Introduction to Molecular Magnetism

Edited by D. Tomecka
Computational Physics Division, Poznan, Poland

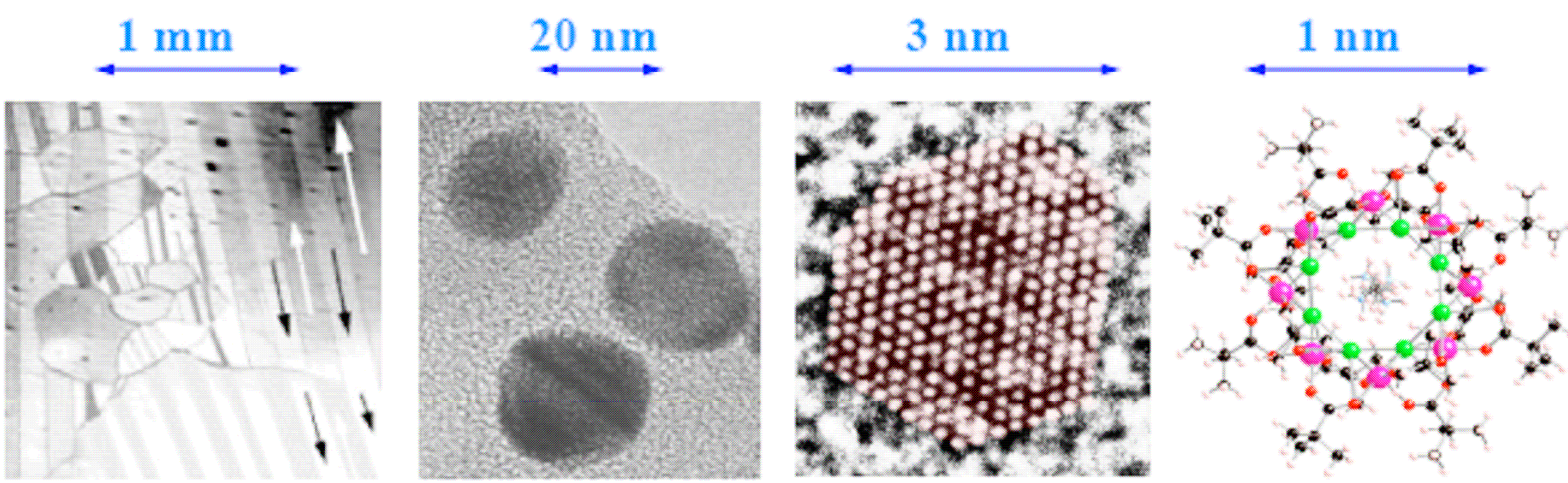
Magnetic structures

← *macroscopic* … *atomic* →

permanent magnets | micron particles | nanoparticles | clusters | molecular clusters | atoms

S = 10^{20} 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1

multi - domains *single - domains* *spins*



W. Wernsdorfer, **Adv. Chem. Phys. <u>118</u>, 99-190 (2001)**; also **arXiv/cond-mat/0101104**.

Molecular Magnets

(molecules containing magnetically interacting metallic ions) first developed in late 1960s, 1970s

Why to use magnetic molecules?

•Transition few-spin system => many-spin system, contribution to understanding of bulk magnetism;
• Transition quantum spin system (s = 1/2) => classical spin system (s_{Fe} = 5/2, s_{Gd} = 7/2);
• Easy to produce, single crystals with => 1017 identical molecules can be synthesized and practically completely characterized;
• Speculative applications: magnetic storage devices, magnets in biological systems, lightinduced nano switches, displays, catalysts,
qubits for quantum computers.

Materials science:

• One molecule can be seen as one bit.
• This leads to unprecedented data densities.
• Conventional materials are reaching the superparamagnetic limit.

Physics:

• These systems are in between classical and quantum magnetic systems.
• They show distinct quantum properties.

Molecular nanomagnets or Single Molecule Magnets

(e.g., Fe_8, Mn_{12})

SMM are a class of magnetic molecules displaying **hysteresis** and **slow relaxation of the magnetization** at the single-molecule level.

SMM:

- *a)* ***high spin ground state,***
- *b)* ***a large negative axial zero-field splitting (ZFS),***
- *c)* ***and the absence of transverse zero-field splitting.***

Differs from a simple paramagnet which would have random spin orientation in the absence of a magnetic field.

Differs from a ferromagnet or ferrimagnet as retention of orientation is not related to movement of domain walls.

As magnetic domains are not involved, no superparamagnetic limit to size of particle/molecule that could store information

• You can dissolve a single molecule magnet in a solvent or put it in some other matrix, like a polymer, and it will still show this property.

Applications of Nanomagnets

Magnetic drug delivery

Ferrofluids

Spintronics

MRI contrast agents

High-density information storage

Hyperthermic treatments

Quantum effects in mesoscopic matter

Magnetocaloric effect

Quantum computation

Natural Nanomagnets:

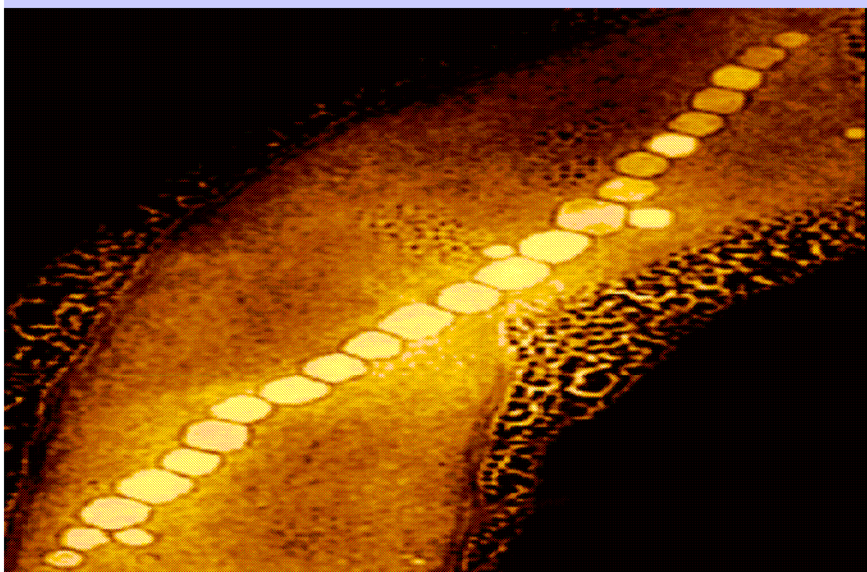
•Ferritin

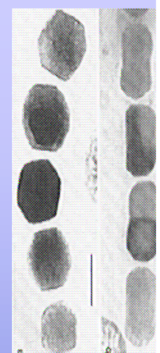
Man on average has 3-4 g of iron 30 mg per day are exchanged in plasma. Ferritin stores iron in mineral form; Ferritins are found in animals, vegetables, mushrooms and bacteria

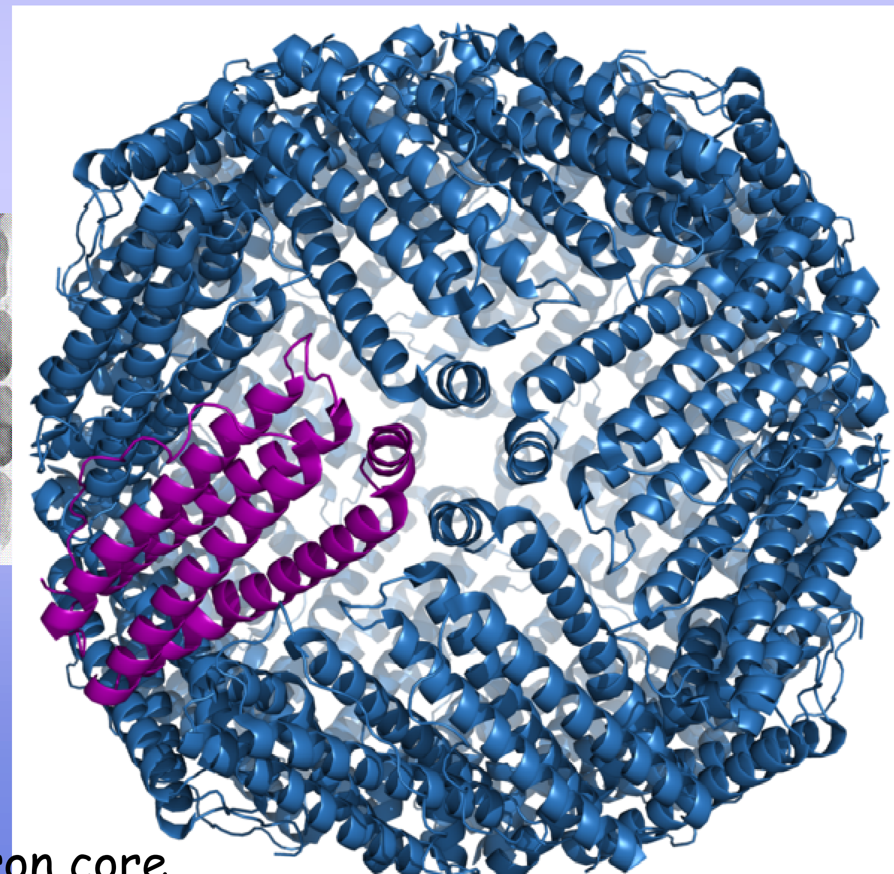
The internal core, 7 nm, may contain up to 4,000 iron(III) ions Approximately FeO(OH) Magnetism depends on the number of ions Magnetic measurements provide information on the number of ions in the core

•Magnetosomes

Nanomagnets embedded in cell membranes





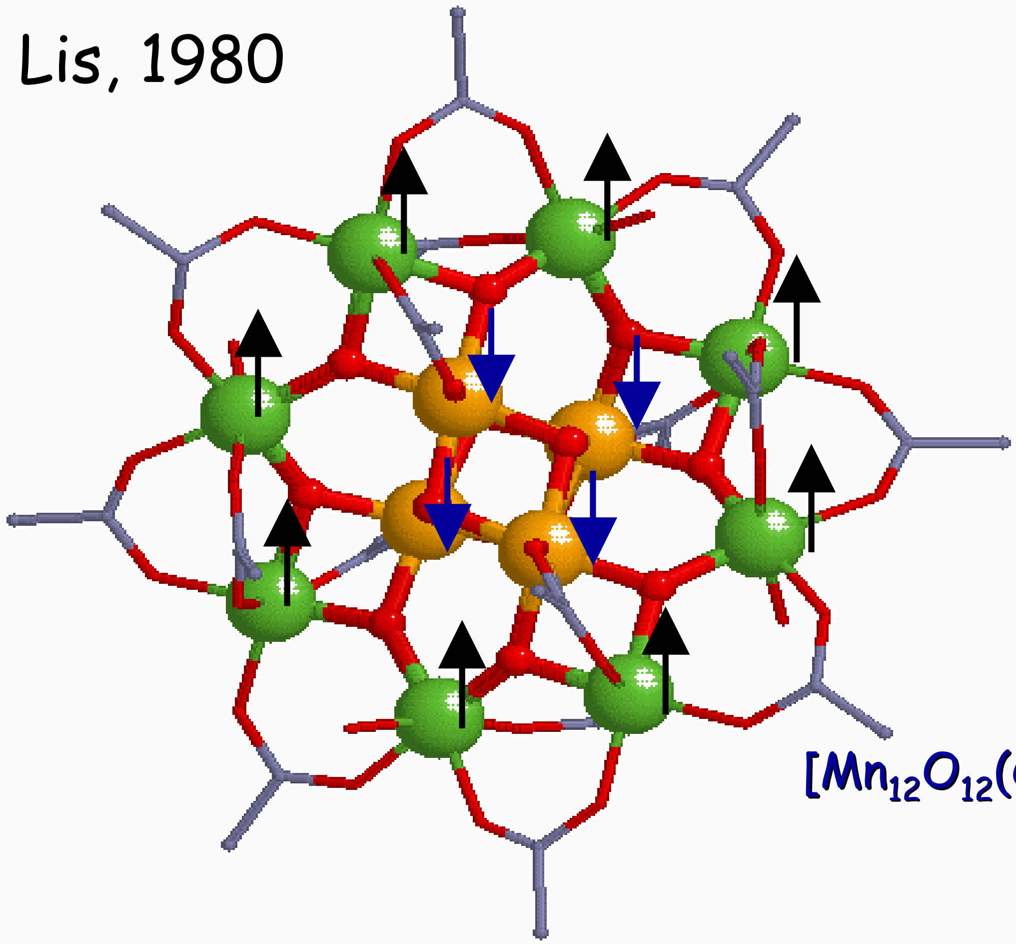


•Magnetotactic bacteria

iron core

The first single molecule magnet: Mn_{12}-acetate

Lis, 1980



Mn(III) — $S = 2$ ↑

Mn(IV) — $S = 3/2$ ↓

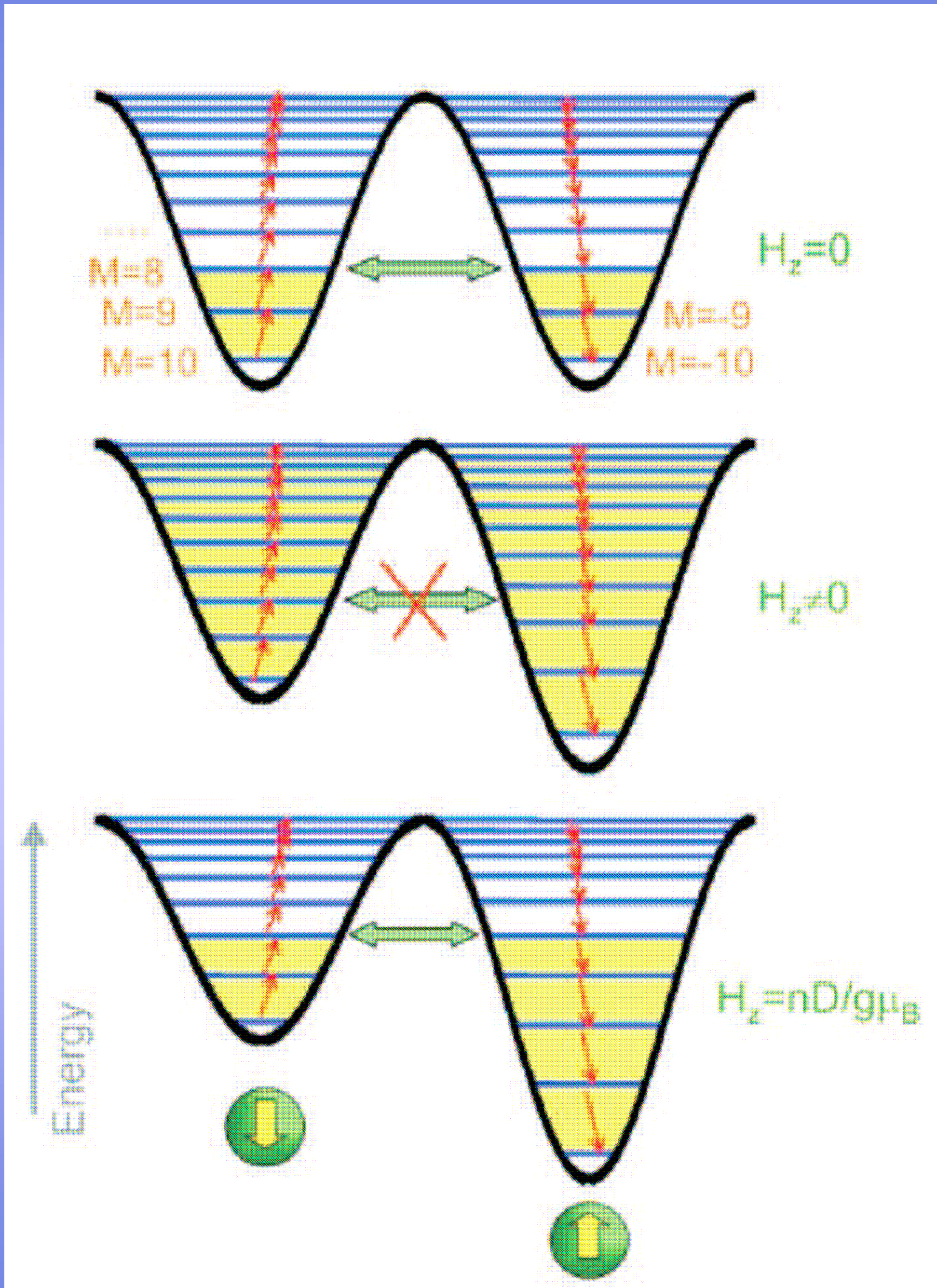
Oxygen

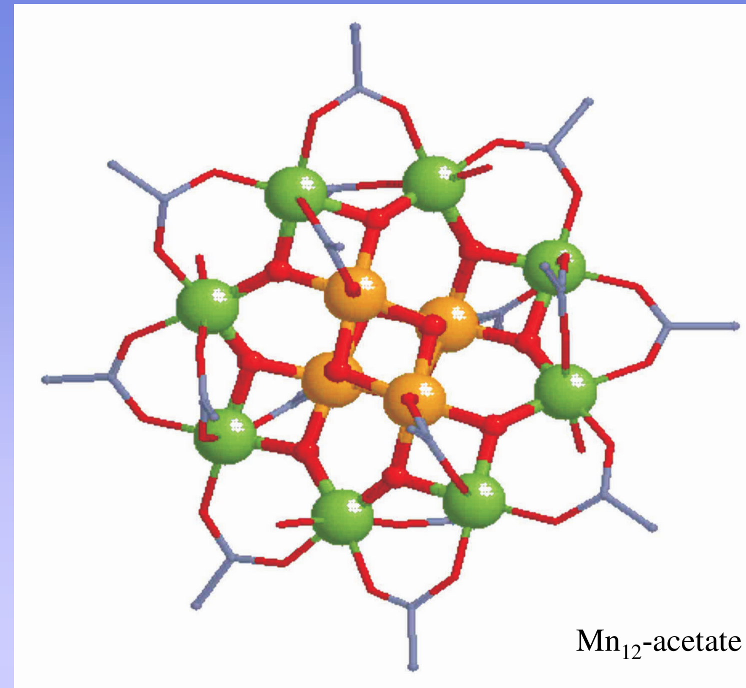
Carbon

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$

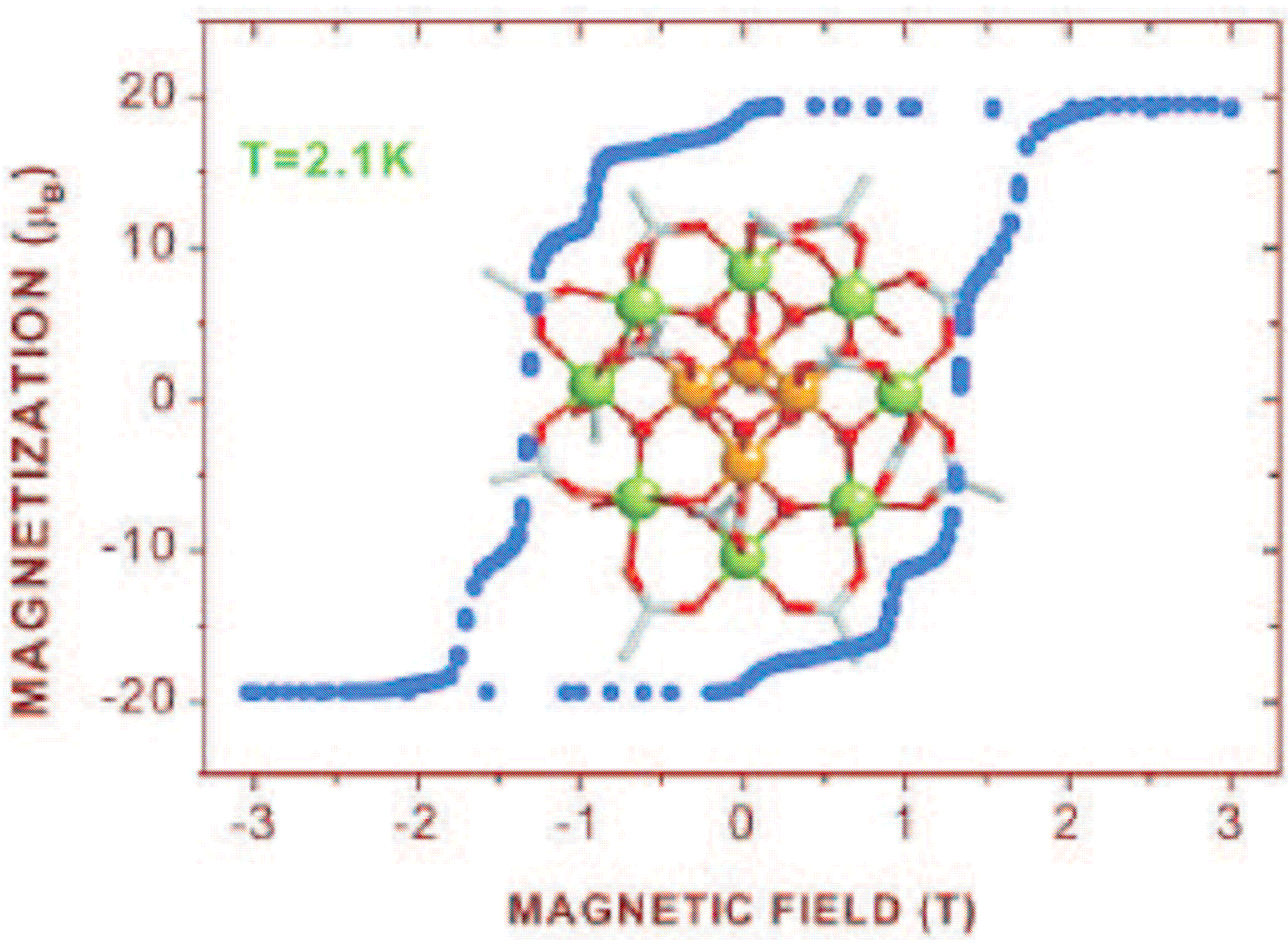
R. Sessoli et al. JACS **115**, 1804 (1993)

- Ferrimagnetically coupled magnetic ions ($J_{intra} \sim 100$ K)
- **Well defined giant spin (S = 10) at low temperatures (T < 35 K)**
- Easy-axis anisotropy due to Jahn-Teller distortion on Mn(III)
- Crystallizes into a tetragonal structure with S_4 site symmetry
- Organic ligands ("chicken fat") isolate the molecules





Energy levels of the S=10 spin manifold split by an axial anisotropy (top). Overcoming of the barrier can occur through a thermal activation or through a tunnel mechanism involving the ground doublet or thermally excited states. When an axial field is applied the levels on the opposite sides of the barrier are no more in coincidence (b) and tunnelling is suppressed unless specific values of the field are reached (c).



Stepped hysteresis cycle of the molecular nanomagnet

*Mn*12-acetate

First proven example: Mn_{12}-ac

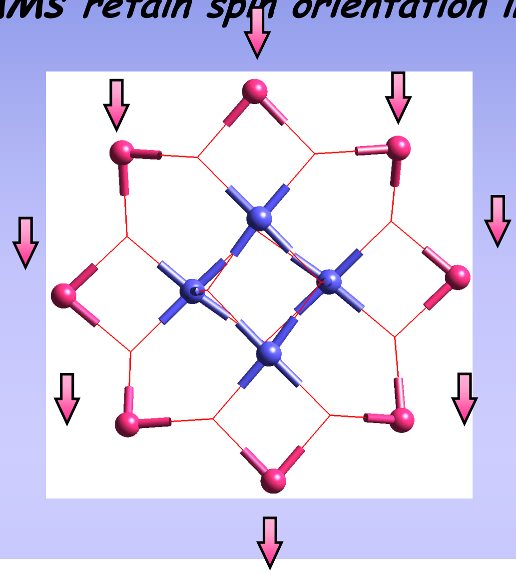
[Mn12O12(O2CMe)12(H2O)4]

(Lis, Acta Crystalogr., Sect. B: Srtuct. Crystallogr. Cryst. Chem. 36, 2042 (1980)

Christou *et al*, *J. Amer. Chem. Soc.*, **1993**, *115*, 1804)

More recent examples: Mn_4, Fe_8, V_4, Fe_4, Fe_{10}, Mn_{10} and Fe_{19} cages

SMMs retain spin orientation in the absence of a magnetic field – i.e. nanoscale magnetic memories



Molecular structure (X-ray diffraction)

A cube containing Mn4+ ions (blue) surrounded by a ring of Mn3+ ions (pink), held together by oxides (red lines).

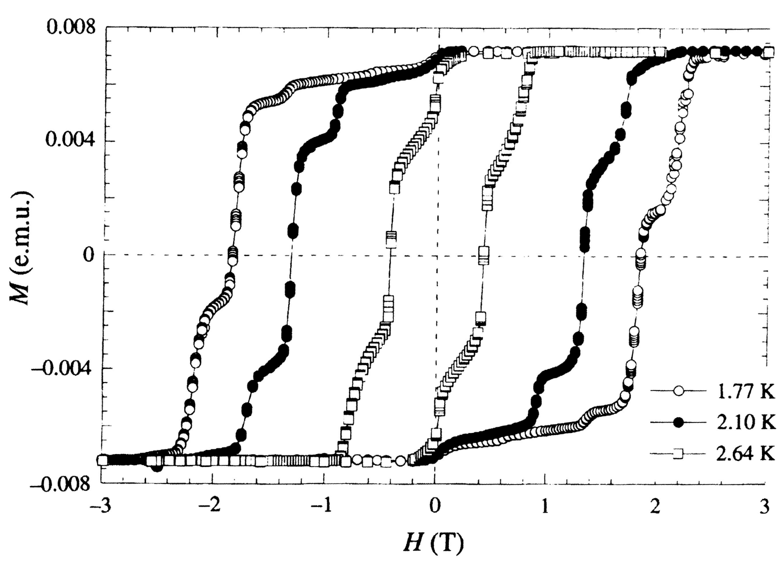
Magnetic structure (deduced)

Spins on Mn4+ sites (S = 3/2) anti-ferromagnetically coupled to spins on Mn3+ sites (S = 2).

Spin ground state = 8 x 2 – 4 x 3/2 = 10

S = 10 is a high spin ground state for a molecule. Not highest known.

Behaviour of spin is unprecedented.



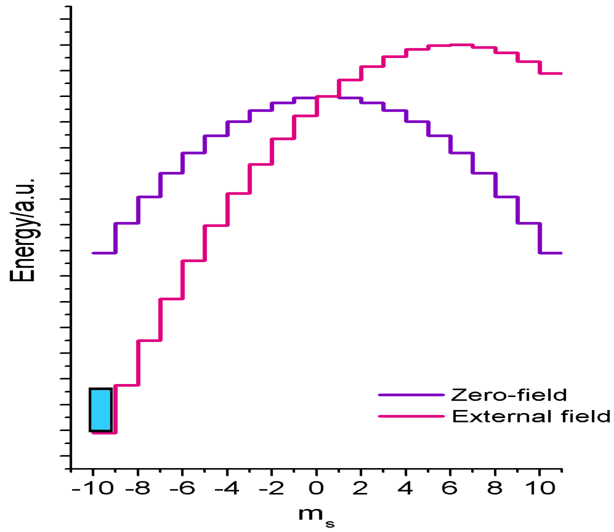
Christou *et al*, *J. Amer. Chem. Soc.*, **1993**, *115*, 1804

Hysteresis for $\{Mn_{12}\}$

Hysteresis in magnetisation vs. field for powders or crystals i.e. an energy barrier to reorientation of molecular spin

Hysteresis loop for crystals is not smooth – shows steps.

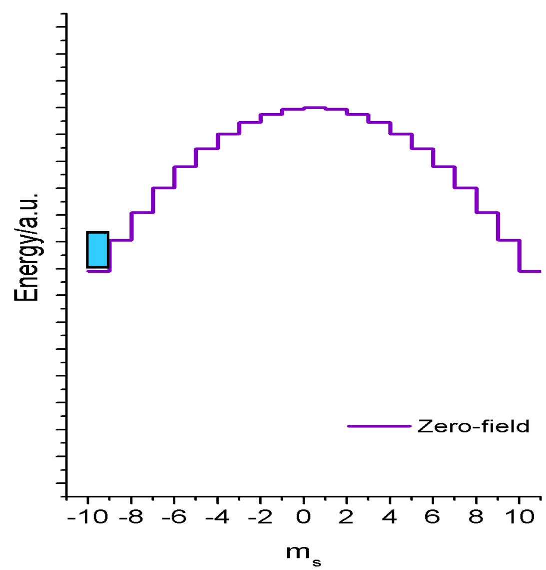
Barbara *et al*, *Nature*, **1996**, *383*, 145.



Energy Barrier for {Mn12}

For {Mn12} cage S = 10,
ms restricted to +10 ms -10
States with different ms values have different energies;
gaps related to parameter D
If D is negative,
ms = ±S lowest in energy
ms = 0 highest in energy.
For {Mn12} D/k = -0.61 K

For {Mn12} Ea/k = 61 K.
Hysteresis in magnetisation vs. field due to this energy barrier



Quantum Tunnelling of Magnetisation

At specific fields (e.g. H = 0) magnetisation suddenly lost – see steps on hysteresis loop.
Reason: magnetisation tunnels through the energy barrier, rather than going over.
Quantum tunnelling in a mesoscopic system is rare.
Also influences relaxation rates – at very low temperature becomes temperature independent.

Mn, Mn_2, Mn_3, Mn_4, $[Mn_4]_2$, Mn_5, Mn_6, Mn_7, Mn_8, Mn_9, Mn_{10}, Mn_{11}, Mn_{12}, Mn_{13}, Mn_{16}, Mn_{18}, Mn_{21}, Mn_{22}, Mn_{24}, Mn_{26}, Mn_{30}, Mn_{70}, Mn_{84}

Fe_2, Fe_3, Fe_4, Fe_5, Fe_6, Fe_7, Fe_8, Fe_{10}, Fe_{11}, Fe_{13}, $Fe_{17/19}$, Fe_{19}, Fe_{30}

Ni_4, Ni_5, Ni_6, Ni_8, Ni_{12}, Ni_{21}, Ni_{24}

Co_4, Co_5, Co_6, Co_7, Co_{10}

Co_2Gd_2, Co_2Dy_2, Cr_{12}, $CrNi_6$, $CrNi_2$, $CrCo_3$, $Fe_{10}Na_2$, Fe_2Ni_3, Mn_2Dy_2, Mn_2Nd_2, V_{15}, Ho, Fe_2Ho_2, $Mn_{11}Ln_4$, ...

Only few of these molecules are SMMs !!

. . . .

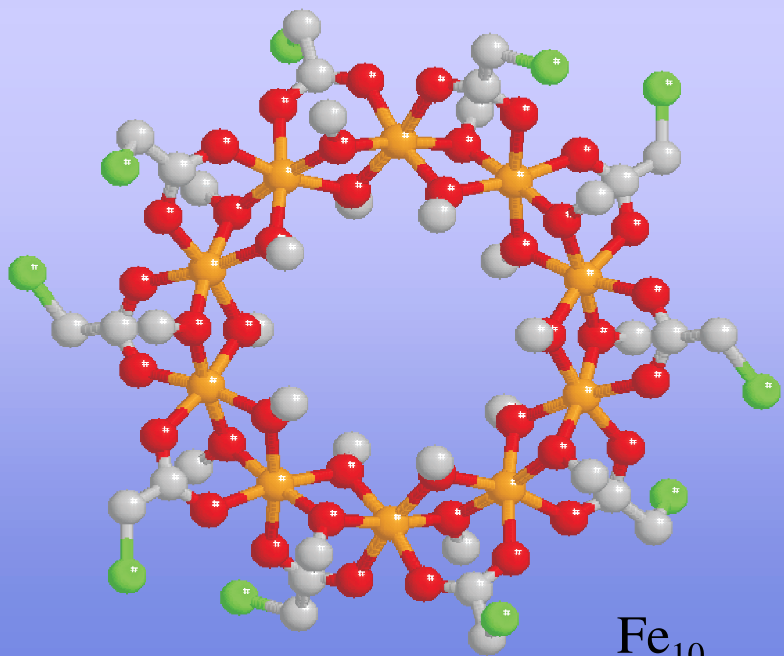
S = 0, 1/2, 1, 3/2, 2, 5/2, 4, 9/2, 5, ... 51/2

W. Wernsdorfer, **Adv. Chem. Phys. 118, 99-190 (2001)**; also **arXiv/cond-mat/0101104**.

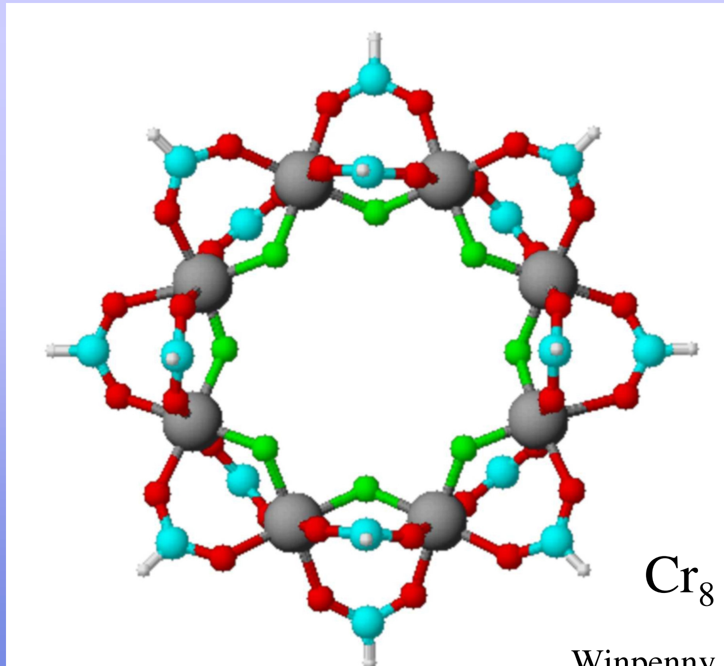
Other classes of magnetic molecules:

Antiferromagnetic rings (e.g., Cr_8, Fe_{10}, Ni_{12})

- Antiferromagnetic n.n. exchange interaction.
- Nonmagnetic S=0 ground state.
- One Cr3+ ion can be replaced by a different ion (ground state with S>0).
- Interesting for fundamental physics (e.g. Neel vector tunneling).
- Ni-substituted Cr_8 : S=1/2, potentially a good candidate qubit.



Fe_{10}



Cr_8

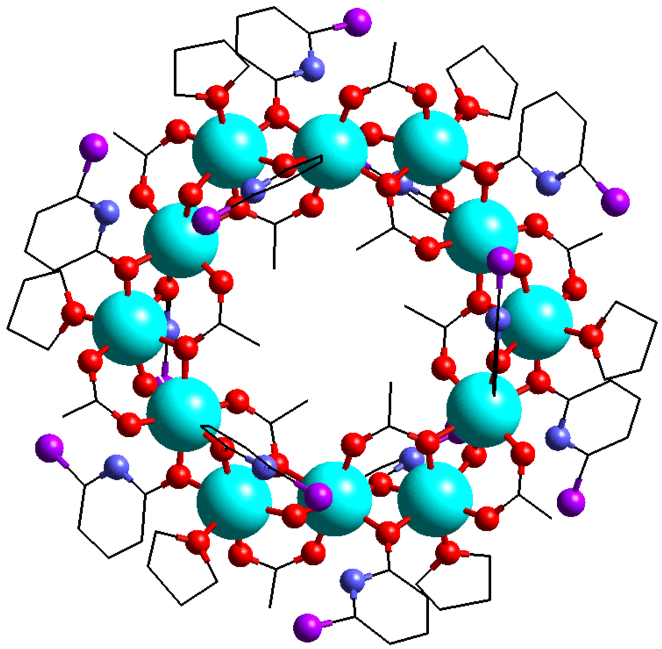
Winpenny

Ni_{12} wheel

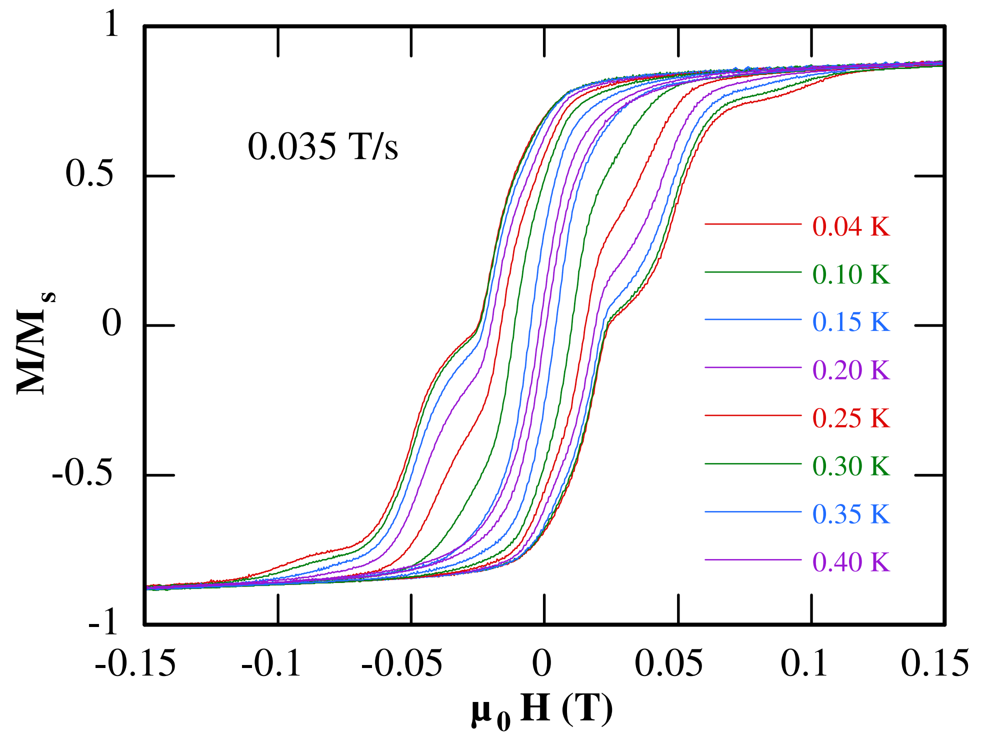
Ferromagnetic exchange leads to an S = 12 ground state.

Hysteresis and Tunnelling in {Ni12}

Cyril Cadiou, Manchester and Wolfgang Wernsdorfer, Grenoble

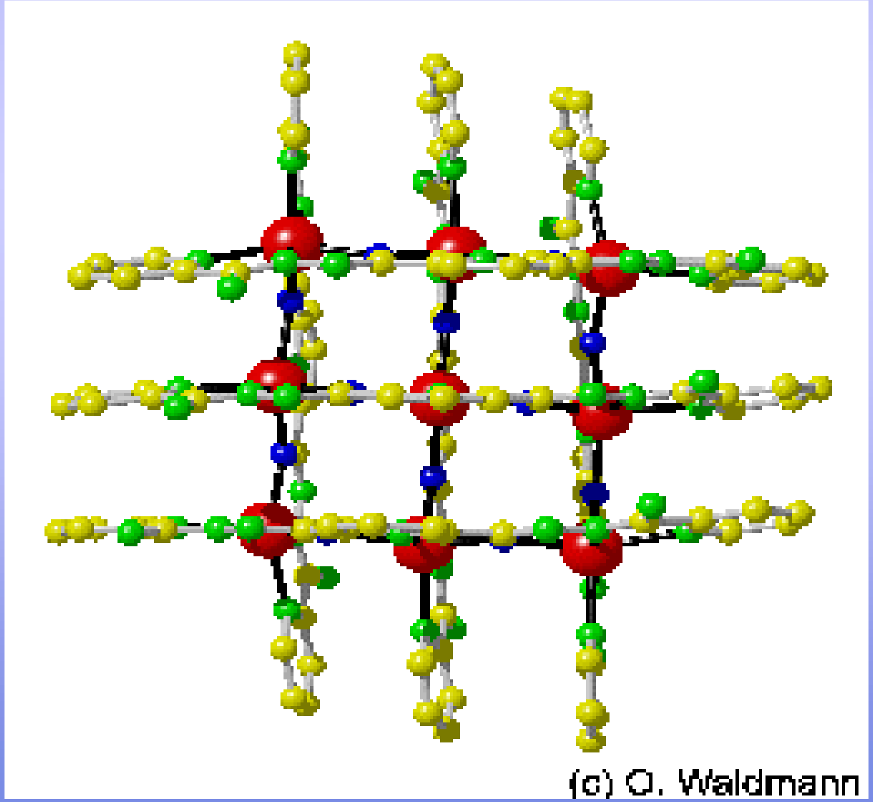


Richard Winpenny, Craig Grant, 1999



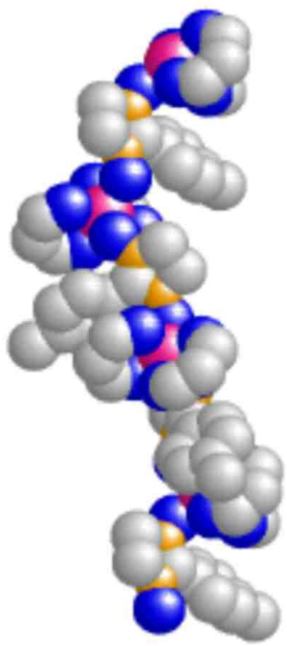
Grids (e.g., Mn3x3)

- Antiferromagnetic n.n. exchange interaction.
- Magnetic S=5/2 ground state.
- 2d topology.
- Quantum oscillations of the total molecular spin induced by applied magnetic field.



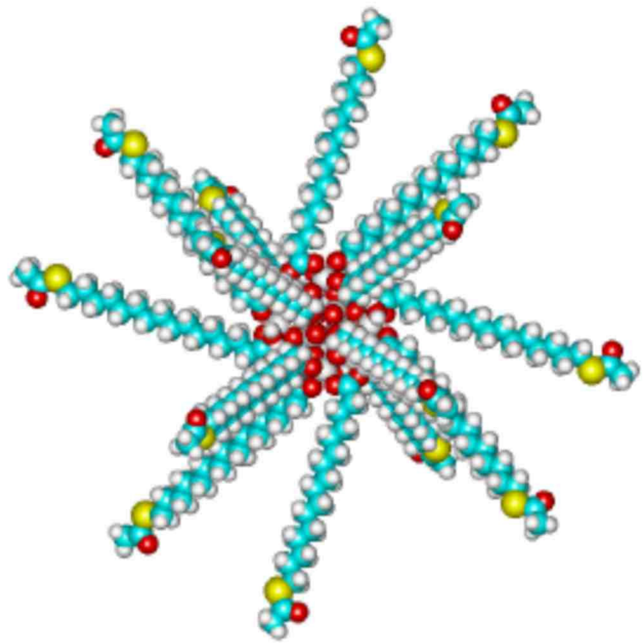
Single Chain Magnets, SCM,

are magnetic polymers and show also a slow relaxation of their magnetization at low temperatures.



Single Chain Molecule example

A. Caneschi et al.Angew. Chem. **2001**

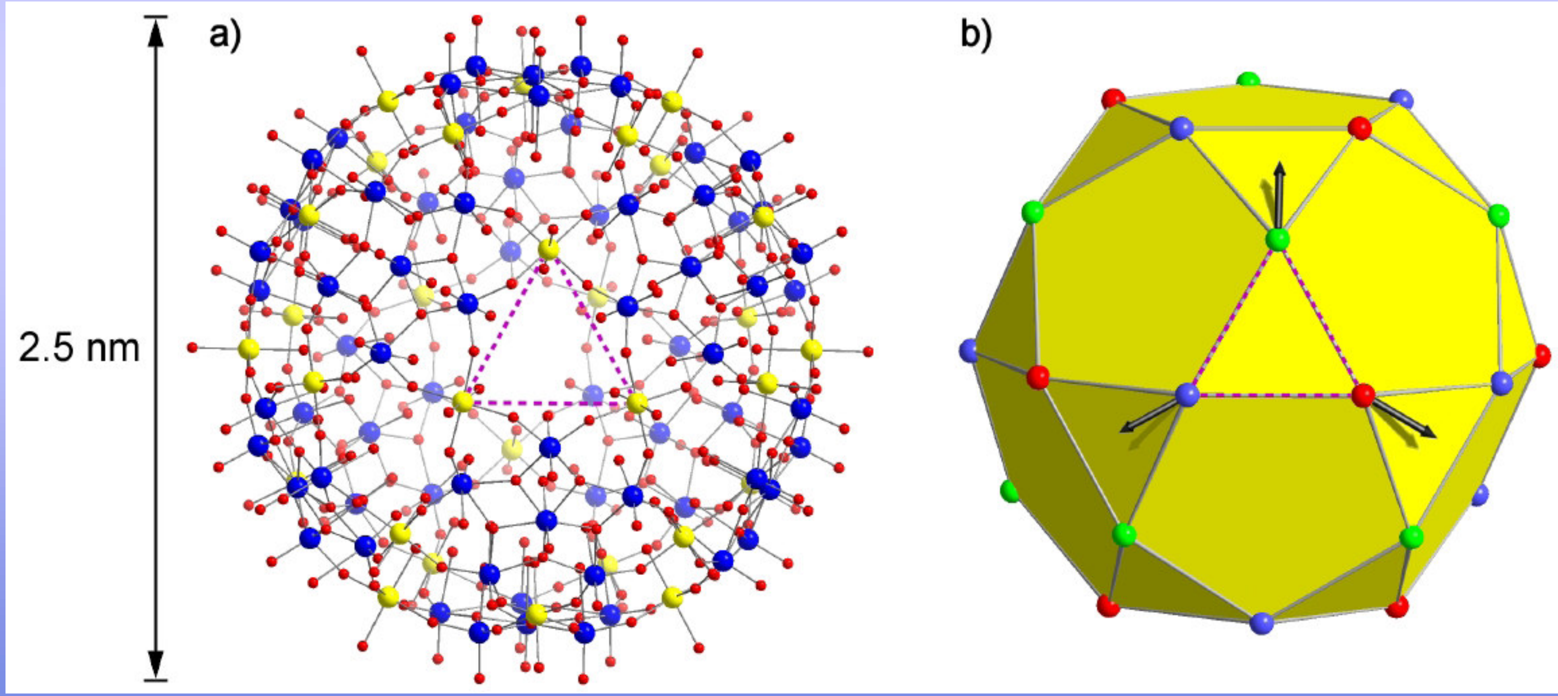


Chain of Mn_{12} molecule

Gatteschi, 2004

{Mo72Fe30}

- Structure: Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (A. M¨uller *et al.*, Chem. Phys. Chem. **2**, 517 (2001))
- Classical ground state of {$Mo_{72}Fe_{30}$}: three sublattice structure, coplanar spins (M. Axenovich and M. Luban, Phys. Rev. B **63**, 100407 (2001));
- Quantum mechanical ground state S = 0 can only be approximated, dimension of Hilbert space $(2s + 1)N \approx 10^{23}$.

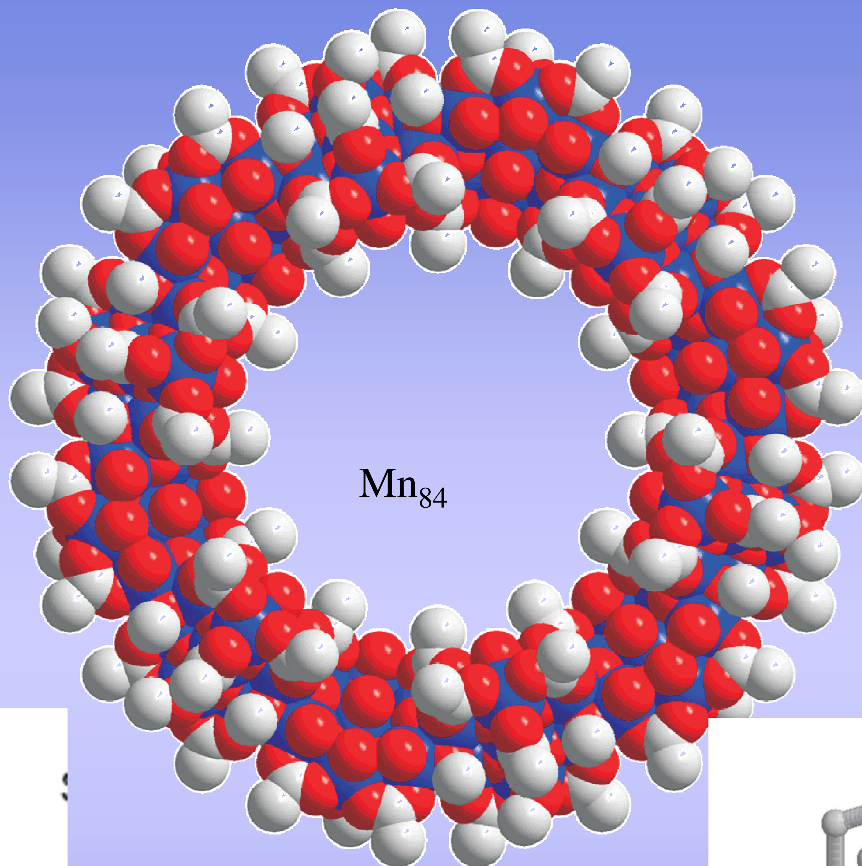


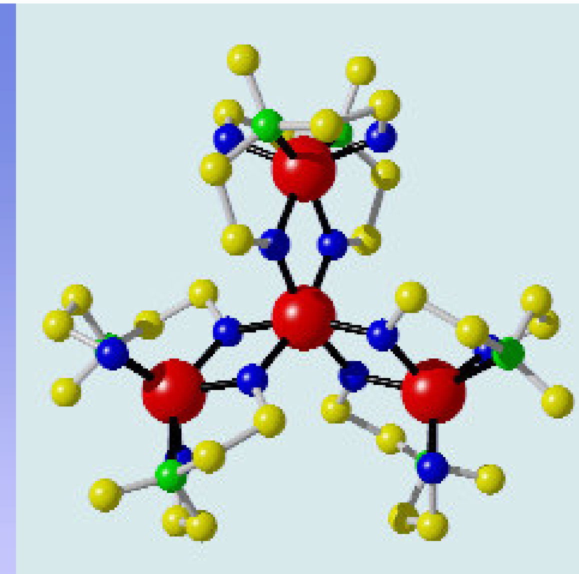
- Giant magnetic Keplerate molecule;

J.Schnack

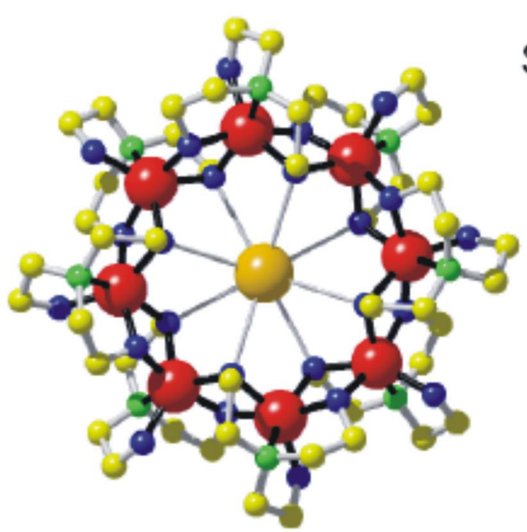
Other interesting examples

Christou 2004

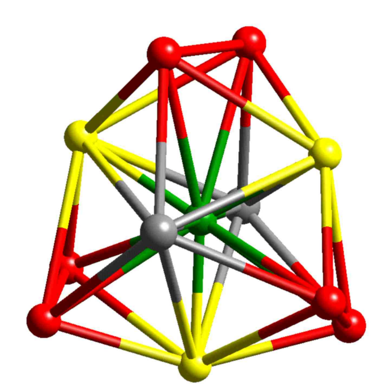


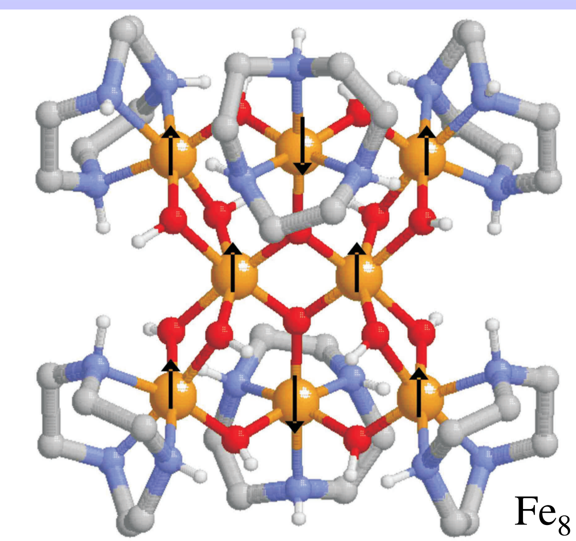


Ni_4



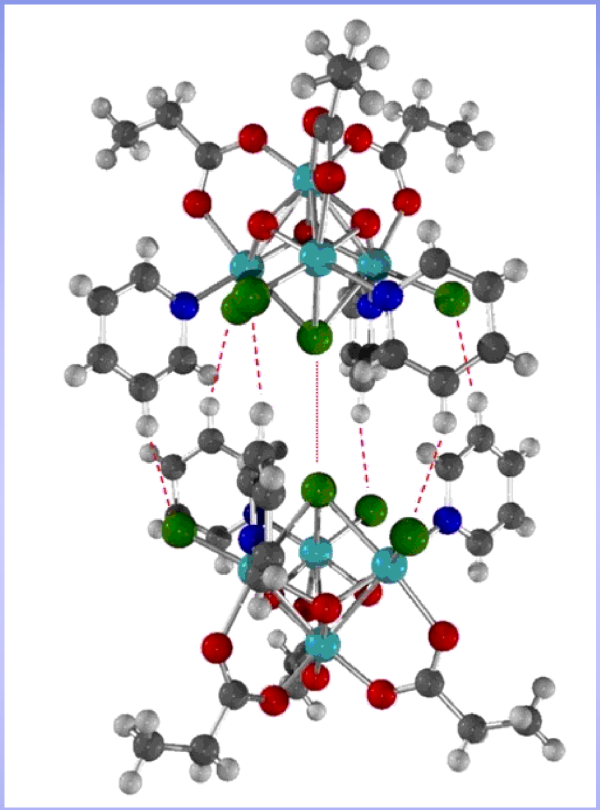
Saalfrank *et al.*

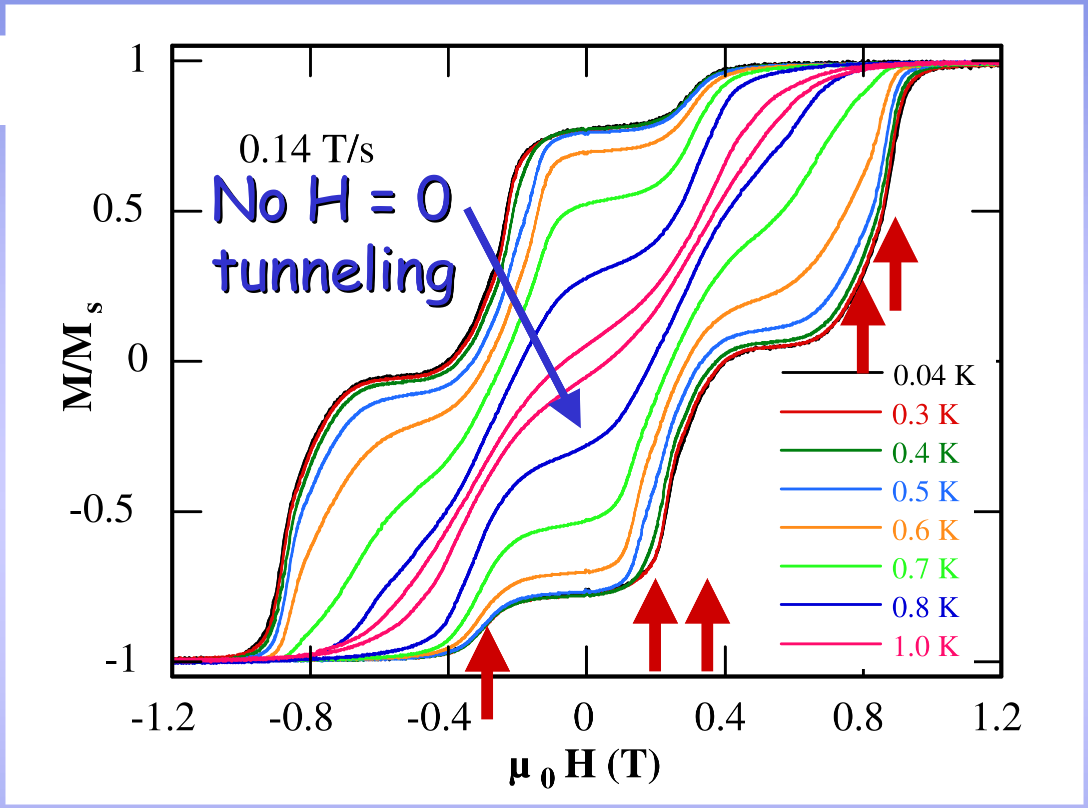




Wiegart, 1984

Dimer Structure of $[Mn_4O_3Cl_4(O_2CEt)_3(py)_3]_2$





$[Mn_4]_2$

***D*1 = –0.72 K** ***J* = 0.1 K**

To zeroth order, the exchange generates a bias field *Jm'*/gμB which each spin experiences due to the other spin within the dimer

Wolfgang Wernsdorfer, George Christou, et al., *Nature*, **2002**, 406-409

Representive Attributes of Molecule-Based Magnets

- Low density
- Mechanical flexibility
- Low-temperature processability
- High strength
- Modulation/tuning of properties by means of organic chemistry
- Solubility
- Low environmental contamination
- Compatibility with polymers for composites
- Biocompatibility
- High magnetic susceptibilities
- High magnetizations
- High remanent magnetizations
- Low magnetic anisotropy
- Transparency
- Semiconducting and/or insulating dc electrical onductivity

{Miller,Epstein}

APPLICATIONS

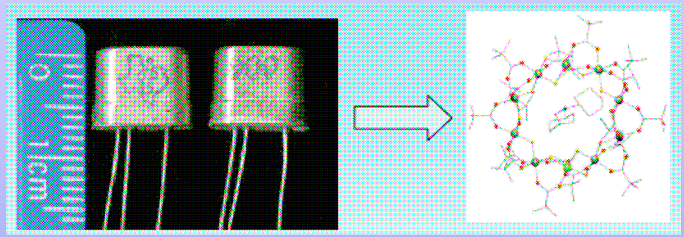
Magnetic molecules are interesting for both fundamental issues and potential applications:

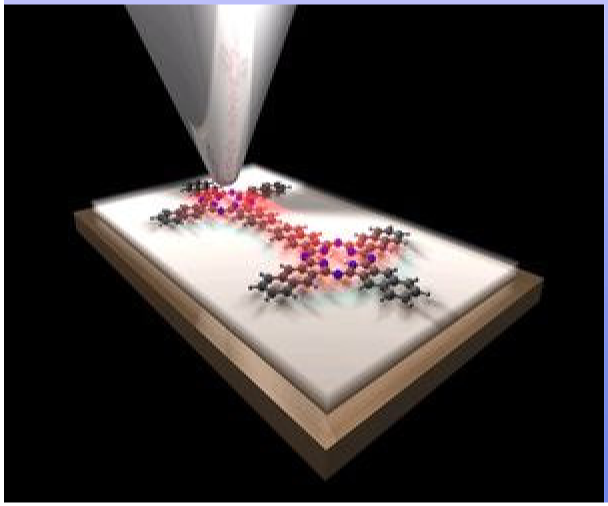
Fundamental issues:

* Highly tunable model systems for studying quantum phenomena (quantum tunnelling of the magnetisation (QTM), coherence, quantum-classical crossover, etc.), and to study microscopic magnetic interactions

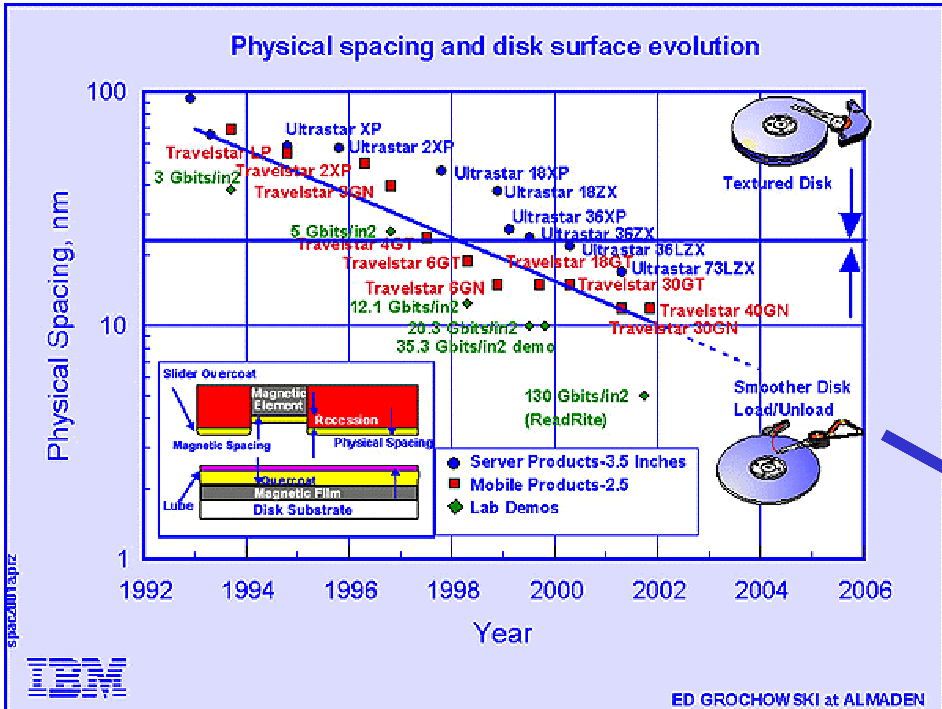
Main potential applications:

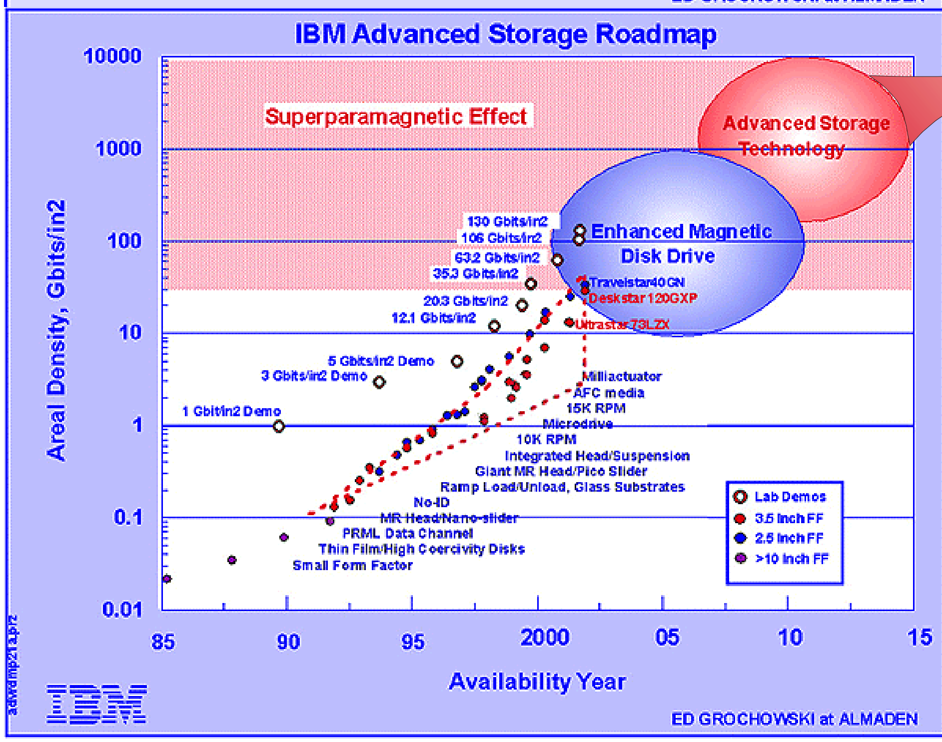
* High-density information storage with nanomagnets
* Magnetocaloric refrigerants (cooling technology based on the magnetocaloric effect)
* Quantum computation





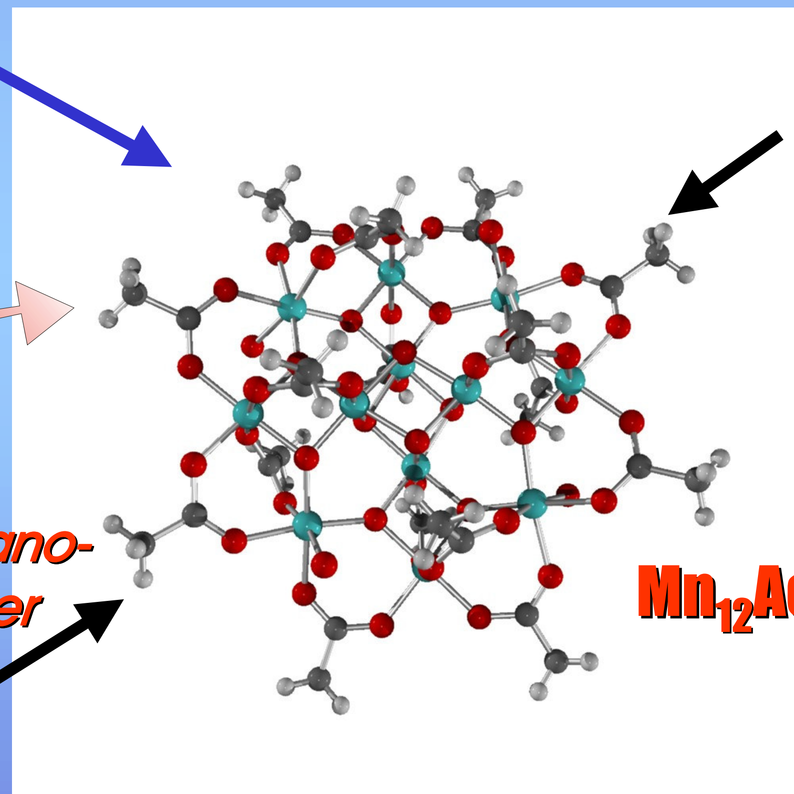
Schematic three-dimensional image of a **molecular "logic gate"** of two naphthalocyanine molecules, which are probed by the tip of the low-temperature scanning tunneling microscope. By inducing a voltage pulse through the tip to the molecule underneath the tip (shown in the back), the two hydrogen atoms in the adjacent molecule (in white at the center of the molecule in front) change position and electrically switch the entire molecule from "on" to "off". This represents a rudimentary logic-gate, an essential component of computer chips and could be the building block for computers built from molecular components. Credit: IBM





Single Molecule Magnets

The Future: writing information to individual molecules



1 Nano-meter

$Mn_{12}Ac$

{Dr. S. Hill}