Trends in molecular magnetism: a personal perspective

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Deutsche Forschungsgemeinschaft DFG

FOR 945

The Leverhulme Trust

Many thanks to my collaborators worldwide

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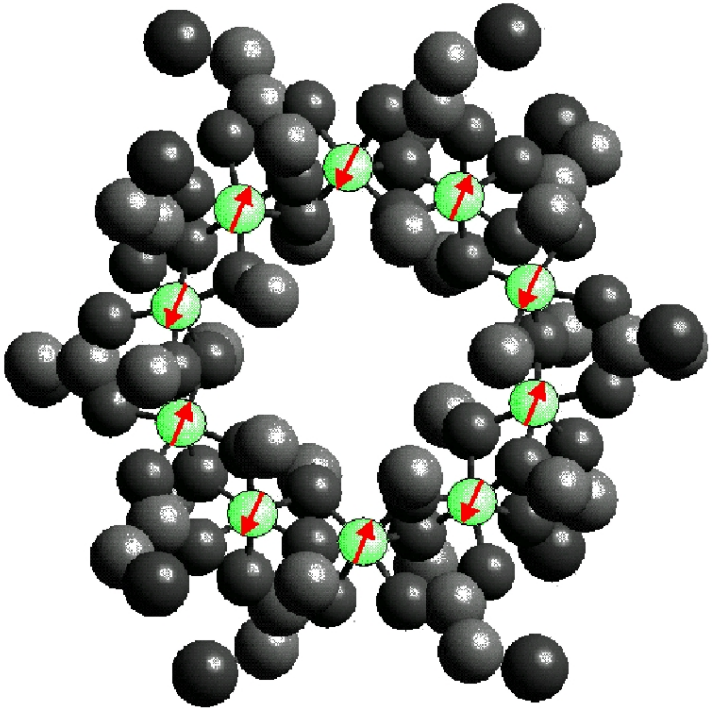
  B. Büchner, V. Kataev, R. Klingeler, H.-H. Klauß (Dresden)

Contents for you today



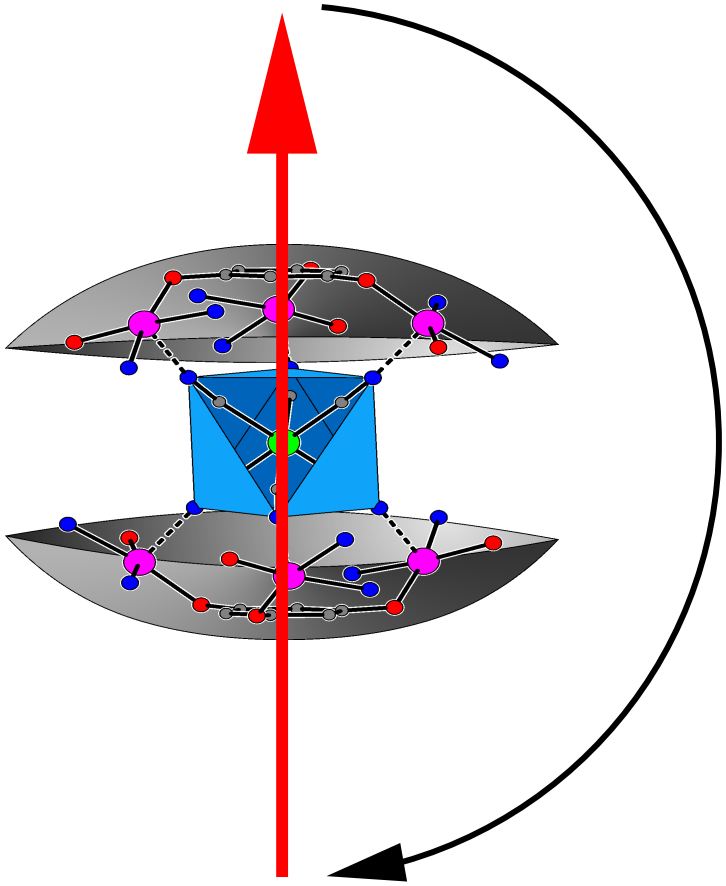
Fe_{10}

1. Single Molecule Magnets
2. Antiferromagnetic Molecules
3. Molecules on Surfaces
4. Coherence Phenomena
5. Forschergruppe 945

If you are missing your topic, please call my lawyer!

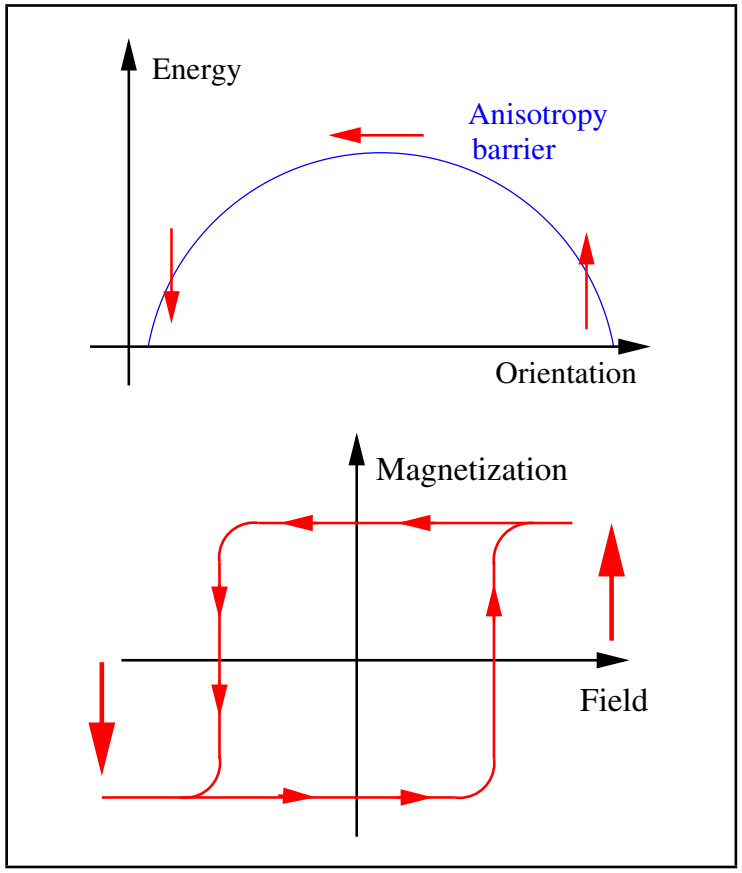
Single Molecule Magnets

Single Molecule Magnets I



- Magnetic Molecules may possess a large ground state spin, e.g. $S = 10$ for Mn_{12} or Fe_8;
- Ground state spin can be stabilized by anisotropy (easy axis).

Single Molecule Magnets II

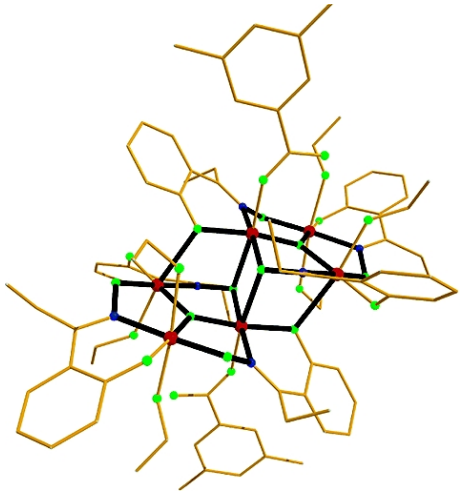


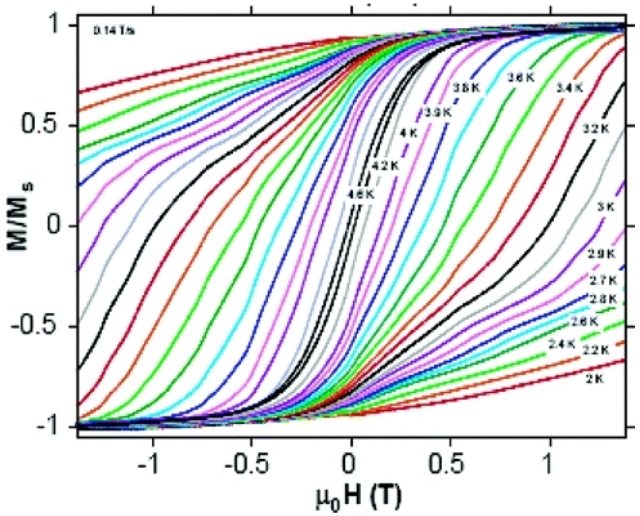
- Single Molecule Magnets (SMM): large ground state moment; anisotropy barrier dominates at low T.

$$\underset{\sim}{H} \approx DS_z^2$$

- Metastable magnetization and hysteresis;
- But also magnetization tunneling due to non-commuting terms, e.g. E, B_x, B_y.

Single Molecule Magnets III





$[Mn_6^{III}O_2(Et\text{-}sao)_6(O_2CPh(Me_2))_2(EtOH)_6]$:

- $S = 12$ ground state with $D = -0.43$ cm^{-1}
- $U_{eff} = 86.4$ K and a blocking temperature of about 4.5 K.
- A record molecule from the group of Euan Brechin (Edinburgh).

C. J. Milios *et al.*, J. Am. Chem. Soc. **129**, 2754 (2007)
S. Carretta *et al.*, Phys. Rev. Lett. **100**, 157203 (2008)

Single Molecule Magnets IV

- "Magnitude of the anisotropy barrier is mainly determined by the strength of the spin-orbit coupling and cannot be engineered by independently optimizing D and S."(1)

- "From this point of view systems with larger energy barriers should be obtained in the case of perfect alignment of the Jahn-Teller axes . . .
However, the challenge here will be the control of the ferromagnetic exchange."(1)

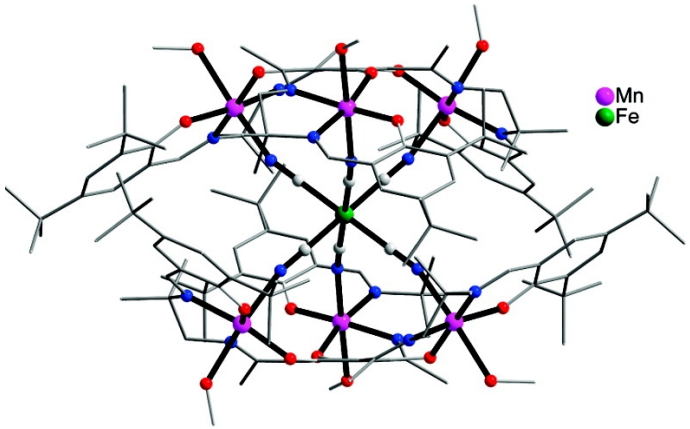
- ". . . the widely considered design rule to increase S is not as efficient as suggested by $\underset{\sim}{H} = DS^2$,. . . the increase is on the order of unity and not S^2."(2)

- "For obtaining better SMMs, it hence seems most promising to work on the local ZFS tensors D_i or to work in a limit where the Heisenberg term is not dominant (i.e., to break the strong-exchange limit)."(2)

(1) E. Ruiz *et al.*, Chem. Commun. 52 (2008).

(2) O. Waldmann, Inorg. Chem. **46**, 10035 (2007).

Single Molecule Magnets V



Rational design of strict C_3 symmetry:

- Idea of Thorsten Glaser:
  C_3 symmetric alignment of local easy axes
  (easy axis $\equiv$ Jahn-Teller axis);
- Various ions could be used so far,
  e.g. Mn_6Cr (1), Mn_6Fe (2), . . .
- Problem: exchange interaction sometimes antiferromagnetic.

T. Glaser *et al.*, Angew. Chem.-Int. Edit. **45**, 6033 (2006).
T. Glaser *et al.*, Inorg. Chem. **48**, 607 (2009).

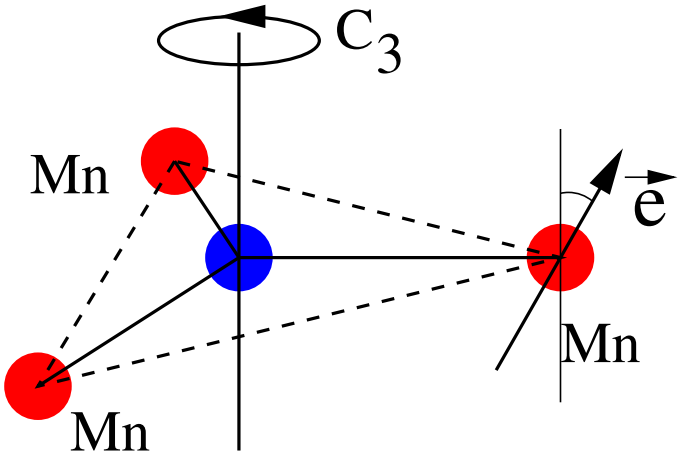
Single Molecule Magnets VI – Theory

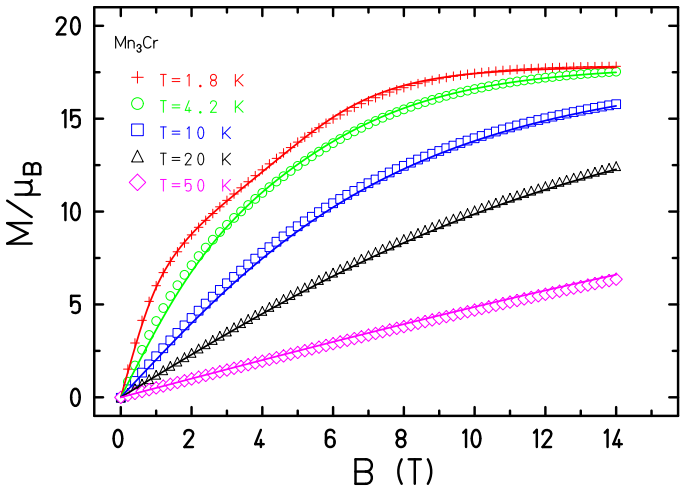
$$\underset{\sim}{H}(\vec{B}) \;=\; -\sum_{i,j} J_{ij}\,\vec{\underset{\sim}{s}}(i)\cdot\vec{\underset{\sim}{s}}(j) \;+\sum_{i} d_i\left(\vec{e}_i\cdot\vec{\underset{\sim}{s}}(i)\right)^2+ \;\mu_B\,\vec{B}\cdot\sum_{i}^{N}\mathbf{g}_i\cdot\vec{\underset{\sim}{s}}(i)$$

- $\left[\underset{\sim}{H},\vec{\underset{\sim}{S}}^2\right]\neq 0$, $\left[\underset{\sim}{H},\vec{\underset{\sim}{S}}_z\right]\neq 0$;
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ for every field (direction and strength)!
  $\Rightarrow$ Orientational average.
- If you are lucky, point group symmetries still exist. Use them!
- Easy: $\dim(\mathcal{H})<30,000$; possible: $30,000<\dim(\mathcal{H})<140,000$

T. Glaser *et al. et* J. Schnack, Inorg. Chem. **48**, 607 (2009).

Single Molecule Magnets VII – Theory



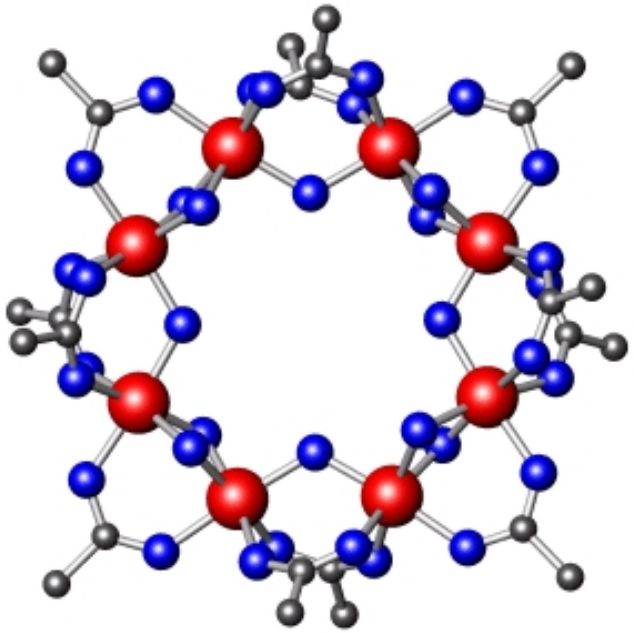


What can be achieved? Mn_3Cr:

- Assume C_3 symmetry;
- Two couplings: J_1 to central Cr, J_2 between Mn;
  Mn: s=5/2, g=2.0; Cr: s=3/2, g=1.95
- Model Mn anisotropy by local axis $\vec{e}(\vartheta, \phi)$.
  Due to C_3 symmetry $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}}$.
  Only relative $\phi = 120°$ determined.
- Model Cr anisotropy by local axis $\vec{e}(\vartheta, \phi)$.
  Due to C_3 symmetry $\vartheta_{\text{Cr}} = 0, \phi_{\text{Cr}} = 0$.
- Result: $J_1 = -0.29\ \text{cm}^{-1}$, $J_2 = -0.08\ \text{cm}^{-1}$,
  $d_{\text{Mn}} = -1.21\ \text{cm}^{-1}$, $\vartheta_{\text{Mn}} = 22°$, $d_{\text{Cr}} = +0.17\ \text{cm}^{-1}$.

Antiferromagnetic Molecules

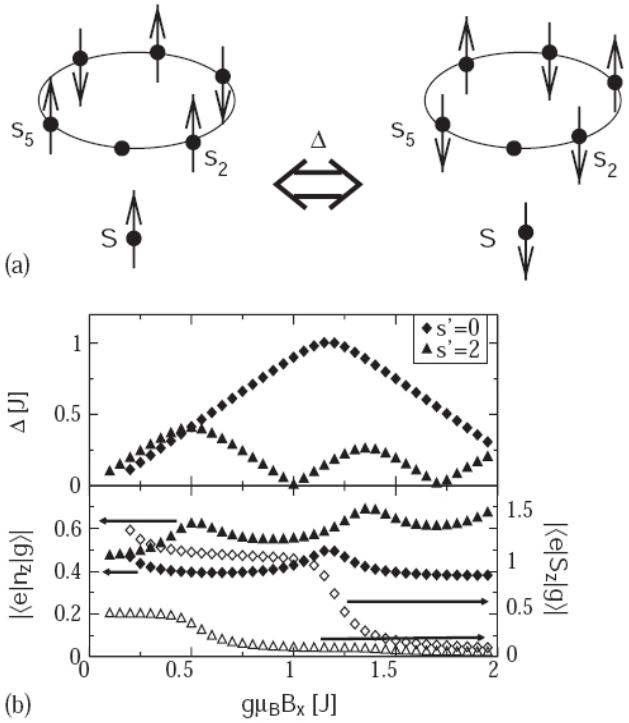
Antiferromagnetic Molecules I – Rings



- To date: many AF rings synthesized, e.g. Fe_6, Fe_{10}, Fe_{12}, . . . , Cr_8, . . . (1)
- Theory: Exact diagonalization; Rotational band model; QMC; Classical (2)

(1) Taft, Delfs, Saalfrank, Rentschler, Winpenny, Timco, Timco, Timco, . . .
(2) Luban, Waldmann, Schnack, Schröder, Carretta, Engelhardt, . . .

Antiferromagnetic Molecules II – Trend A



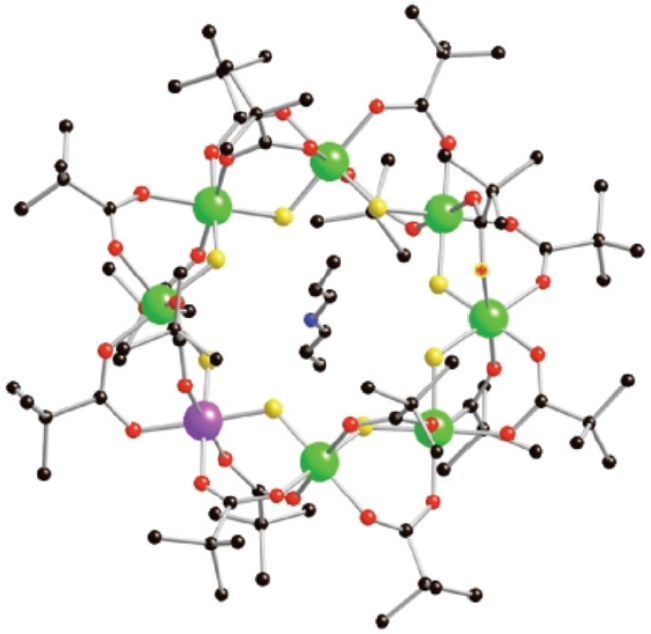
from (4)

Investigation of spin dynamics and coherent tunnelling

- Tunneling of the Neel vector at low lemperatures (1,2,3);
- Tunneling in doped af rings (4).

(1) O. Waldmann, Europhys. Lett. **60**, 302 (2002).
(2) A. Honecker, F. Meier, D. Loss, and B. Normand, Eur. Phys. J. B **27**, 487 (2002).
(3) F. Meier and D. Loss, Phys. Rev. Lett. **86**, 5373 (2001).
(4) F. Meier and D. Loss, Physica B **329-333**, 1140 (2003).

Antiferromagnetic Molecules III – Trend B



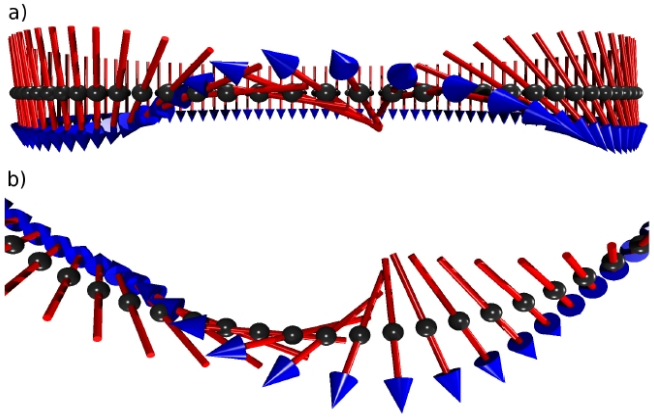
Cr_7Ni by Timco

Synthesis of odd or heterometallic or coupled af spin rings

- Odd membered rings very rare; one reason: steric hindrance (1);
- Heterometallic rings derived from homometallic, especially from Cr_8 (2);
- Coupling of heterometallic rings for quantum computing (3).

(1) O. Cador *et al.*, Angew. Chem. Int. Edit. **43**, 5196 (2004);
H. C. Yao *et al.*, Chem. Commun. 1745 (2006);
(2) F. K. Larsen *et al.*, Angew. Chem. Int. Ed. **42**, 101 (2003); E. Micotti *et al.*, Phys. Rev. Lett. **97**, 267204 (2006); L. P. Engelhardt *et al.*, Angew. Chem. Int. Edit. **47**, 924 (2008), i.e. Timco, Timco, Timco, . . . ; (3) G. A. Timco *et al.*, Nature Nanotechnology (2009), accepted.

Antiferromagnetic Molecules IV – Trend C

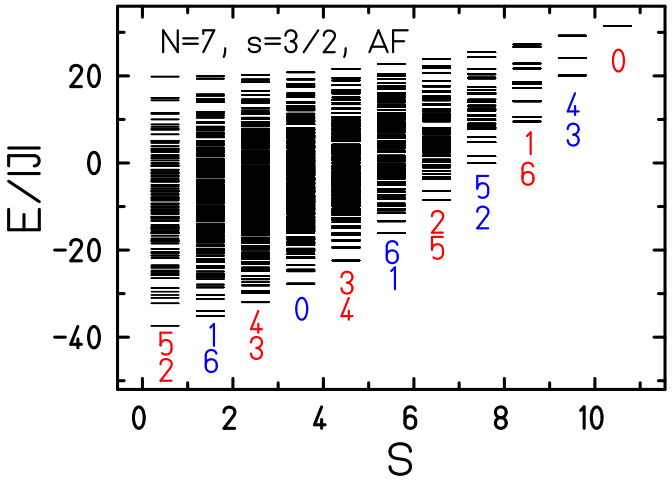


Soliton dynamics

- Theoretical realization of classical solitons on af Heisenberg spin rings (1)
- Do quantum solitons exist and if, how do they look like? (2)

(1) H.-J. Schmidt, C. Schröder, and M. Luban, cond-mat/0801.4262.
(2) J. Schnack and P. Shchelokovskyy, J. Magn. Magn. Mater. **306**, 79 (2006).

Antiferromagnetic Molecules V – Trend D



Extending theorems of Lieb, Schultz, and Mattis

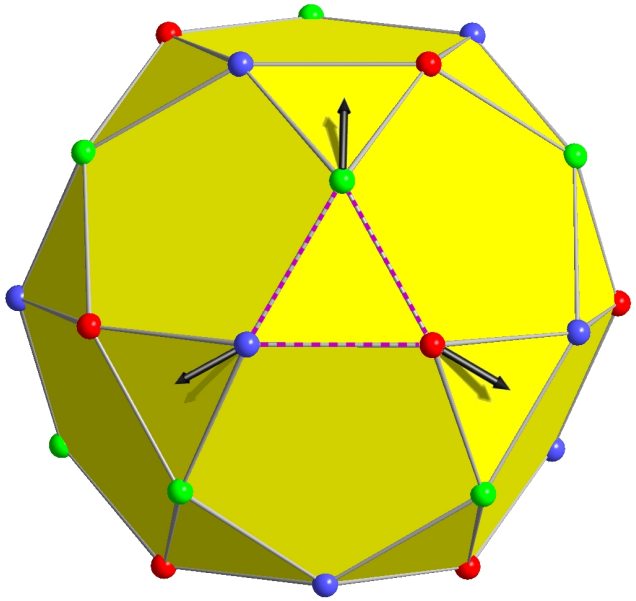
- For odd N and half integer s, i.e. $s = 1/2, 3/2, 5/2, \ldots$ we find that (1)
  - the ground state has total spin $S = 1/2$;
  - the ground state energy is **fourfold** degenerate.

- Reason: In addition to the (trivial) degeneracy due to $M = \pm 1/2$, a degeneracy with respect to k appears (2)

For all rings: $$k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \mod N \,, \quad a = Ns - M \,, \quad (4)$$

(1) K. Bärwinkel, H.-J. Schmidt, J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
(2) $\lfloor \cdot \rfloor$ largest integer, smaller or equal
(3) J. Schnack, Phys. Rev. B **62**, 14855 (2000)
(4) K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B **68**, 054422 (2003)

Antiferromagnetic Molecules VI – Frustration Effects



Fe_{30} by A. Müller

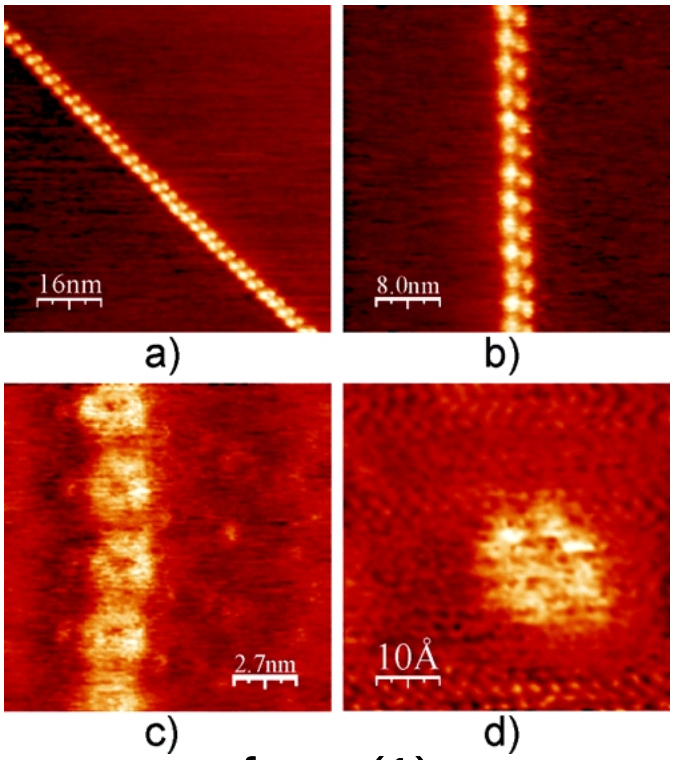
Learn about antiferromagnets from molecules

- Archetypical frustrated molecules: cuboctahedra, icosahedra, icosidodecahedra, truncated tetrahedra (1);
- Cuboctahedra and icosidodecahedra share properties with kagome lattice (2);
- Phase transition at $T = 0$ for icosahedron (3);
- Enhanced magnetocaloric effect (4).

(1) A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001); meanwhile Fe_{30}, Cr_{30}, V_{30}, see U. Kortz *et al.*, Cood. Chem. Rev. (2009), accepted.
A. J. Blake *et al.*, J. Chem. Soc.-Dalton Trans. 485 (1997); C. P. Pradeep, D.-L. Long, P. Kögerler, and L. Cronin, Chem. Commun. 4254 (2007).
(2) J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002);
(3) C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)
(4) J. Schnack, R. Schmidt, J. Richter, Phys. Rev. B **76**, 054413 (2007)

Molecules on Surfaces

Molecules on Surfaces I



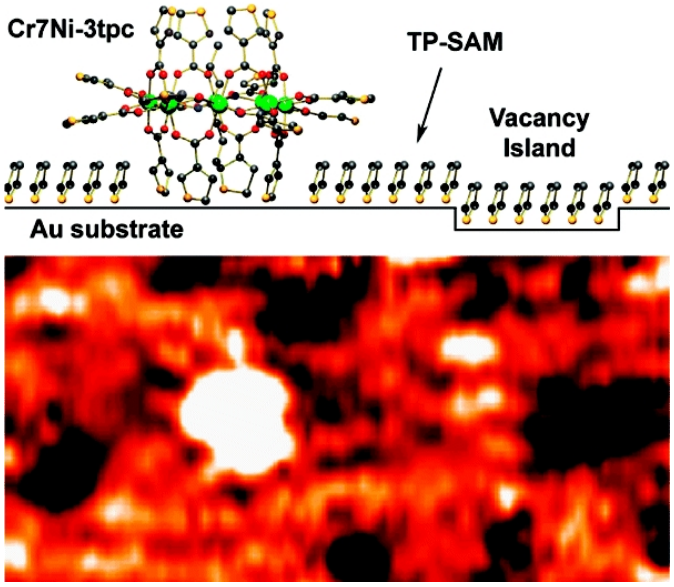
from (1)

Early attempts by Paul Müller

- Cu_{20} on Highly Orientated Pyrolytic Graphite (HOPG) (1);
- Scanning tunnelling microscopy (STM) (2);
- Scanning tunnelling spectroscopy (STS) (2);
- Current induced tunnelling spectroscopy (CITS) (2).
- Theory: Schoeller, Wegewijs, Timm, Postnikov, Kortus.

(1) M. S. Alam *et al.*, Inorg. Chem. **45**, 2866 (2006).
(2) M. Ruben, J. M. Lehn, and P. Müller, Chem. Soc. Rev. **35**, 1056 (2006).

Molecules on Surfaces II



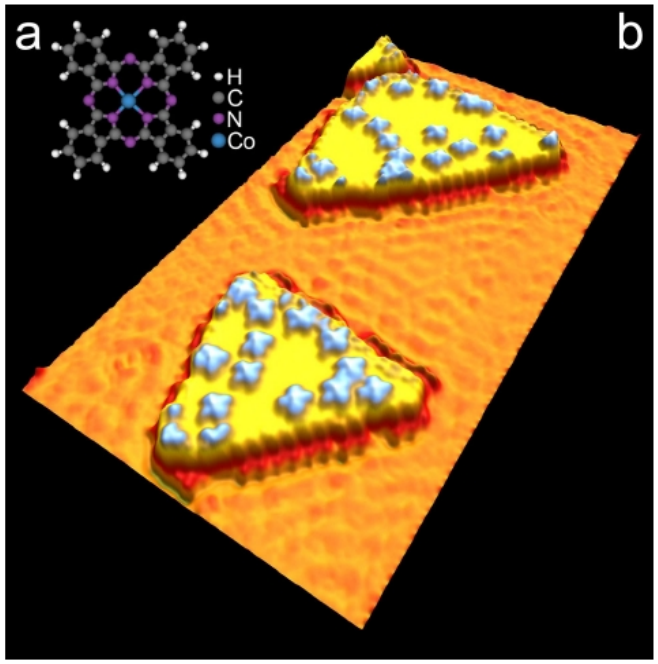
from (1)

Rings on surfaces

- Sulfur-functionalized clusters Cr_7Ni on gold (1);
- Deposited from the liquid phase on Au(111);
- Scanning tunneling microscopy (STM) and X-ray photoemission spectroscopy (XPS);
- "The stoichiometric behavior of the core level intensities, which are the direct fingerprint of the ring, confirms that the ring integrity is preserved."(1)

(1) V. Corradini *et al.*, Inorg. Chem. **46**, 4937 (2007). (2006).

Molecules on Surfaces III



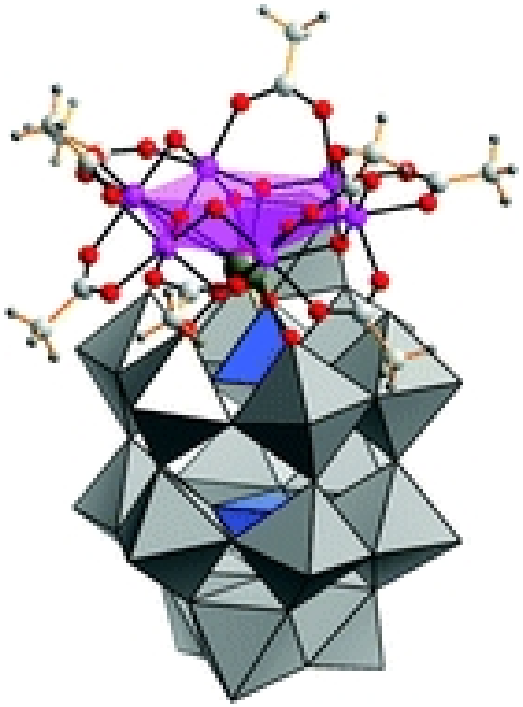
from (1)

Spin-polarized measurements

- Cobalt-phthalocyanine molecules on cobalt islands (1);
- Spin-polarized STM and STS;
- Transport through polarized Co islands;
- Identification of ferromagnetic molecule-lead exchange interaction (1)

(1) C. Iacovita *et al.*, Physical Review Letters **101**, 116602 (2008).

Molecules on Surfaces IV



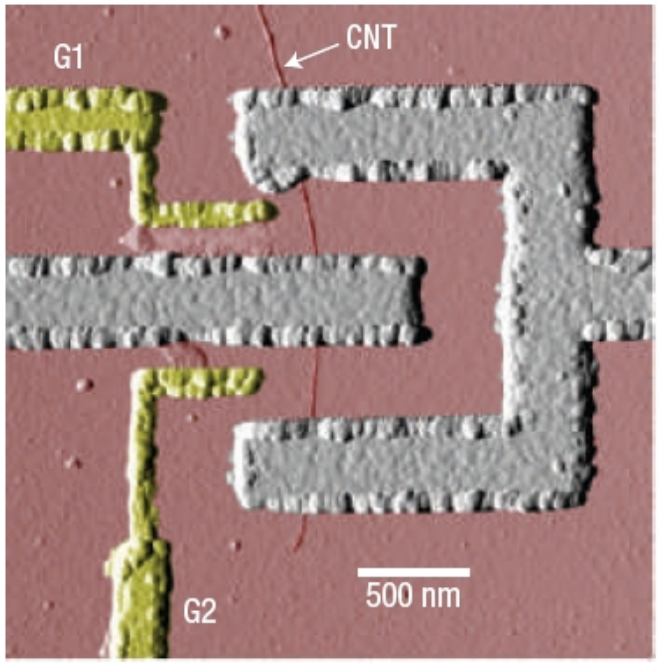
from (1)

“Backslash”on molecule

- How much of the deposited molecule survives?
- Study of a Mn_6 cluster grafted on a Polyoxometalate (POM) (1);
- Intra-molecular interactions change compared to free molecule (1).

(1) Xikui Fang and P. Kögerler, Chem. Commun. 3396 (2008).

Molecules on Surfaces V



from (1)

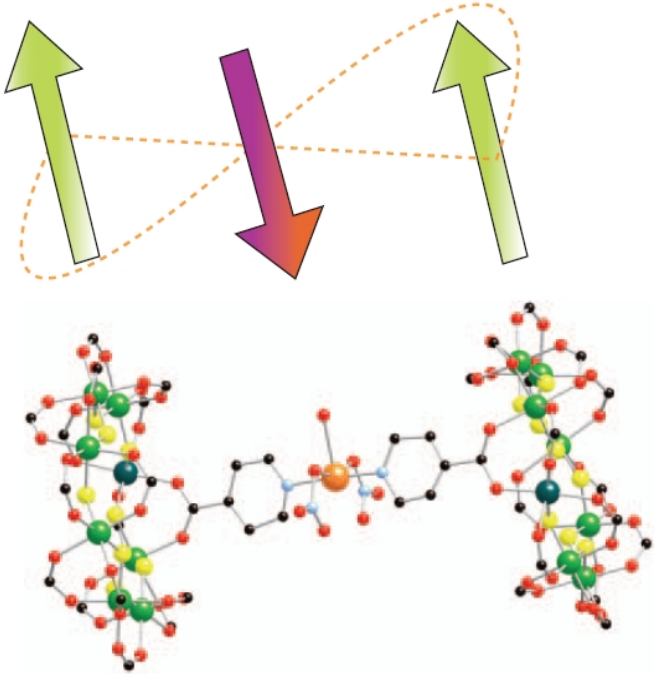
Carbon nanotube squid

- Use of single-walled carbon nanotube (CNT) Josephson junctions;
- Discrete quantum dot (QD) energy level structure controlled by gates (1);
- CNT-SQUIDs sensitive local magnetometers to study the magnetization reversal of individual magnetic particles (1).

(1) J. P. Cleuziou *et al.*, Nature Nanotechnology **1**, 53 (2006).

Coherence Phenomena

Coherence Phenomena I



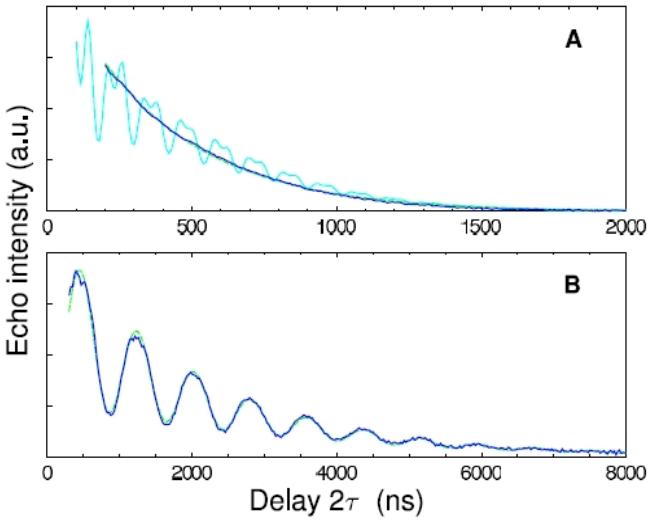
from (1)

Quantum computing

- Chemical realization through coupled molecules with switchable coupling;
- Original ideas, see e.g. (2);
- Molecular transistors; transport in weak or strong coupling regime (3).
- Needed: long coherence times.

(1) G. A. Timco *et al.*, Nature Nanotechnology (2009), accepted; R. E. P. Winpenny, Angew. Chem. Int. Ed. **47**, 7992 (2008); M. Affronte *et al.*, Dalton Transactions 2810 (2006); M. Affronte *et al.*, J. Magn. Magn. Mater. **310**, E501 (2007).
(2) M. N. Leuenberger and D. Loss, Nature **410**, 789 (2001).
(3) L. Bogani and W. Wernsdorfer, Nature Materials **7**, 179 (2008).

Coherence Phenomena II

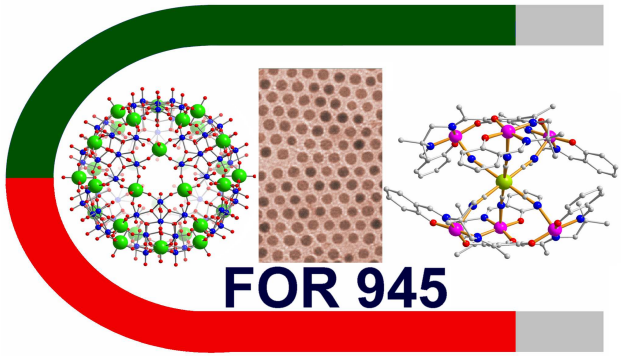


from (1)

Spin relaxation times

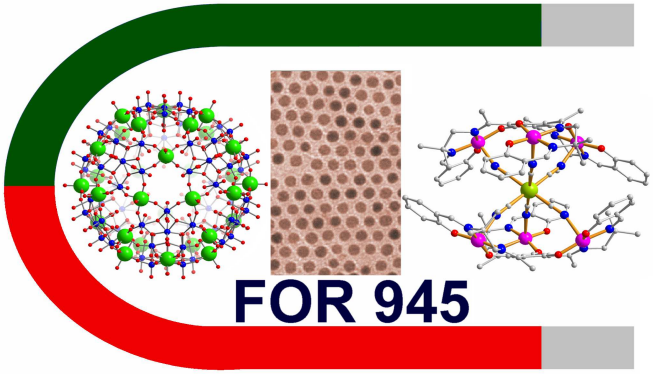
- EPR/NMR, Hahn echo techniques, T_1, T_2 times;
- Decoherence due to e.g. nuclei, phonons, dipolar interaction;
- Deuteration improves coherence times considerably;
- μs (!) can be reached. (1)

(1) A. Ardavan *et al.*, Phys. Rev. Lett. **98**, 057201 (2007).
(2) S. Bahr, K. Petukhov, V. Mosser, and W. Wernsdorfer, Phys. Rev. Lett. **99**, 147205 (2007);
W. Wernsdorfer, Nature Materials **6**, 174 (2007).
(3) S. Bertaina *et al.*, Nature **453**, 203 (2008).
(4) C. Schlegel *et al.*, Phys. Rev. Lett. **101**, 147203 (2008).



Forschergruppe 945

Forschergruppe 945

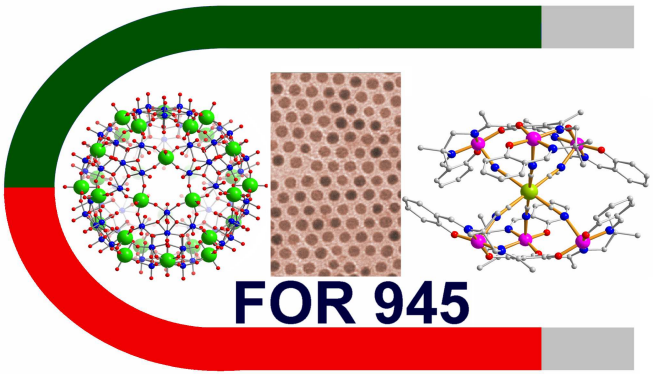


Members

- Chemistry: Thorsten Glaser, Achim Müller, Peter Jutzi, Norbert Mitzel (Bielefeld);
- Physics: Andreas Hütten, Ulrich Heinzmann, Günter Reiss, Jürgen Schnack, Christian Schröder (Bielefeld);
- Physics: Paul Müller, Konstantin Petukhov (Erlangen).

http://www.for945.uni-bielefeld.de/

Forschergruppe 945



Research program

- Synthesis and Characterization of Nanomagnets:
  AF molecules, SMM, core-shell particles;
- Theoretical modeling;
- Deposition and investigation on surfaces.

http://www.for945.uni-bielefeld.de/

I would like to apologize for not mentioning . . .

- Eugenio Coronado (Valencia) and his results;
- George Christou (Gainesville) and his results;
- Roland Wiesendanger (Hamburg) and his results;
- Italy much more;
- Chain magnets;
- Spin-crossover systems;
- YOU;
- . . .

Thank you very much for your attention.

German Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. DFG SPP 1137