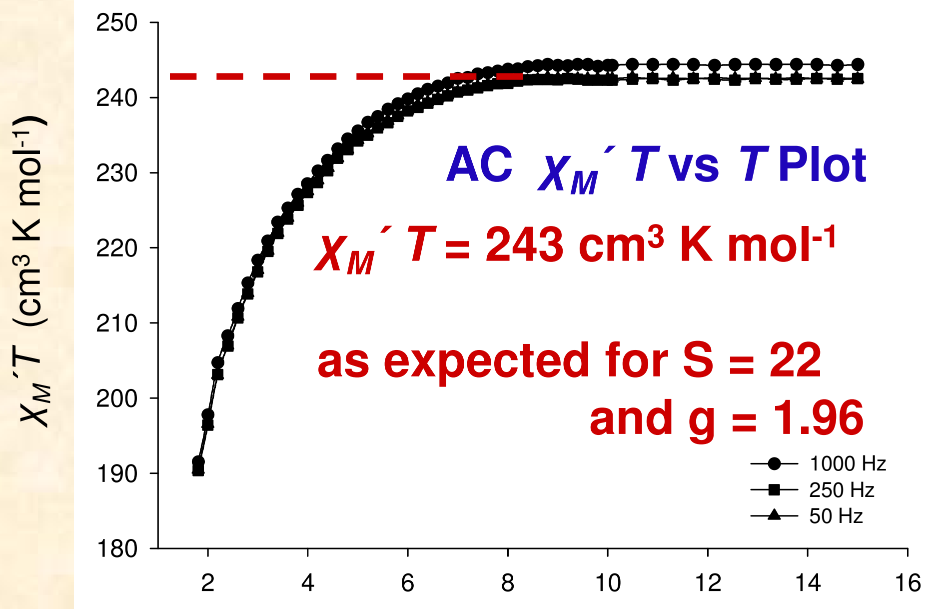
Not a SMM – it has cubic symmetry: point group *T*
Therefore, no anisotropy.

Theocharis Stamatatos, *Angew. Chem. Int. Ed.*, in press

Confirmation of the S = 22 Ground State





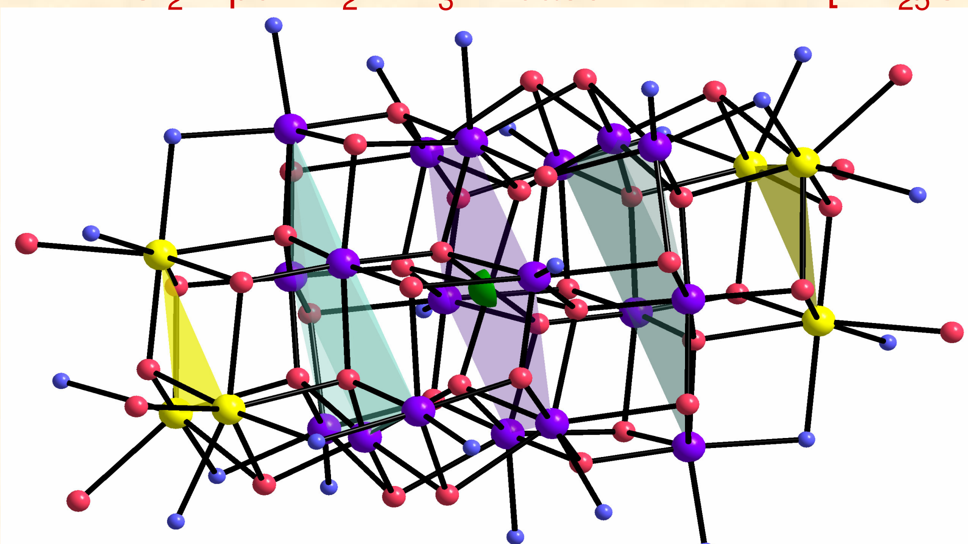


Theocharis Stamatatos,

***Angew. Chem. Int. Ed.*, in press**

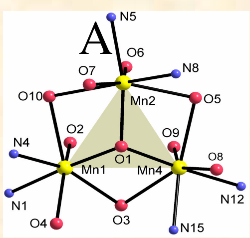
A Mn_{25} SMM with a Record S = 51/2 Spin for a Molecular Species

$MnCl_2$ + $pdmH_2$ + N_3^- + base → $[Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6]^{2+}$

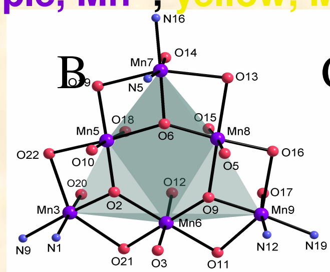


green, Mn^{IV}; purple, Mn^{III}; yellow, Mn^{II}; red, O; blue, N

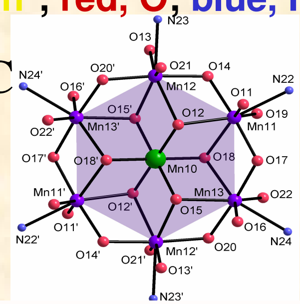
A



B



C



S = 15/2 + 0 + 21/2 + 0 + 15/2 = 51/2

A B C B A

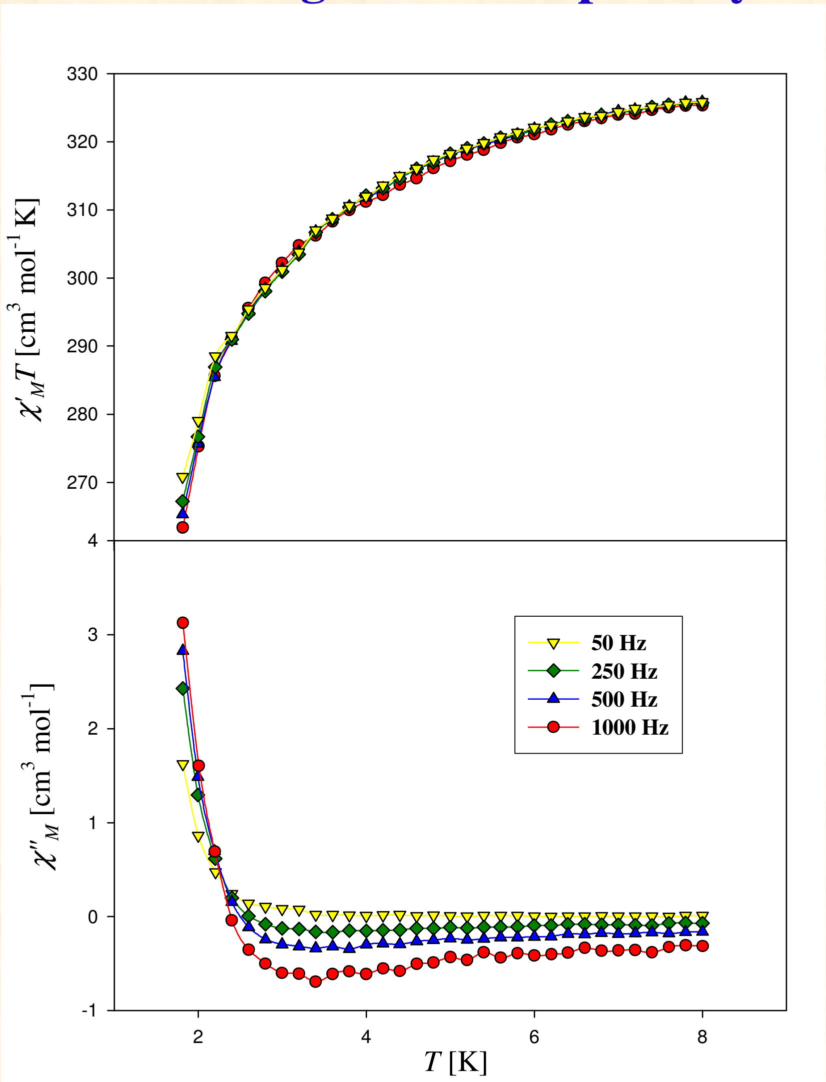
Mn^{IV}, 18 Mn^{III}, 6 Mn^{II}

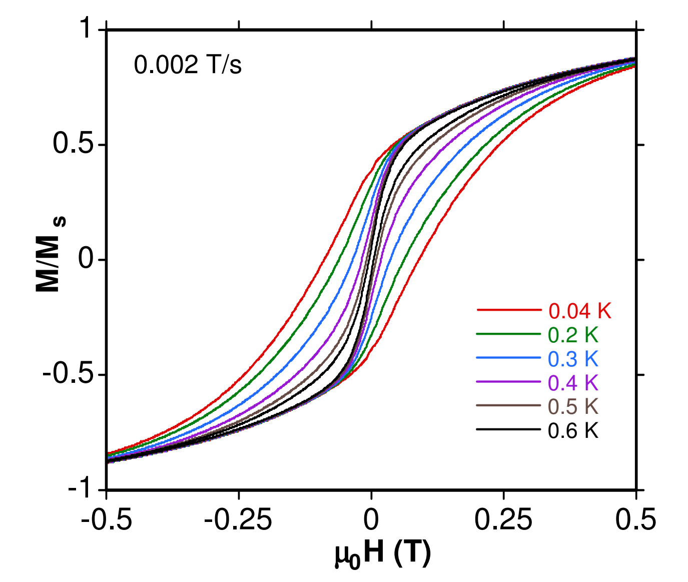
S = 51/2, D = - 0.022 cm^{-1}

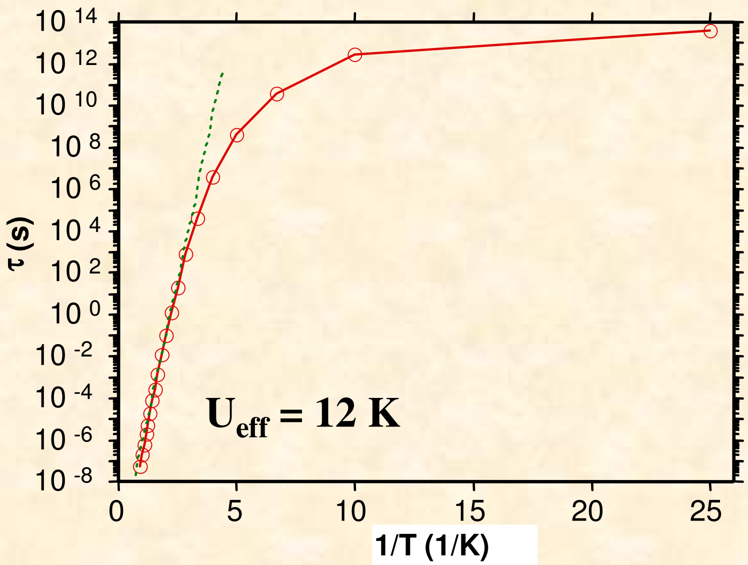
Murugesu *et al.*, *JACS*, 2004, *126*, 4766

Magnetic Properties of Mn_{25}

AC Magnetic Susceptibility

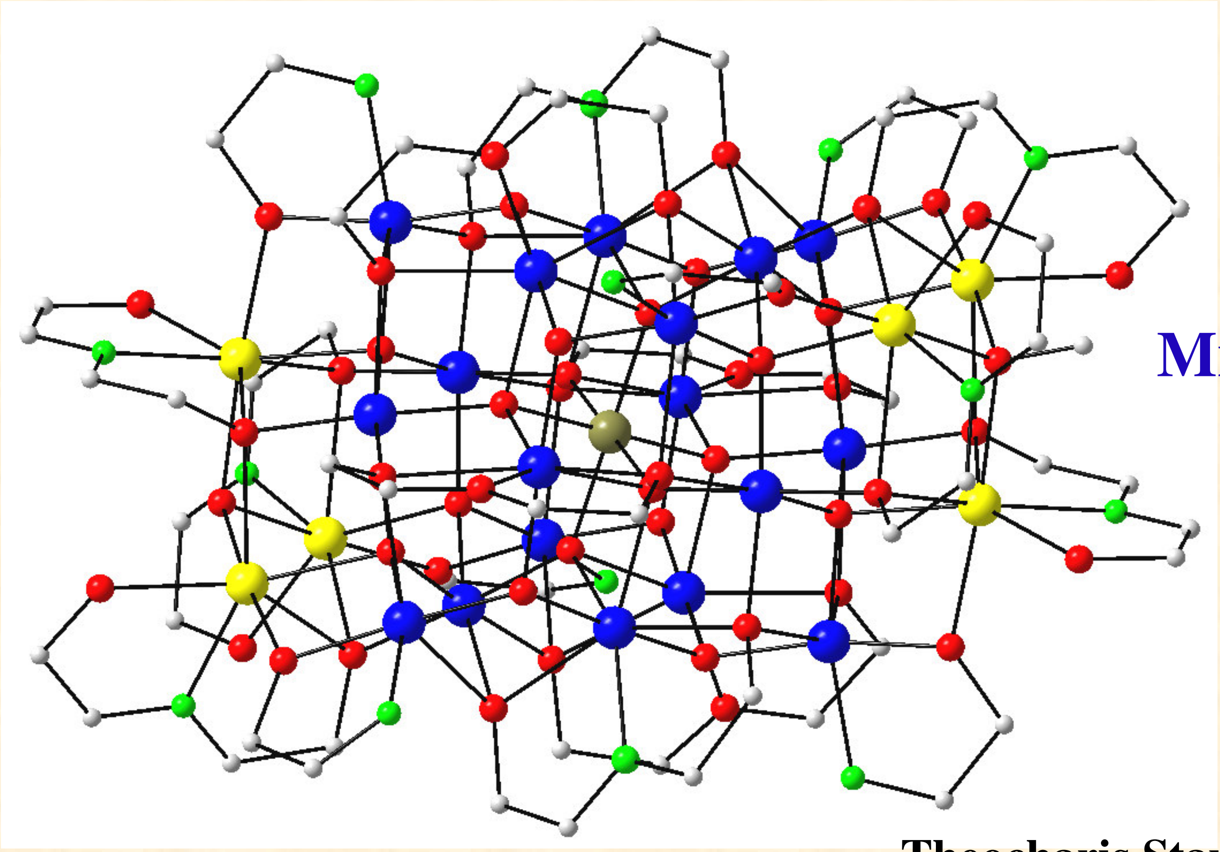






A New Mn_{25} SMM with a Record S = 61/2 Spin for a Molecular Species

$[Mn_{25}O_{18}(OH)_2(hmp)_6(pdmH)_6(pdm)_6]^{8+}$

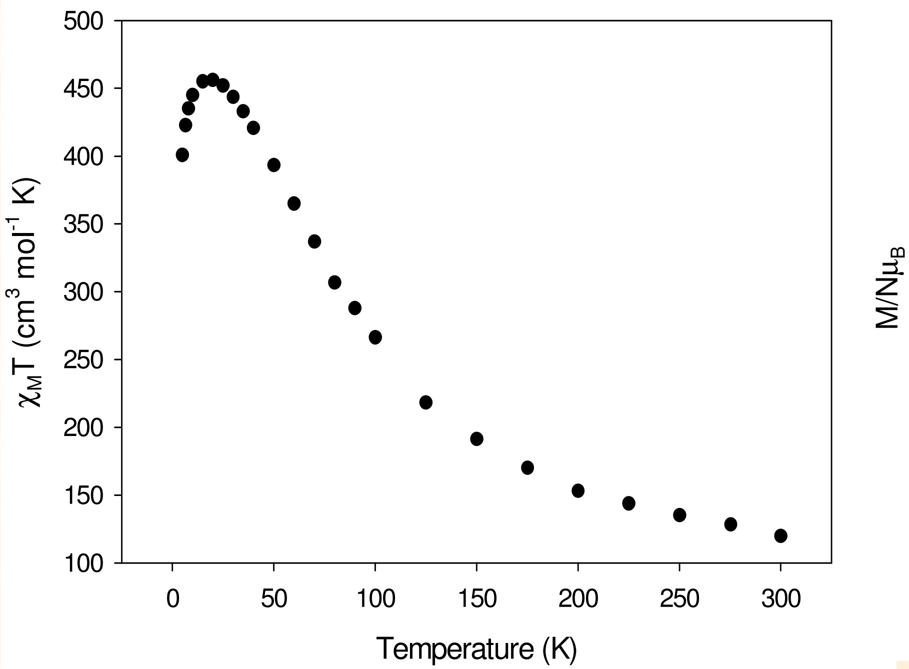


Mn^{IV}, 18 Mn^{III}, 6 Mn^{II}

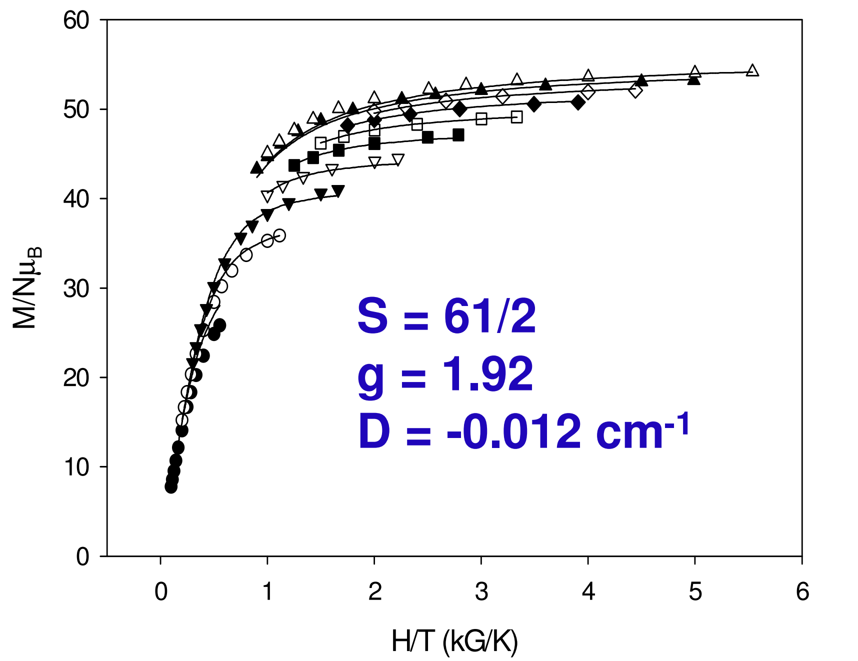
Theocharis Stamatatos, in preparation

Magnetic Susceptibility and Magnetization Fits establish *S* = 61/2

$X_M T$ in a 0.1 tesla DC field



Fit of magnetization vs H and T



$X_M T = 456\ cm^3\ mol^{-1}\ K$
indicates S = 59/2 – 63/2
for g = 1.9 – 2.0

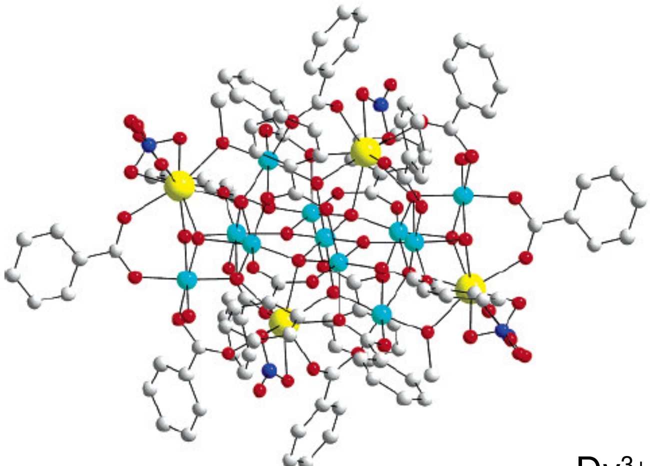
J|A|C|S
COMMUNICATIONS

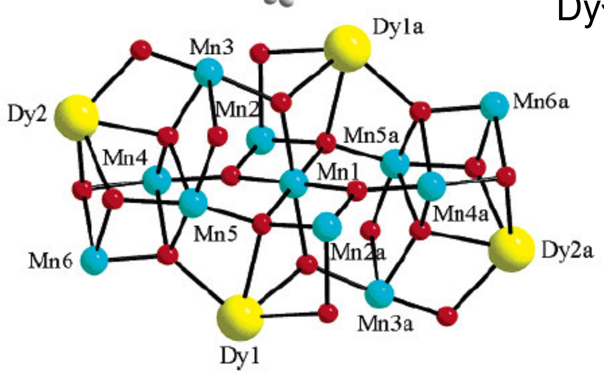
Published on Web 11/12/2004

Initial Observation of Magnetization Hysteresis and Quantum Tunneling in Mixed Manganese−Lanthanide Single-Molecule Magnets

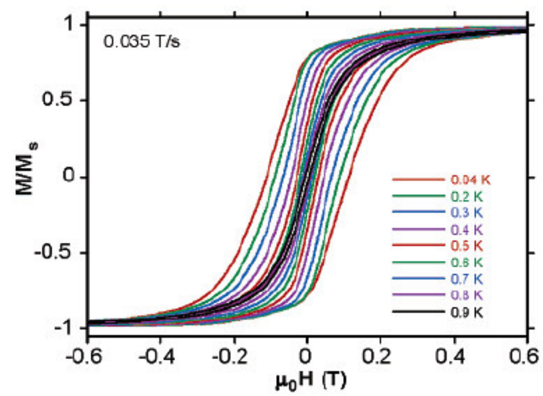
Abhudaya Mishra,† Wolfgang Wernsdorfer,‡ Khalil A. Abboud,† and George Christou*,†

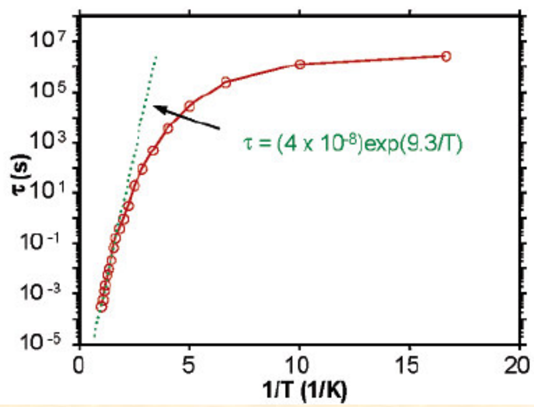
Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, and Laboratoire Louis Néel-CNRS, 38042 Grenoble, Cedex 9, France





Dy^{3+} (S = 5/2, L = 5, $^6H_{15/2}$)





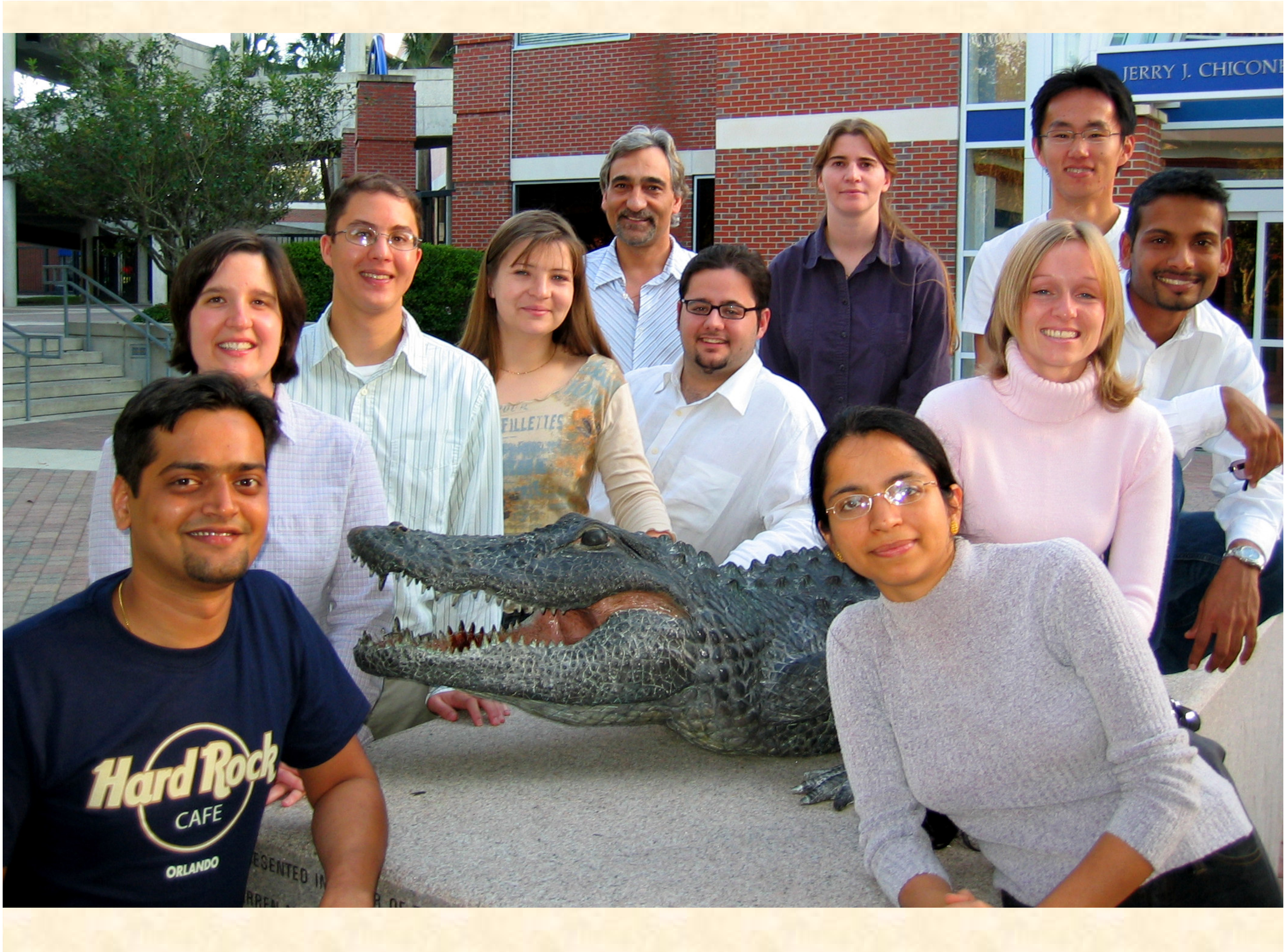
Summary and Conclusions

- The challenge is improve S or D without losing the significant magnitude of the other, while at the same time keeping the exchange-coupling within the molecule strong to ensure excited states are well separated from the ground state.

- --- and keeping the symmetry high!

- Giant SMMs represent a meeting of the two worlds of nanoscale magnetism, the traditional (‘top-down’) and molecular (‘bottom-up’) approaches

- New SMMs of various structural types and nuclearities continue to be discovered as new synthetic procedures are developed


JERRY J. CHICONE
FILLETTES
Hard Rock
CAFE
ORLANDO

One final prediction…..

England 2   Paraguay 0