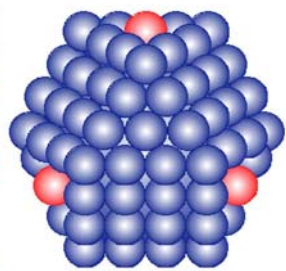
MAGMA Net
NETWORK OF EXCELLENCE

Molecular Magnets

Dante Gatteschi
Università di Firenze-INSTM
dante.gatteschi@unifi.it



MAGMA Net
NETWORK OF EXCELLENCE

Everyday life
is full of useful *magnets*
which traditionally take the form
of three-dimensional solids,
oxides, metals and alloys

MAGMA Net
NETWORK OF EXCELLENCE

Magnetic Toys

Magnets in Automotive Devices

Confort

- **Compass**
- **Door Lock Actuators**
- **Hvac Fan Motor**
- **SEAT Position**
- **Sensors**
- **Seat Position Motor**
- **Speakers**
- **Sun Roof Motor**
- **Suspesion Control**
- **System Trunk Latch Actuator**
- **Window Lift Motor**

Safety

- Air bag sensor
- Seat Belt Sensor

Cockpit control

- Cruise control
- Electric power steering
- Key sensor
- Instrumentation gauges
- Liquid level sensors
- Magnetic switches

External systems

- Antenna lift motor
- Headlight door motors
- Headlight aiming motors
- Mirro positioning motors
- Windshield wash pump motor
- Windshield wiper motor

Engine system

- Alternator
- Cooling fan motor
- Cramshaft position snesor
- Emission control vent motor
- Fuel pump motor
- Idle speed control
- Starter motor
- Throttle position sensor

Drive and brake systems

- ABS speed sensors
- Brake pedal position sensor
- Camless position sensor
- Electric brake actuators
- Traansmission chip collector
- Transmission shift sensor

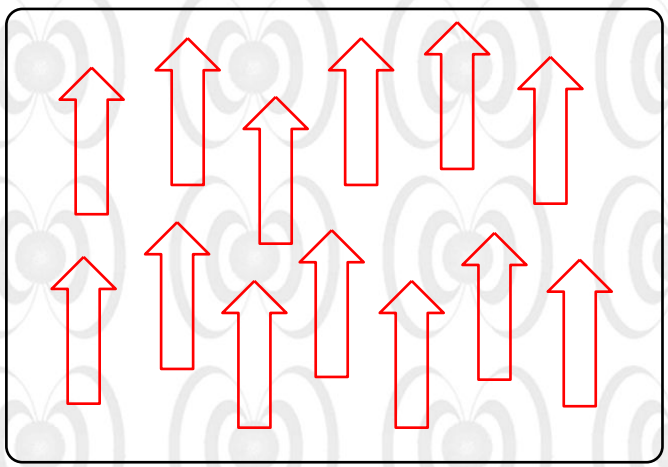
Up to 30 kg of high intensity magnetic material in hybrid, electric and drive by wire CARS

MAGMA Net
NETWORK OF EXCELLENCE

Magnetism is everywhere

The magnetic moments order at Curie temperature

A set of molecules / atoms :



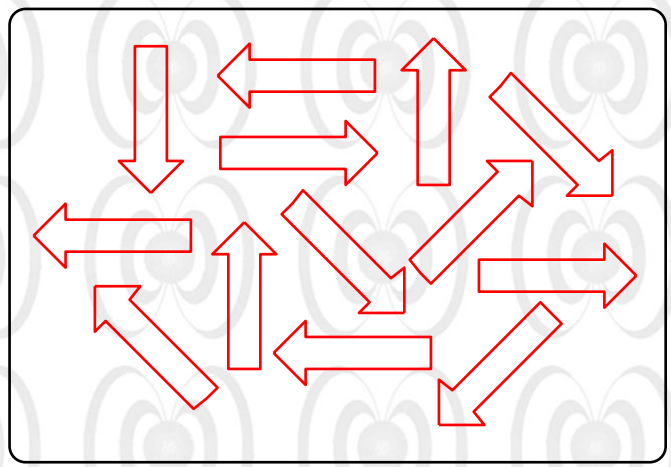
Solid, Magnetically Ordered
thermal agitation (kT) weaker than the interaction (J) between molecules

kT << J

T_C

$kT \approx J$

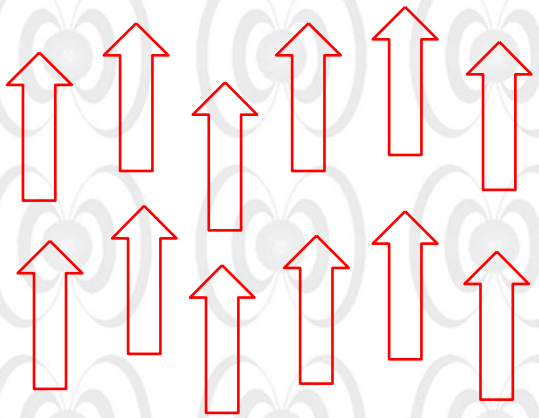
Magnetic Order Temperature or Curie Temperature



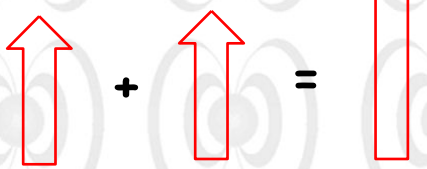
… Paramagnetic solid : thermal agitation (kT) larger than the interaction (J) between molecules

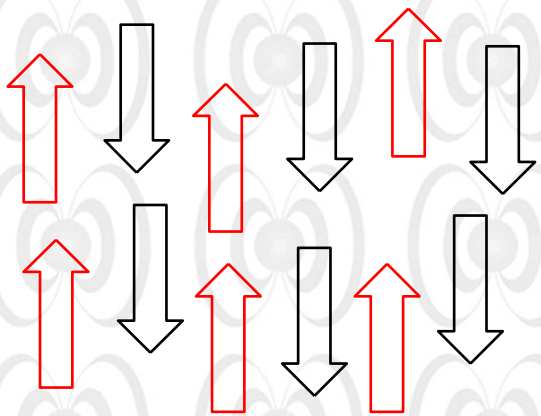
kT >> J

Magnetic Order : ferro-, antiferro- and ferri-magnetism

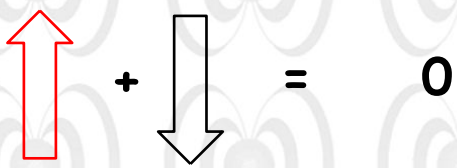


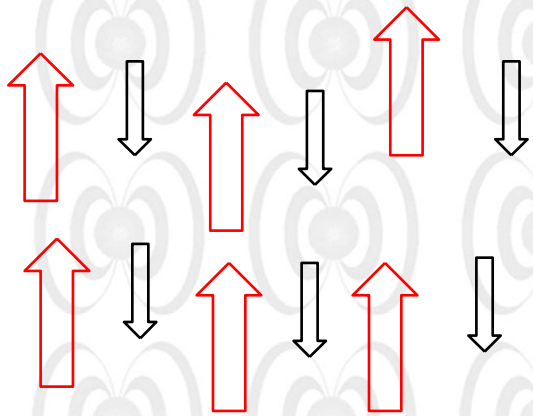
Ferromagnetism :
Magnetic moments
are identical
and parallel



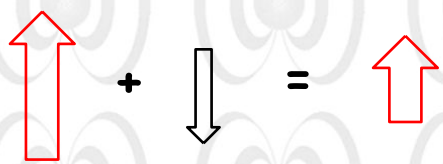


Antiferromagnetism :
Magnetic moments
are identical
and anti parallel





Ferrimagnetism (Néel) :
Magnetic moments
are different
and anti parallel



MAGMA Net
NETWORK OF EXCELLENCE

Magnetochemistry

- The use of magnetic properties (essentially paramagnetism) for structural information
- Mononuclear and dinuclear compounds
- Spin cross-over

MAGMA Net
NETWORK OF EXCELLENCE

Molecular Magnetism

- Design and synthesis of new materials for new magnetic properties
- Molecular materials with permanent magnetization
- Two- and one-dimensional magnetic materials
- Magnetic molecules
- Tailor made Spin cross-over
- Molecular techniques to magnetic nanoparticles

Molecular Magnetism: a Multidisciplinary area

- Efficient models for design
- Synthetic ability
- Sofisticated physical techniques
- Theoretical models
- An eye to biology
- Creativity

Some examples

- Fully organic magnets
- New animals in the magnetic zoo (one dimensional ferrimagnets….)
- Extremely hard magnets
- Magnets with unusual properties (localized vs delocalized, magneto-optical properties, chiral magnets, etc)

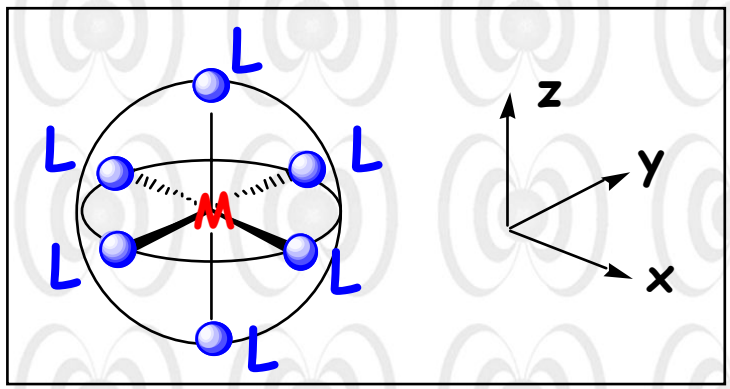
Neutrons in Molecular Magnetism

- Structures
- Polarized Neutron Diffraction for Magnetization Density
- Inelastic Neutron Scattering for information on low lying levels

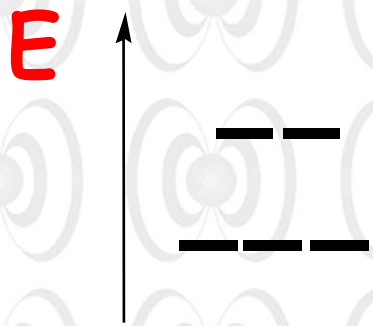
MAGMA Net
NETWORK OF EXCELLENCE

Spin Cross-over

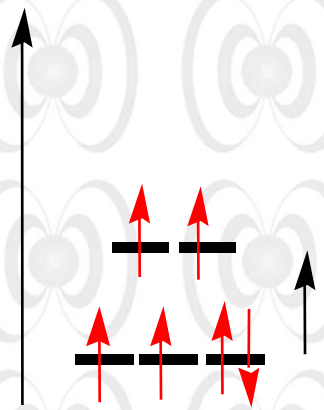
Mononuclear complex ML_6



Splitting of the energy levels



How large is the splitting ?

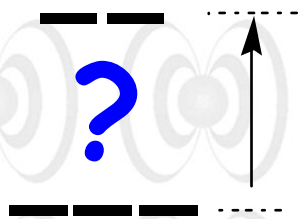


Weak Field

High spin

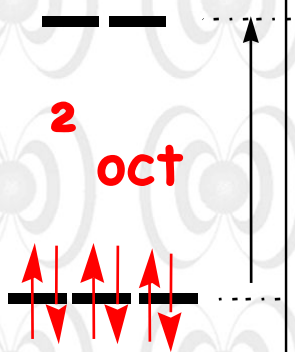
L = H_2O

$[C_2O_4]^{2-}$



Intermediate Field

Temperature Dependent Spin Cross-Over

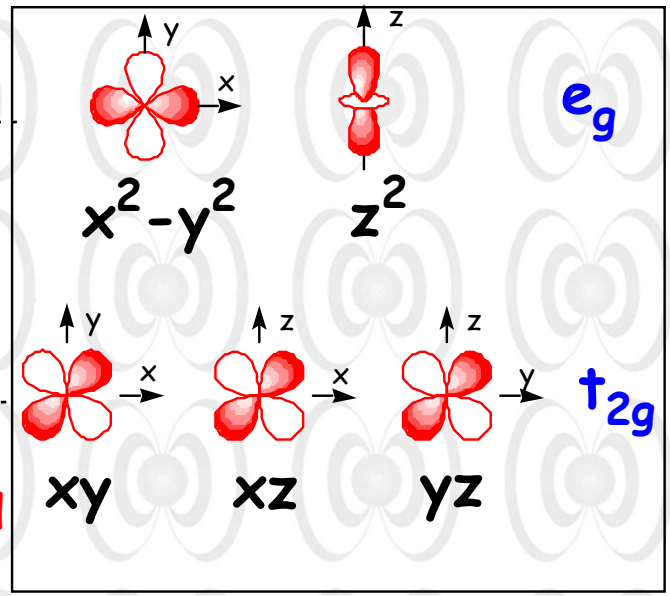


^{2} oct

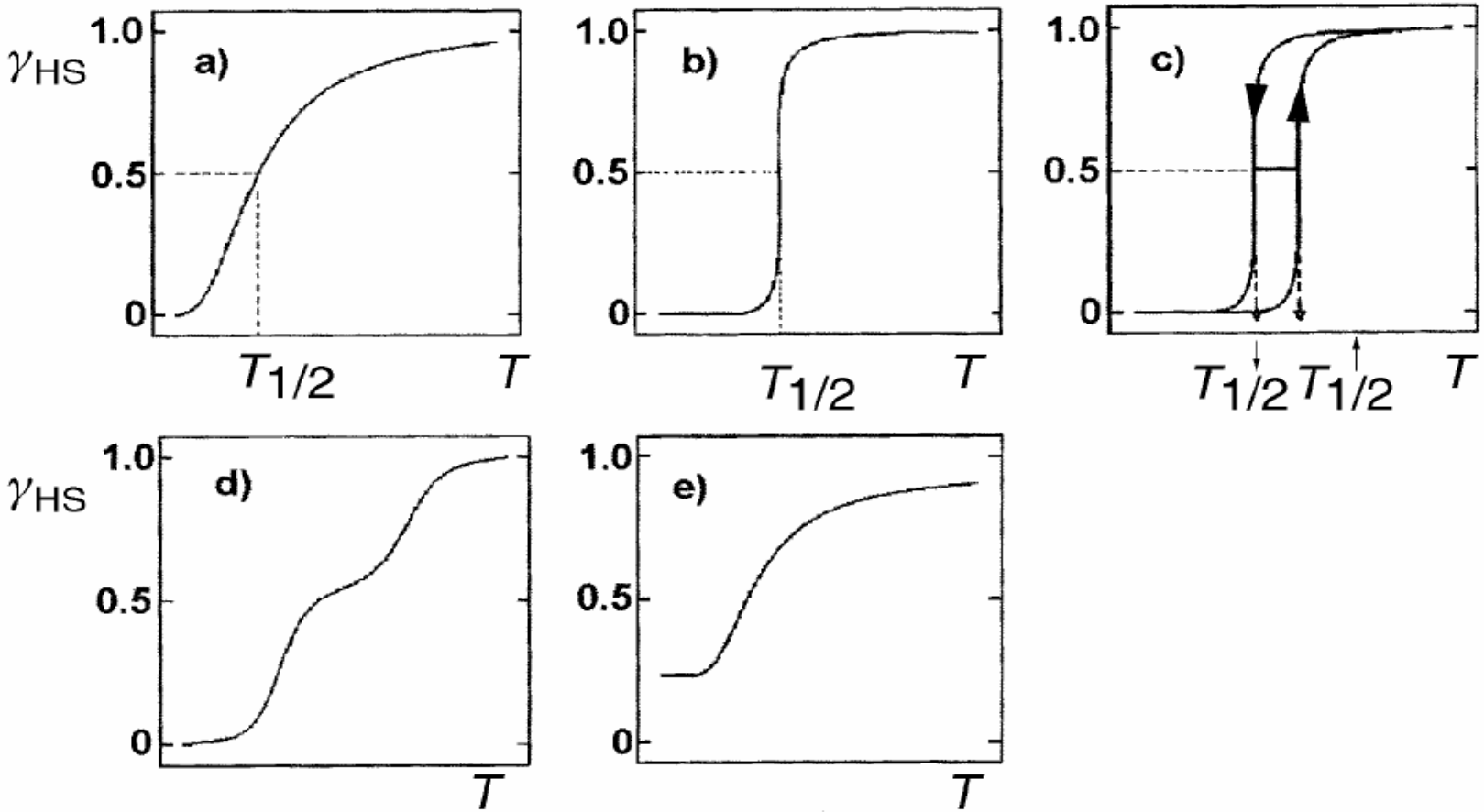
Strong Field

Low spin

L = CN-

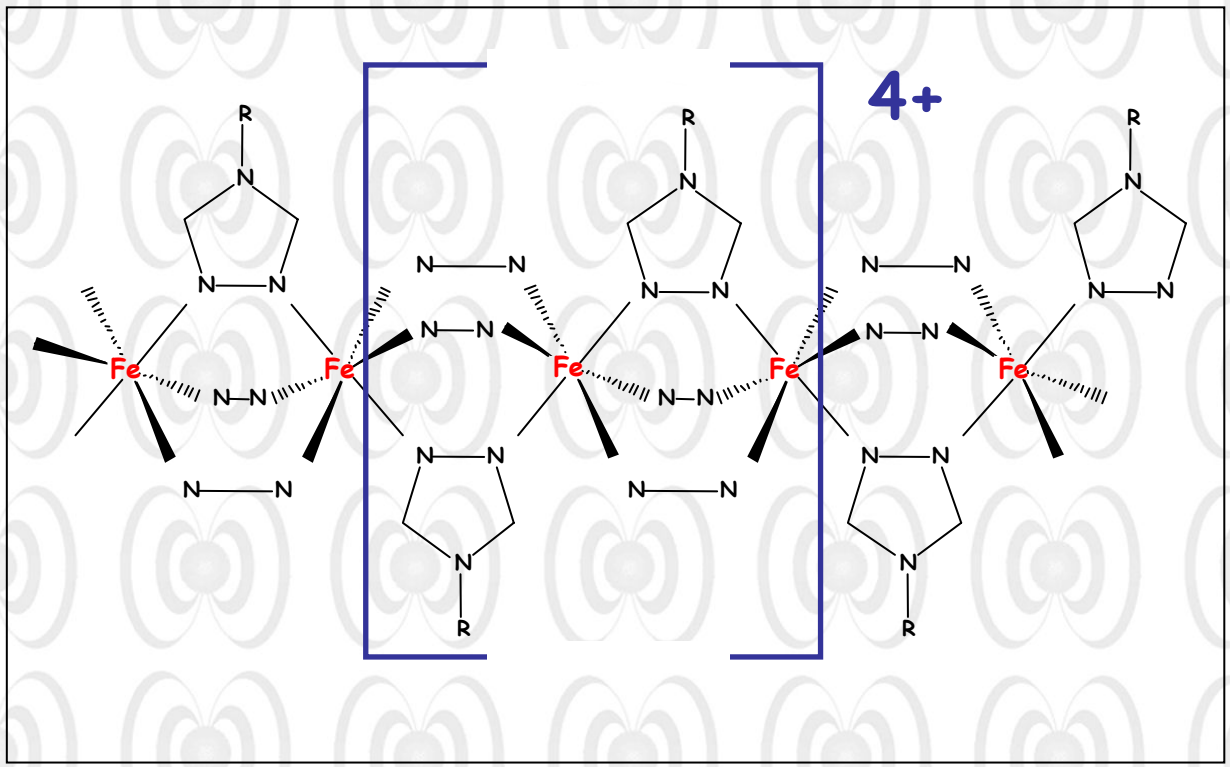


Different Transitions



Spin Cross-Over

A Fe(II) « Chain » with spin cross-over

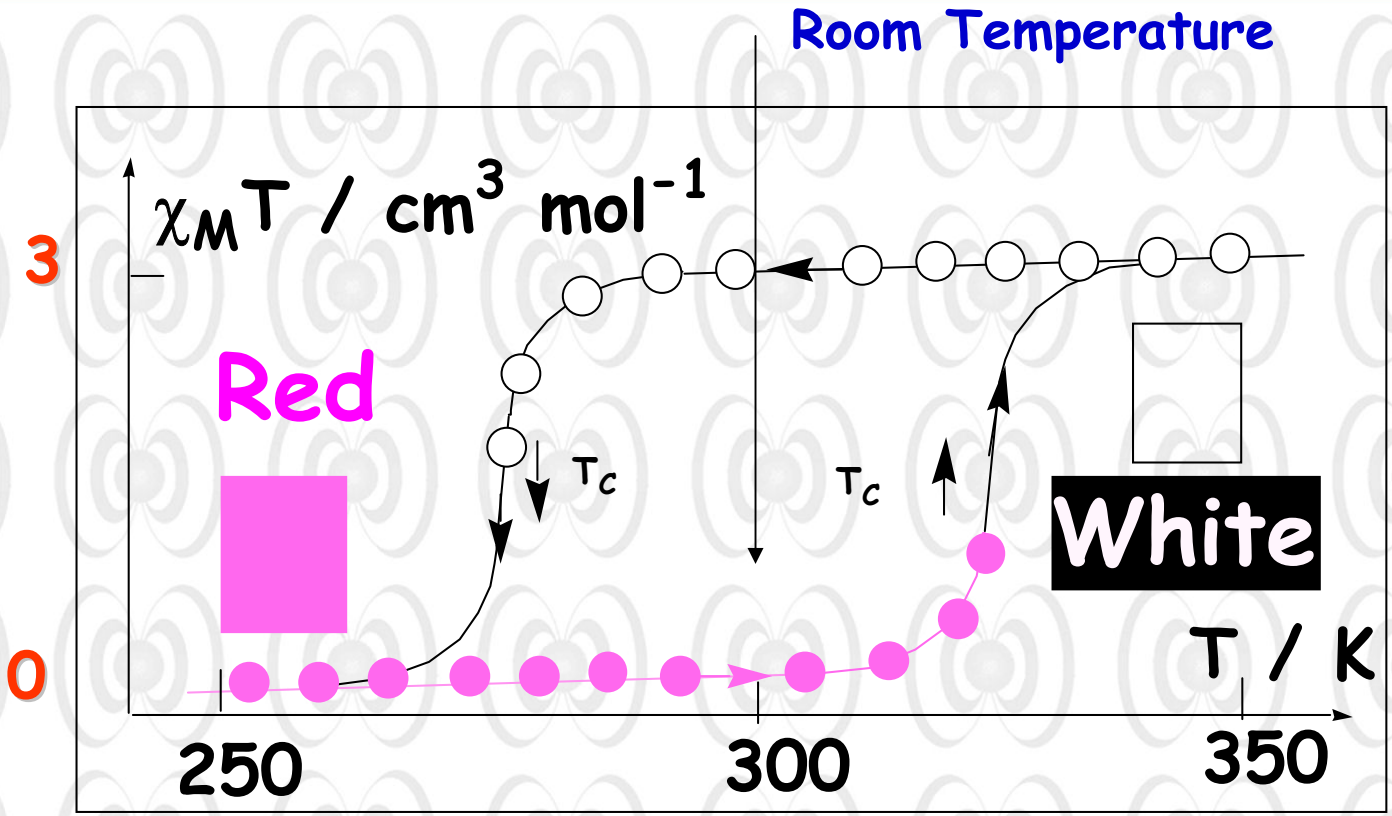


Triazole substituted Ligand (R) ; insulated by counter-anions

Many groups : Leiden, Mainz, Kojima, O. Kahn, C. Jay, Y. Garcia, ICMC Bordeaux

Spin Cross-Over

Bistability Domain

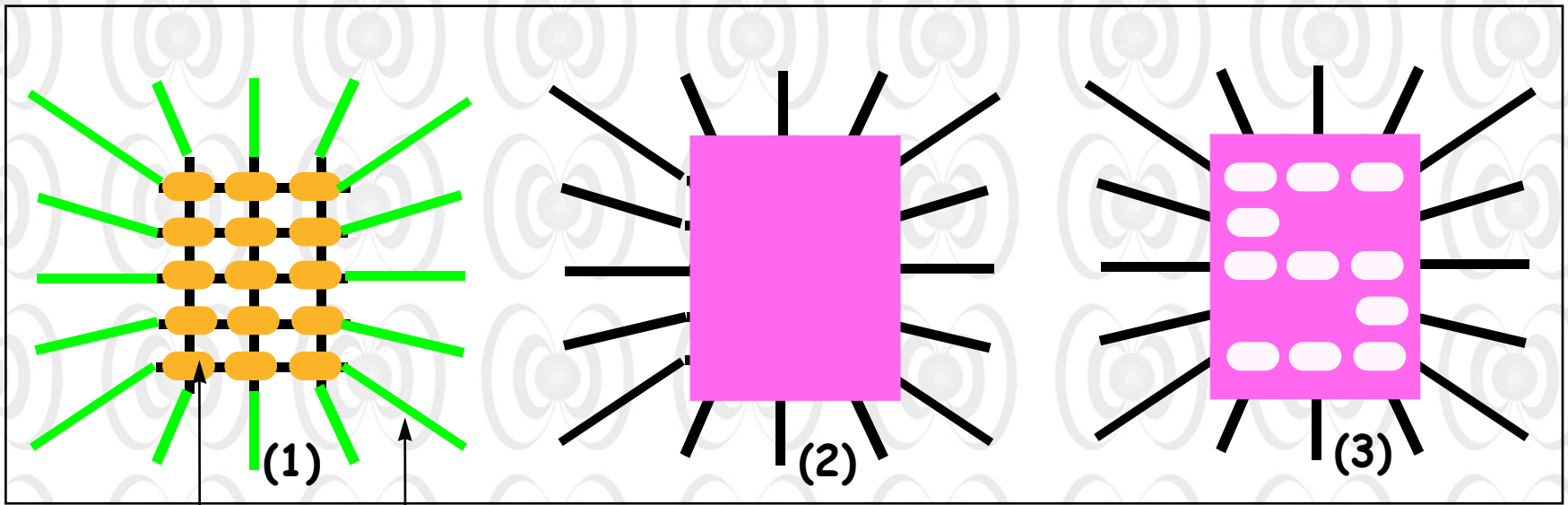


The system « remembers » its thermal past !

O. Kahn, C. Jay and ICMC Bordeaux

Spin Cross-over

Display Device



Joule and Peltier Elements

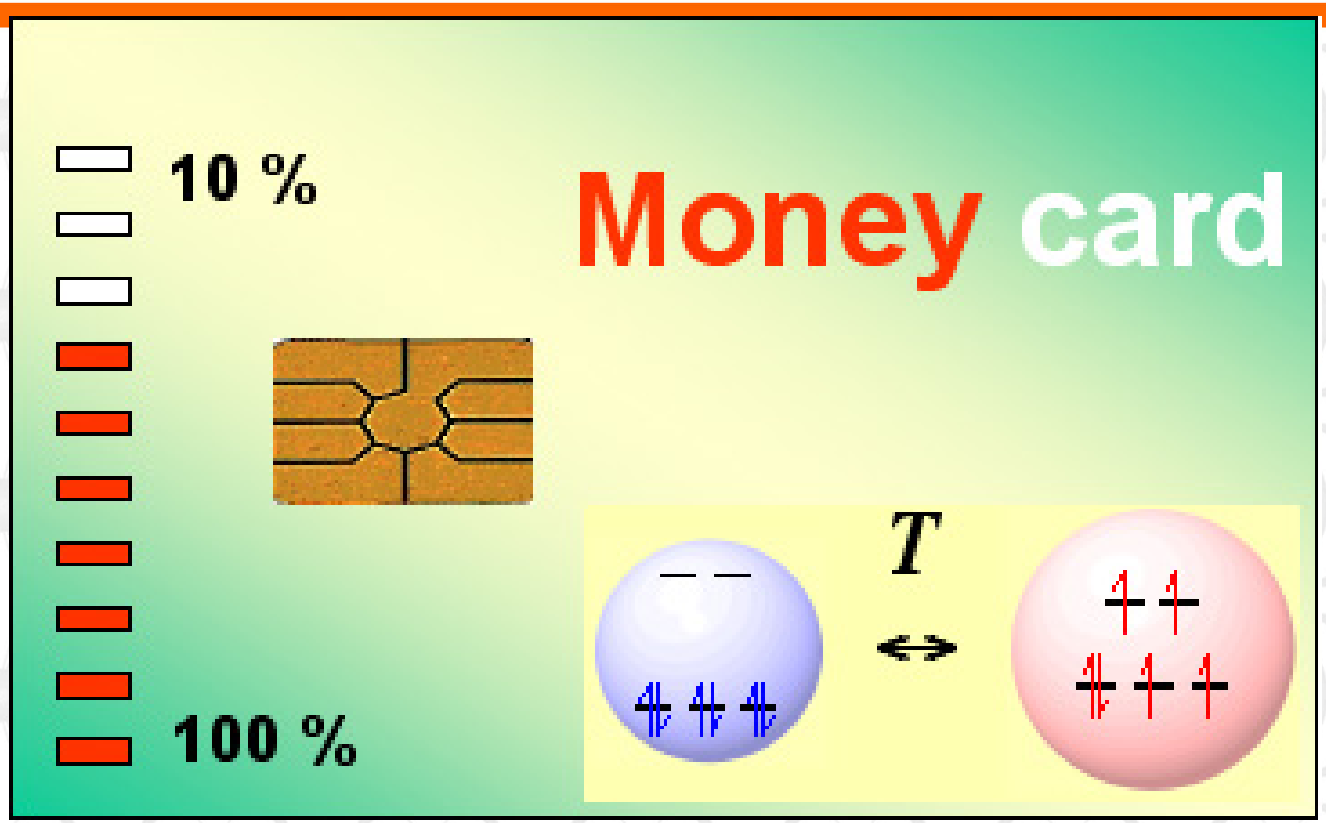
Connections

Compound in Low spin state (Thin Layer)

Display

O. Kahn, J. Kröber, C. Jay *Adv. Mater.* 1992, 718

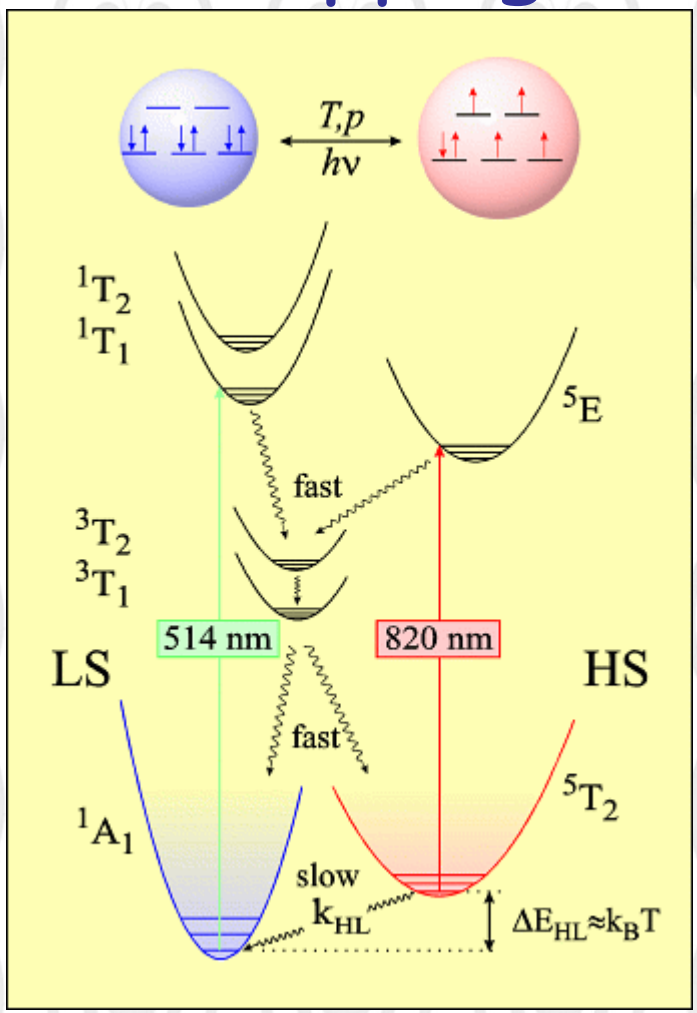
Kahn O., *La Recherche*, 1994, 163



M. Verdaguer

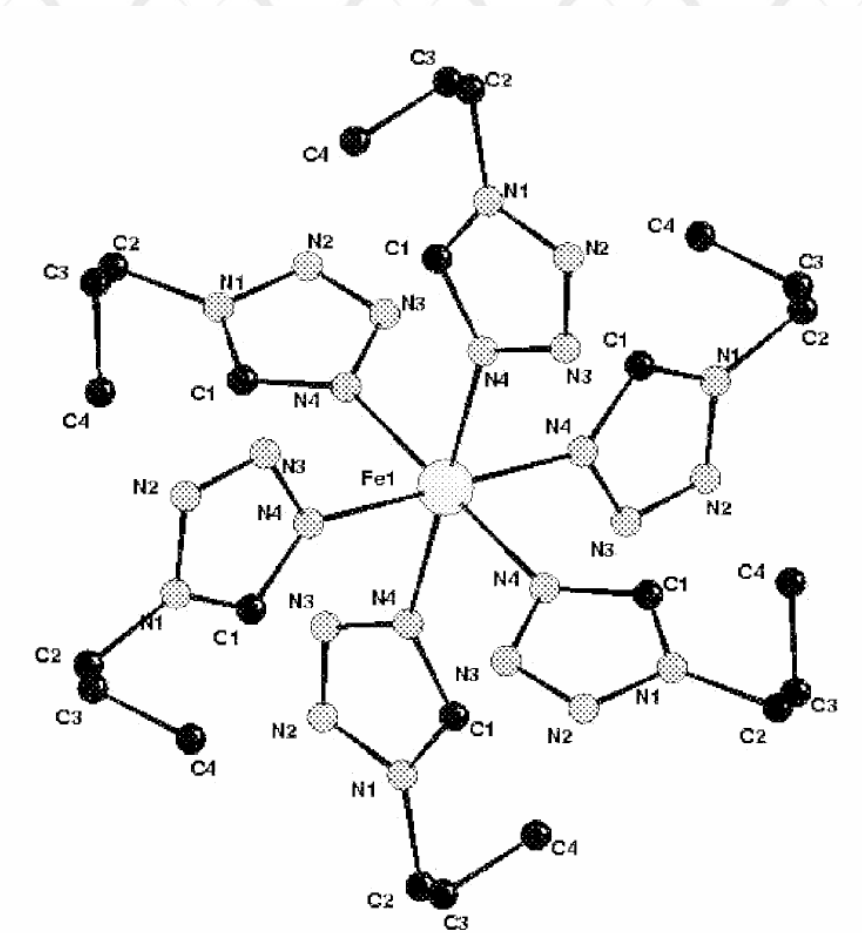
O. Kahn, Y. Garcia, Patent

LIESST
Light Induced Electron Spin State Trapping



MAGMA Net
NETWORK OF EXCELLENCE

$[Fe(ptz)_6]^{2+}$



MAGMA Net
NETWORK OF EXCELLENCE

PND

$$R(\mathbf{K}) = \frac{I_+}{I_-} = \frac{F_N^2 + 2p\sin^2\alpha F_N F_M + \sin^2\alpha F_M^2}{F_N^2 - 2p\sin^2\alpha F_N F_M + \sin^2\alpha F_M^2}$$

$$F_N(\mathbf{K}) = \sum_j b_j e^{i\mathbf{K}\mathbf{r}_j} e^{-W_j}$$

$$F_M(\mathbf{K}) = \int_{cell} m(\mathbf{r}) e^{i\mathbf{K}\mathbf{r}} d^3\mathbf{r}$$

MAGMA Net
NETWORK OF EXCELLENCE

Direct methods

$$s(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{K}} F_M(\mathbf{K}) e^{-i\mathbf{K}\mathbf{r}}$$

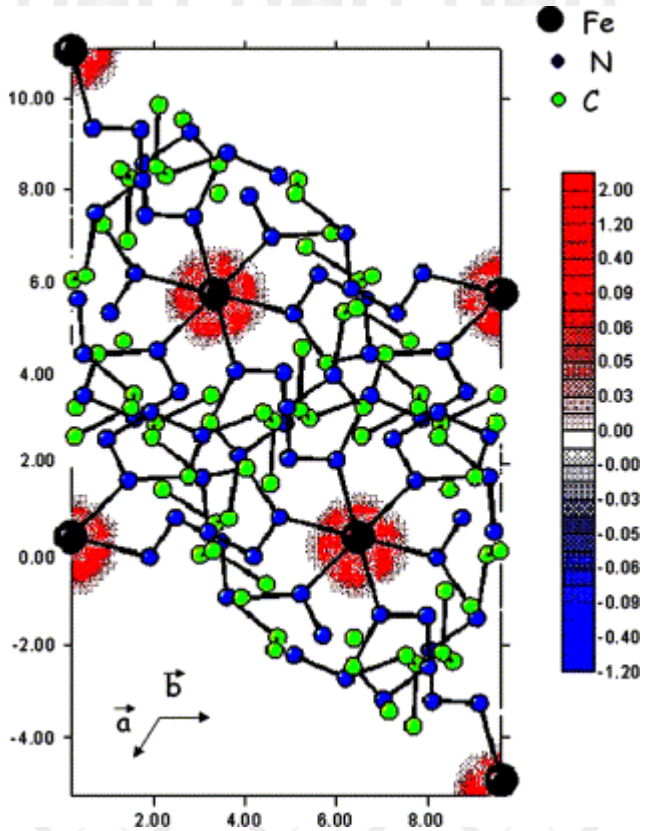
Maximum Entropy Method

- It evaluates, for each possible reconstructed map, the probability of this map
- The probability is the product of the likelihood and the prior
- Likelihood is the probability for the set of experimetal data to be observed
- Prior represents the intrinsic probability of the map

Modelling the spin density

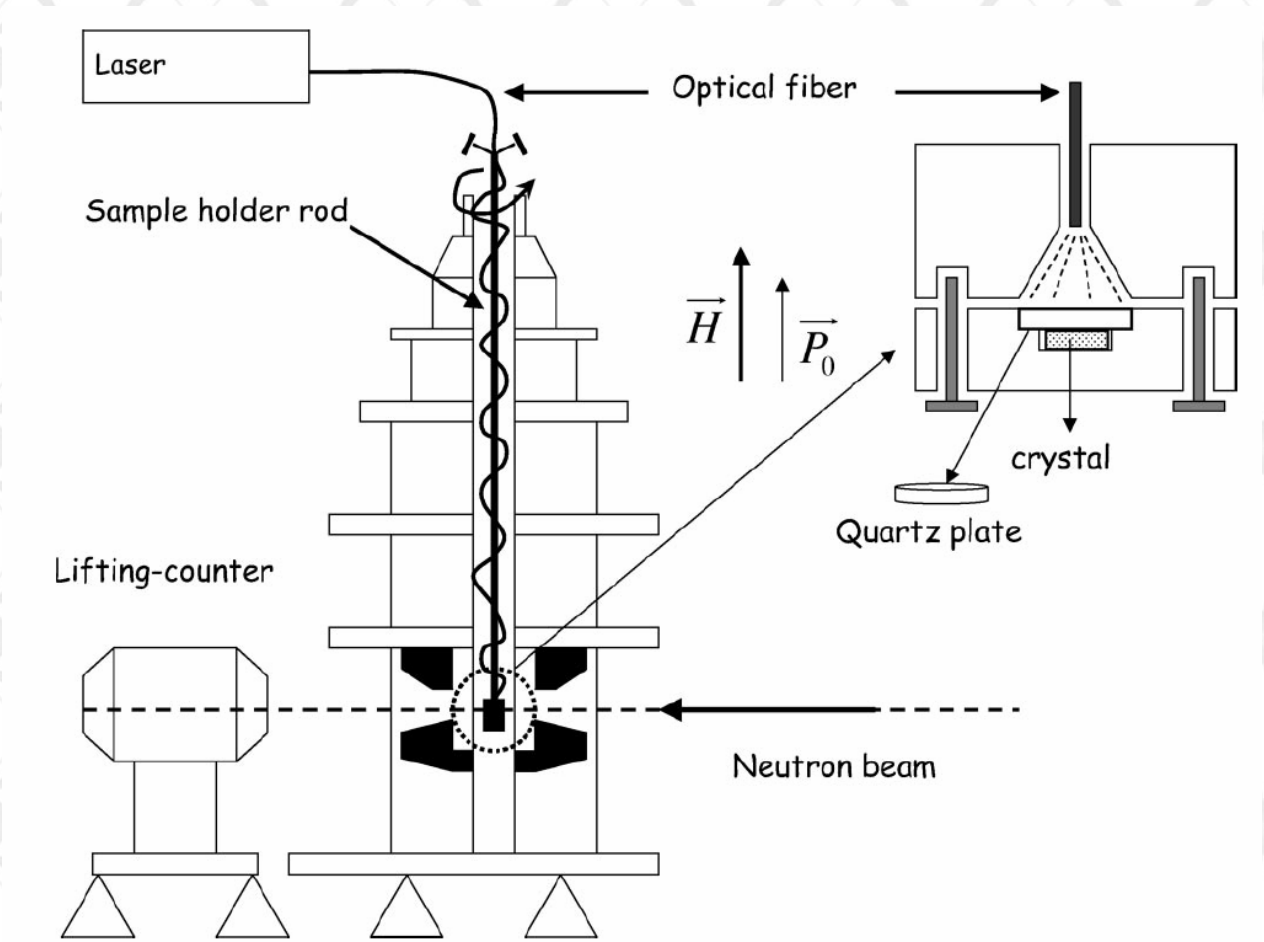
$$s(\mathbf{r}) = \sum_{atoms} \sum_{l} R_l(r) \sum_{m=-l}^{+l} P_{lm} Y_{lm}(\mathbf{r})$$

Spin density map of photo-induced state at 2 K



MAGMA Net
NETWORK OF EXCELLENCE

The set-up



Laue diffraction

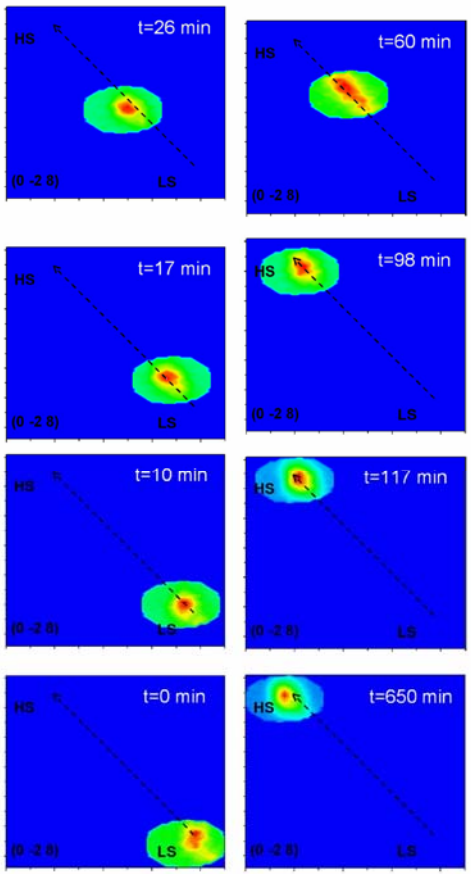


FIG. 3. (Color online) Shift of the $(0,-2,8)$ reflection of $[Fe(ptz)_6](BF_4)_2$ upon photoexcitation at 473 nm, 2 K.

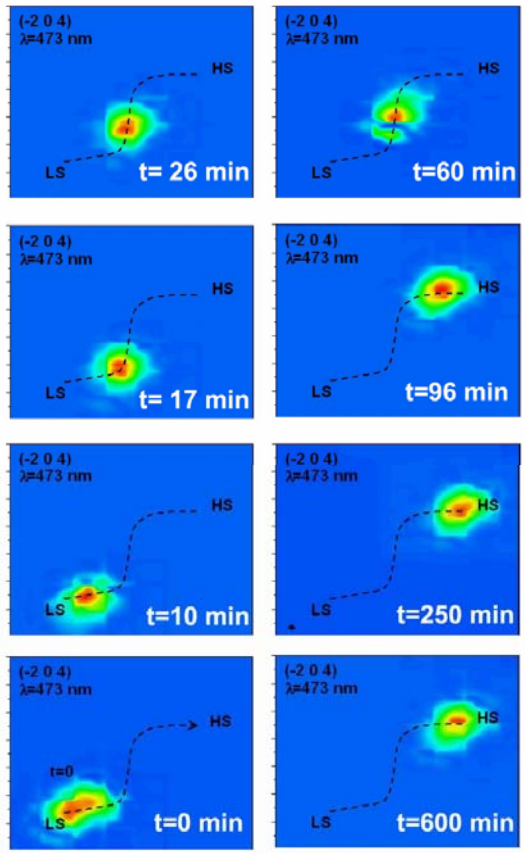


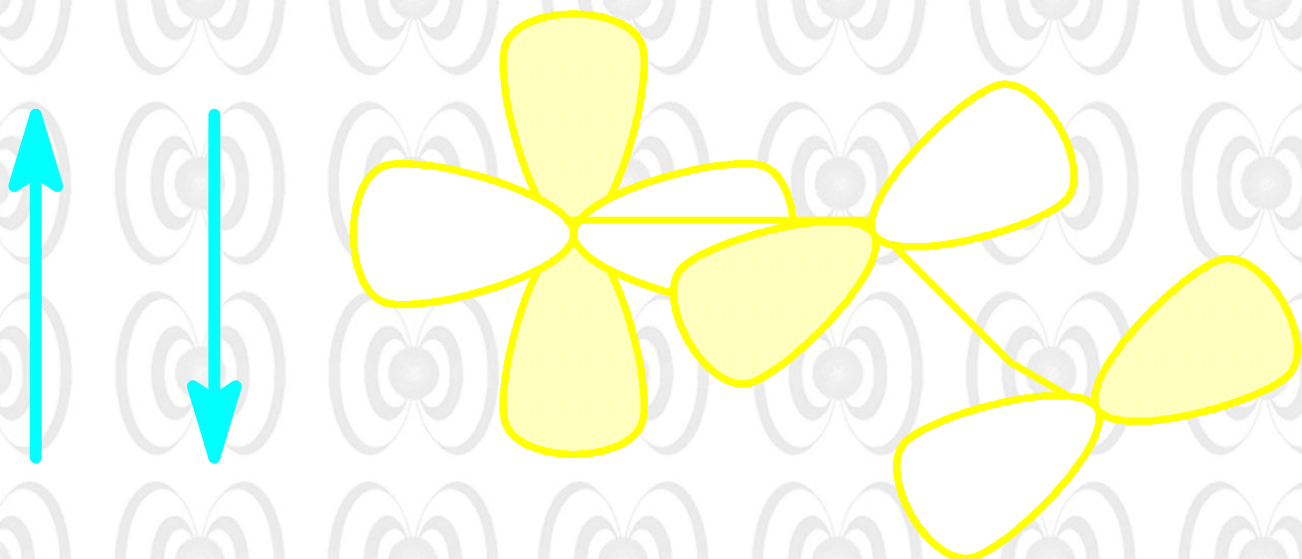
FIG. 5. (Color online) Shift of the $(-2,0,4)$ reflection of $[Fe(ptz)_6](BF_4)_2$ upon photoexcitation at 473 nm, 2 K.

MAGMA Net
NETWORK OF EXCELLENCE

Magnetic interactions

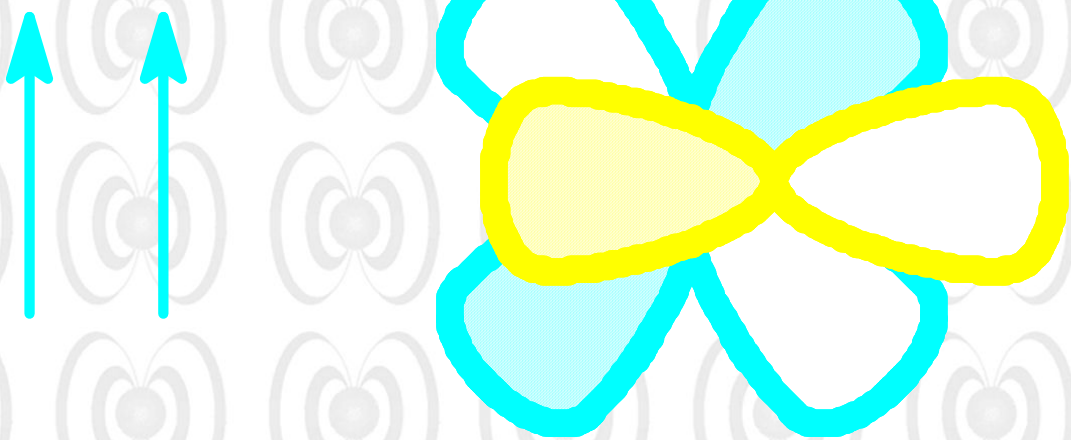
MAGMA Net
NETWORK OF EXCELLENCE

Direct Exchange: AF

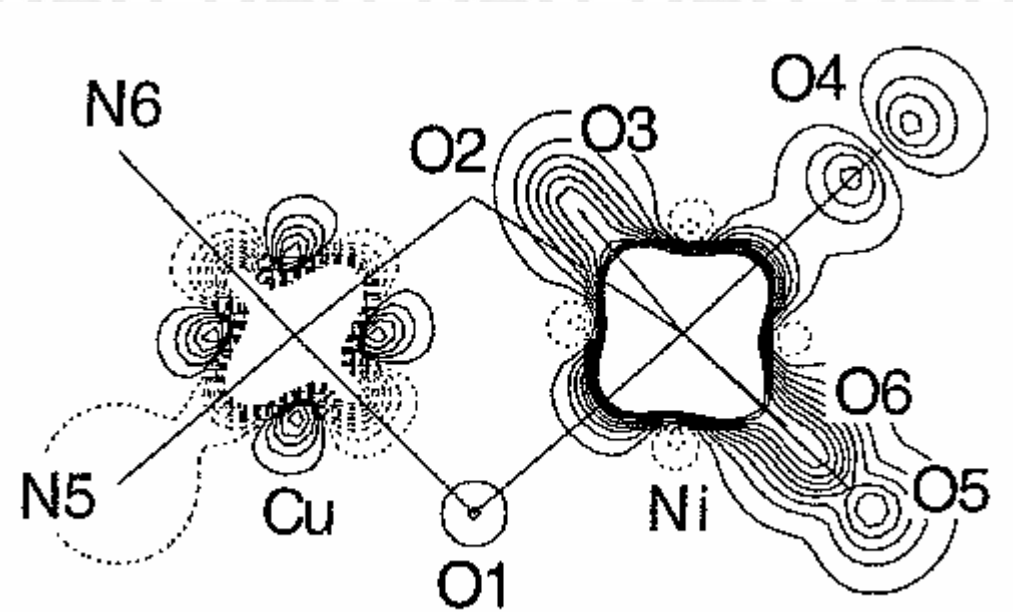


Magnetic orbitals with non-zero overlap :
antiferromagnetic coupling

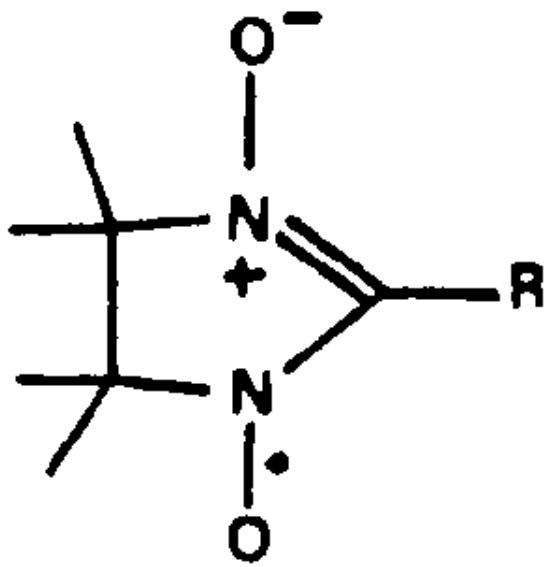
Direct Exchange: F



Orthogonal magnetic orbitals: ferromagnetic coupling (Hund's rule)


N6
O2
O3
O4
O6
N5
Cu
O1
Ni
O5

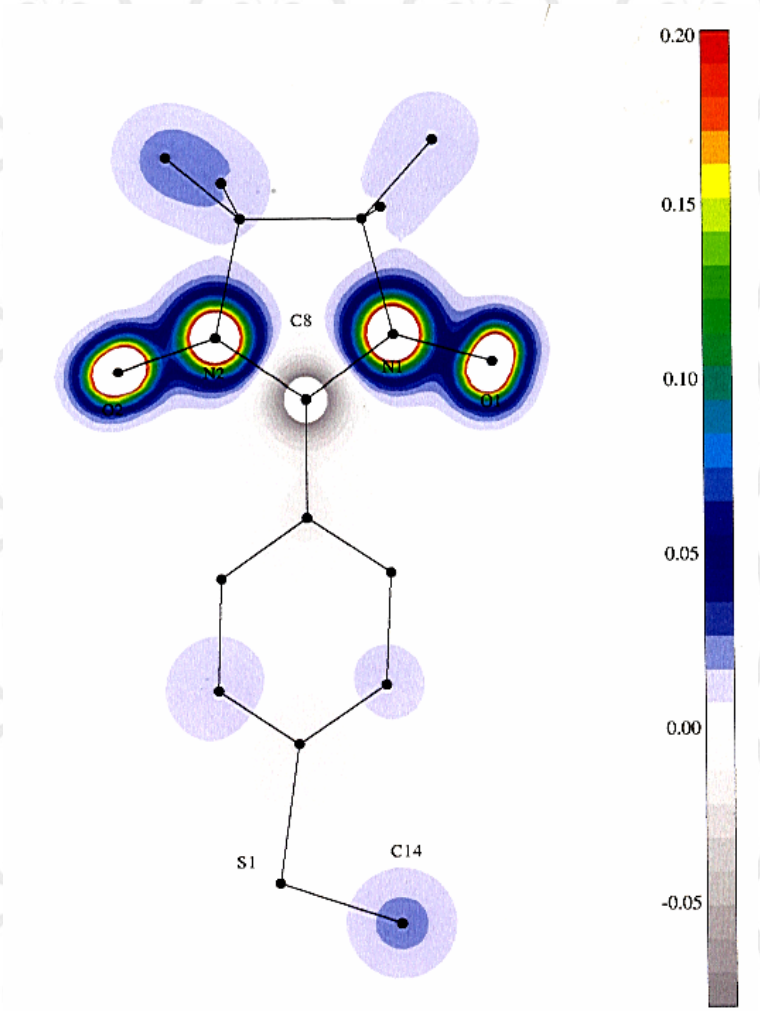
Nitronyl nitroxides

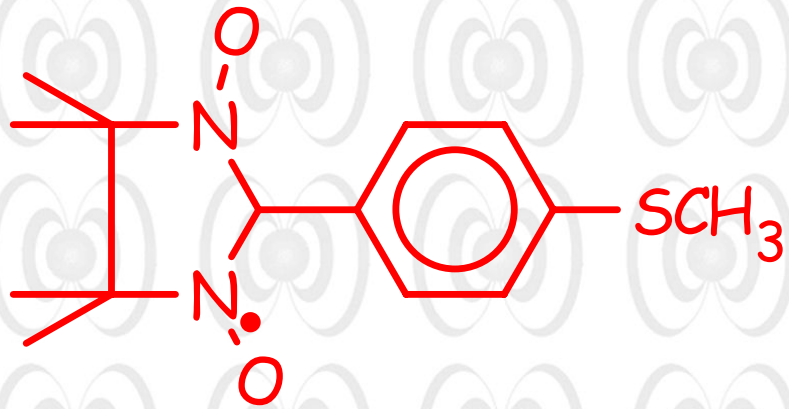


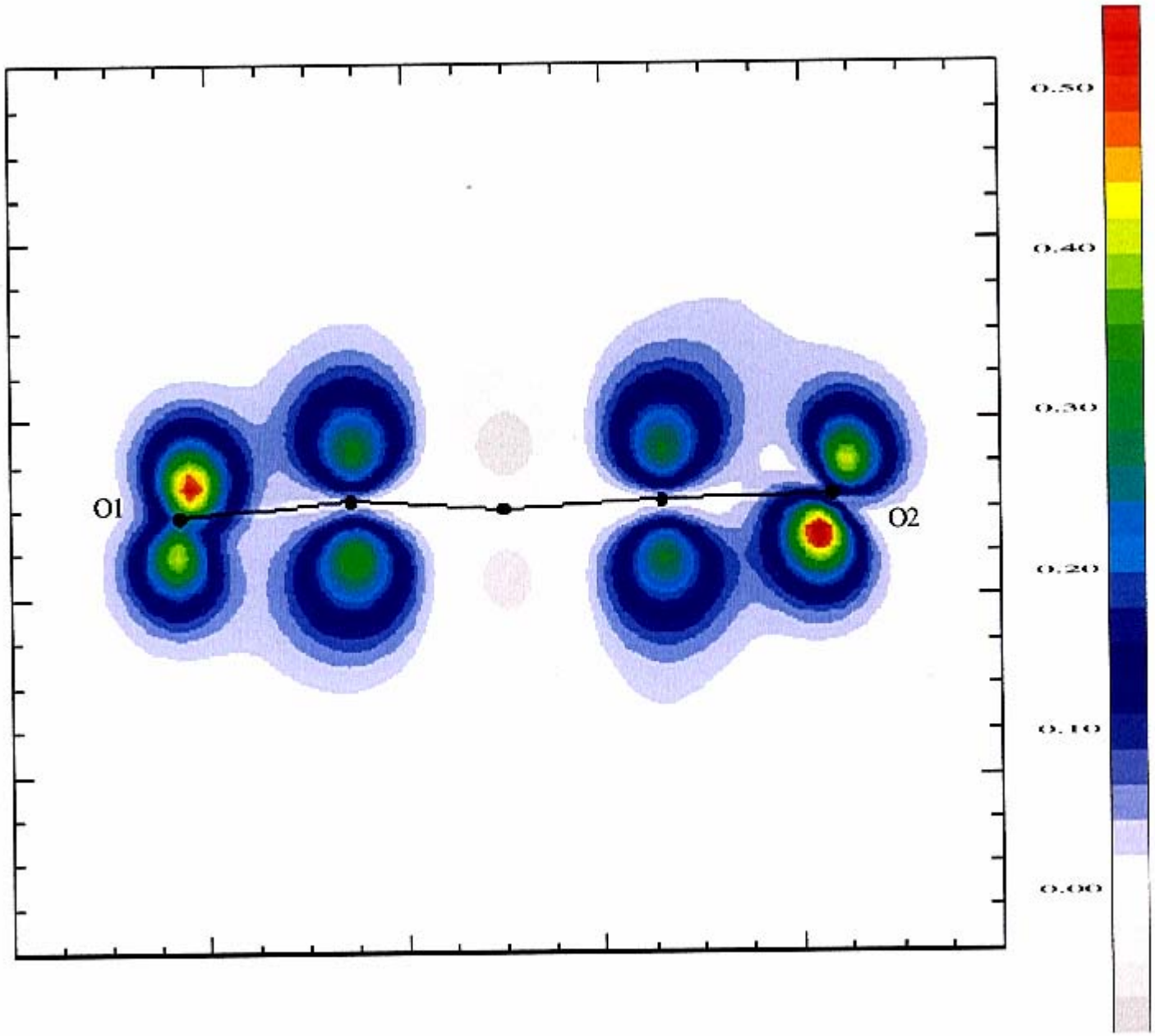
R = Ph, NITPh

R = Me, NITMe

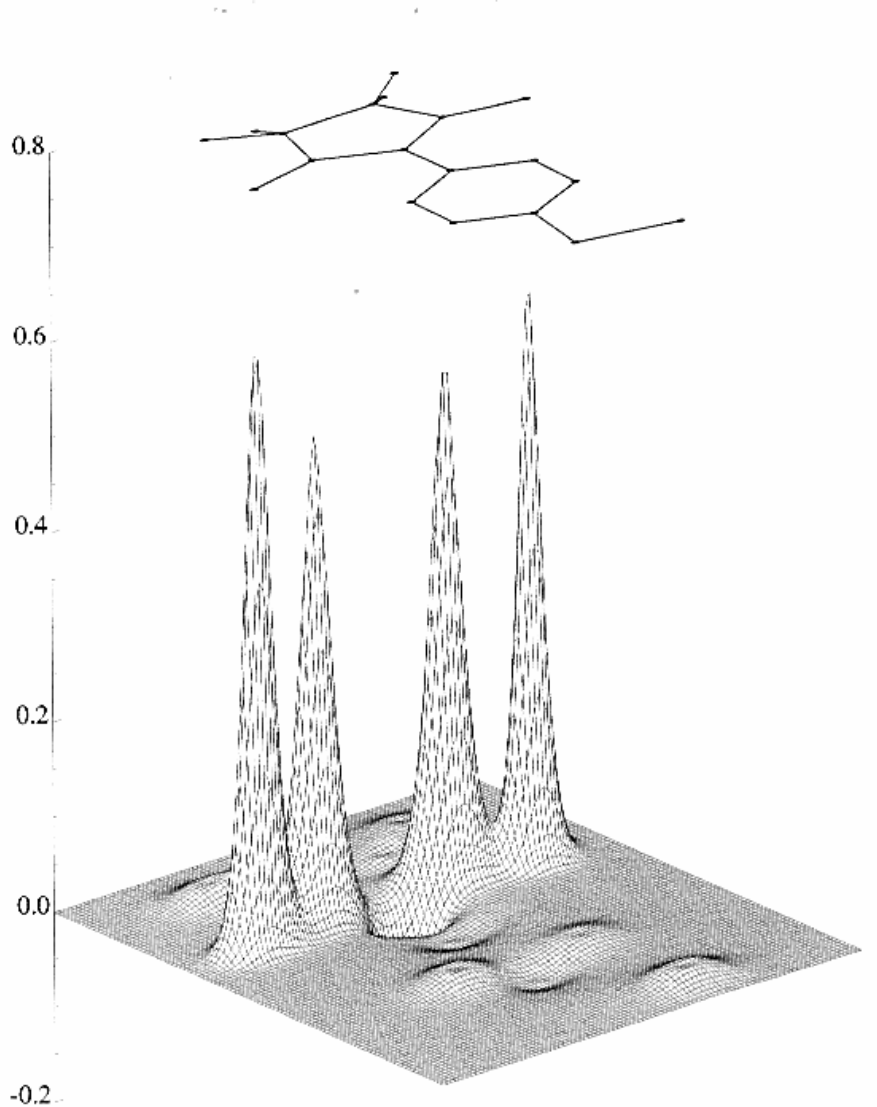
Interazione tra nitronil nitrossidi






O1
O2
0.50
0.40
0.30
0.20
0.10
0.00

MAGMA Net
NETWORK OF EXCE



MAGMA Net
NETWORK OF EXCELLENCE

$Cu(hfac)_2NITMe$: ferro

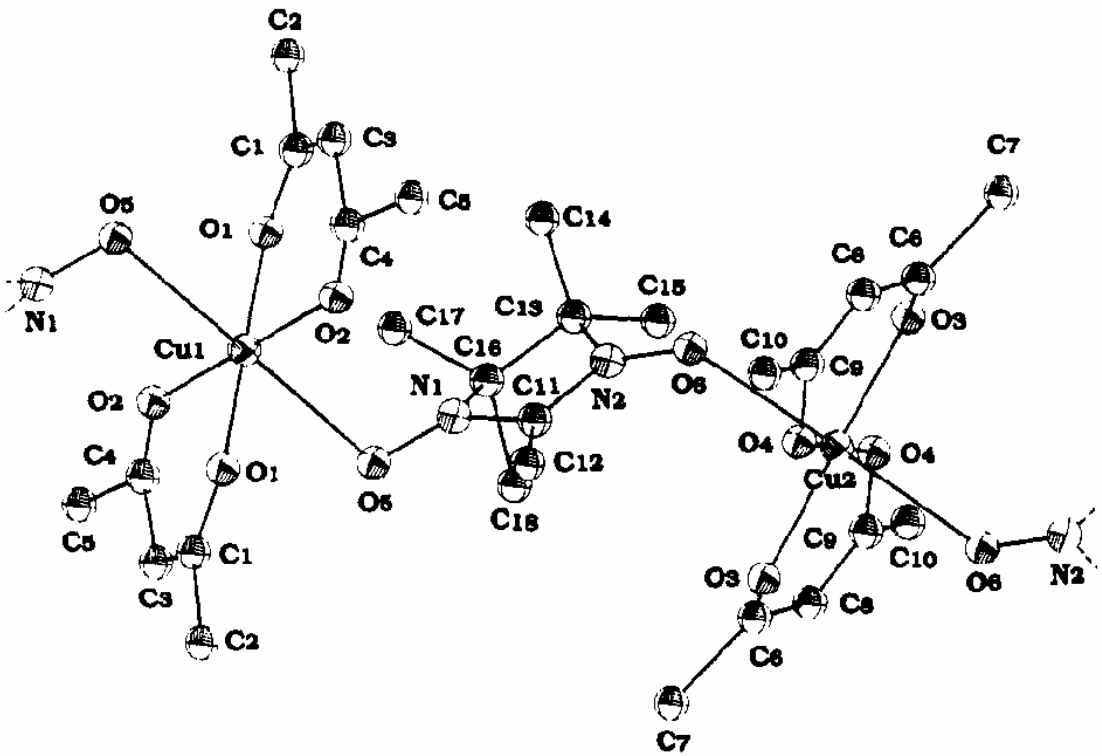
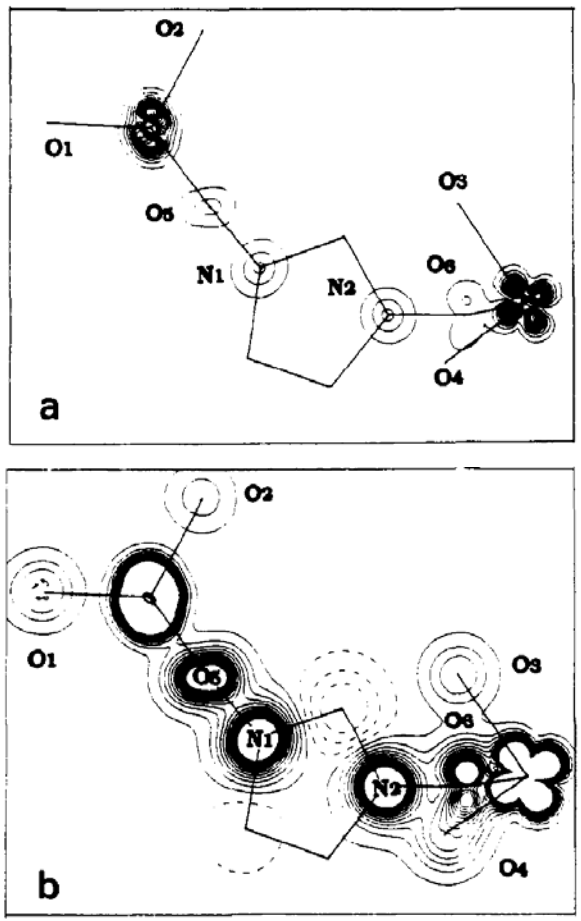


Figure 2. View of the structure of $(Cu(hfac)_2NITMe)_n$ (1) showing the numbering of the atoms. Fluorine and hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 90% probability level.

Spin density map: ferro



CuCl2(NITPh)2: AF

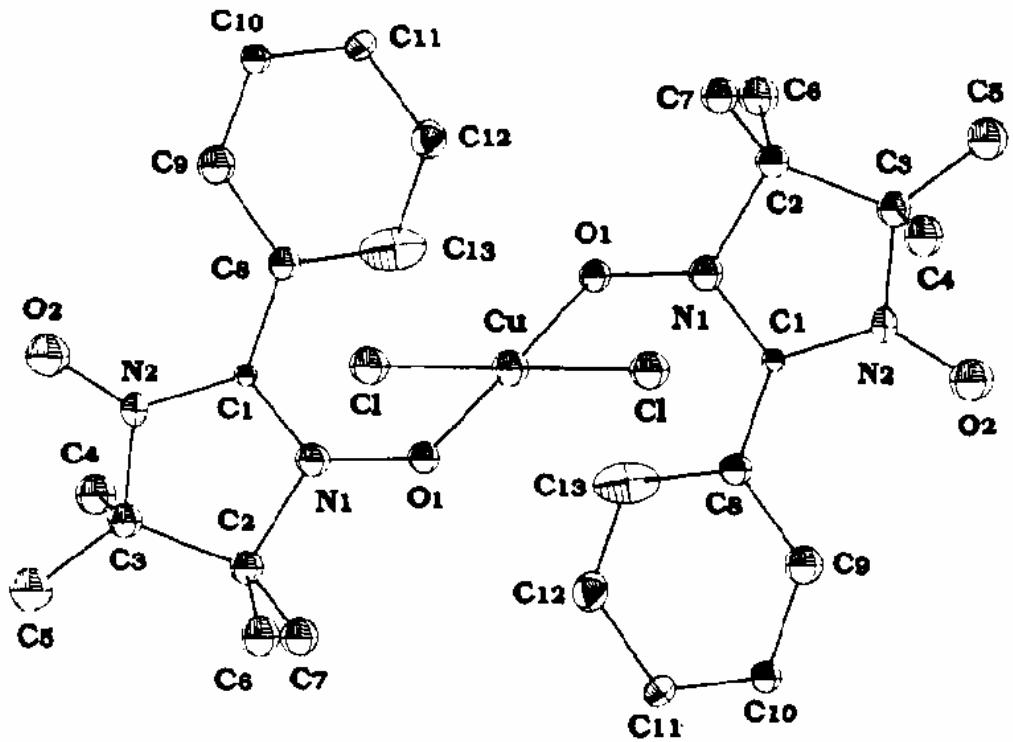
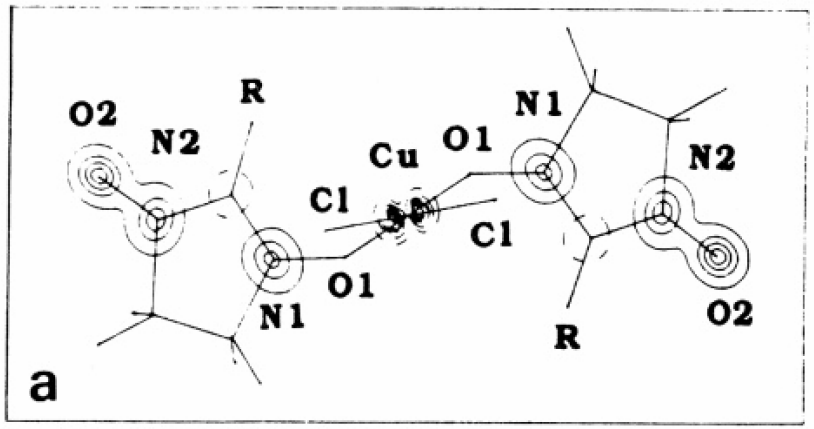
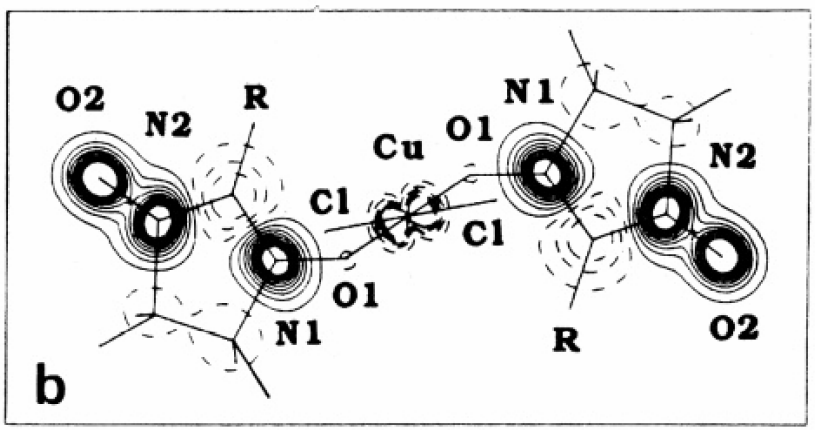


Figure 3. View of the structure of $CuCl_2(NITPh)_2$ (**2**) showing the numbering of the atoms. Hydrogen atoms have been omitted. Thermal ellipsoids are drawn at the 90% probability level.

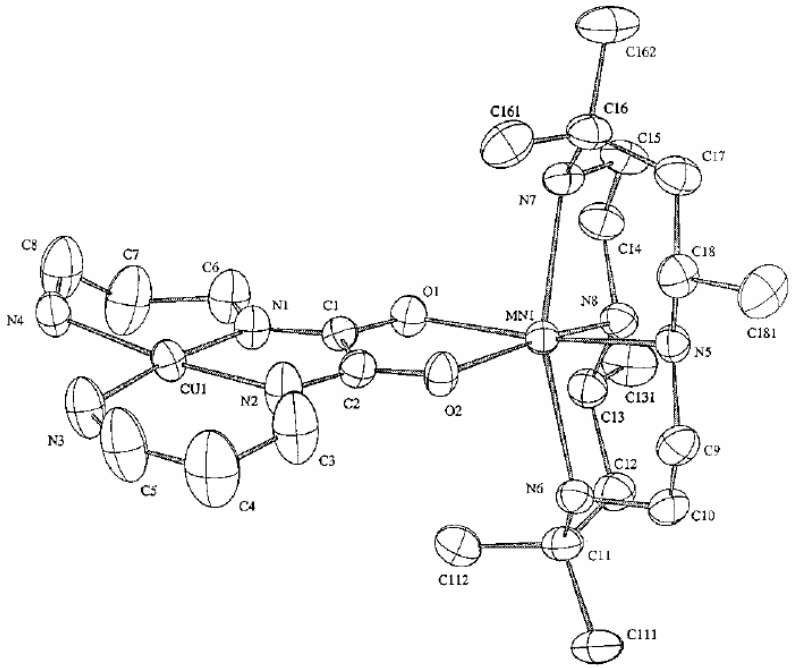
Spin density map: AF

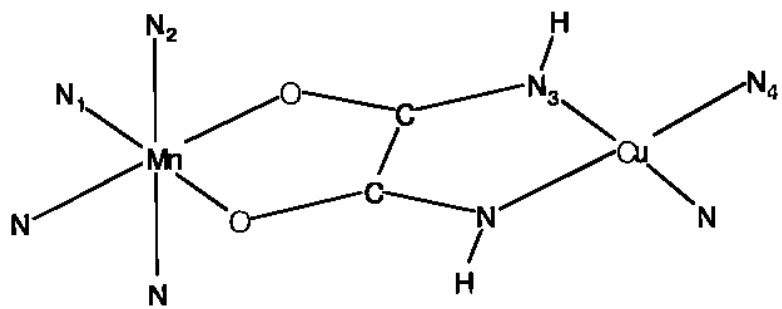




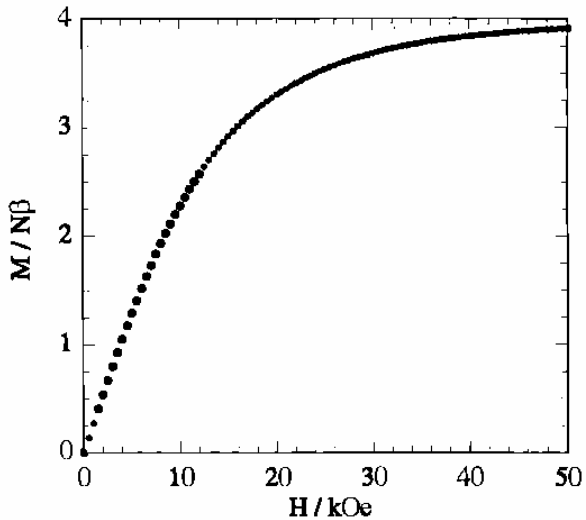
MAGMA Net
NETWORK OF EXCELLENCE

Cu-Mn: AF

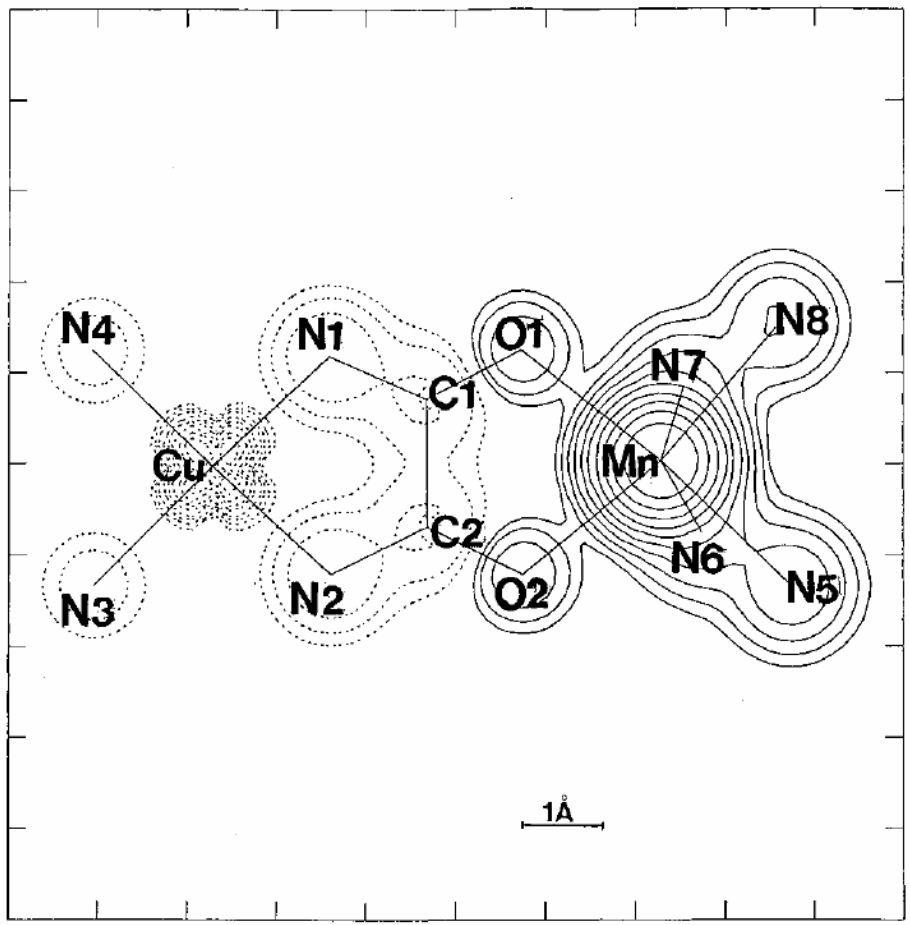




J. Am. Chem. Soc., Vol. 118, No. 47, 1996



Spin density map for Cu-Mn



The mechanism?

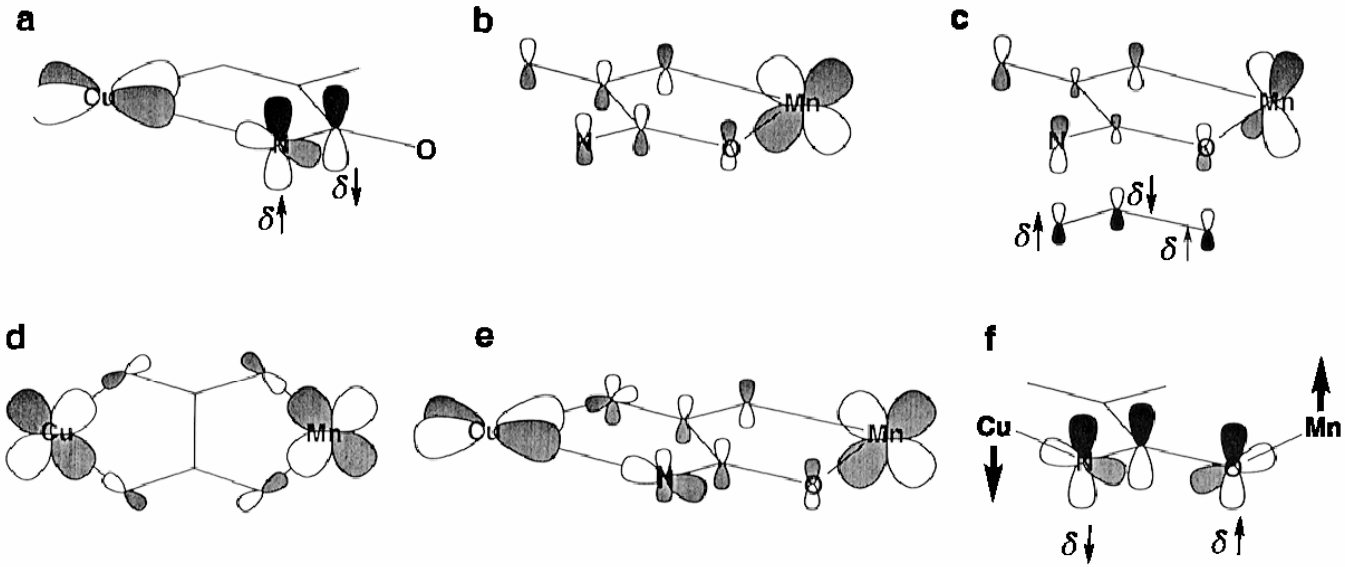


Figure 5. Mechanisms of spin transfer toward the bridges. (a) The donation of α and β spin density from the bridge toward the singly occupied d_{xy} copper orbital leaves an excess of α spin density on the bridge. (b) Interaction with a manganese d_{zx} orbital. The π orbital on the bridge in this case has a very small coefficient on the carbon atoms, and thus an underlying π orbital will be polarized. (c) All the π orbitals have roughly the same weight, so that there will be no resulting spin polarization. (d) Spin delocalization from Cu(II) and Mn(II) through the σ-bonds. (e) Spin delocalization from the oxamido π orbitals to the Mn(II) empty d orbitals. (f) Spin polarization of the bridge (see text).

DFT Results

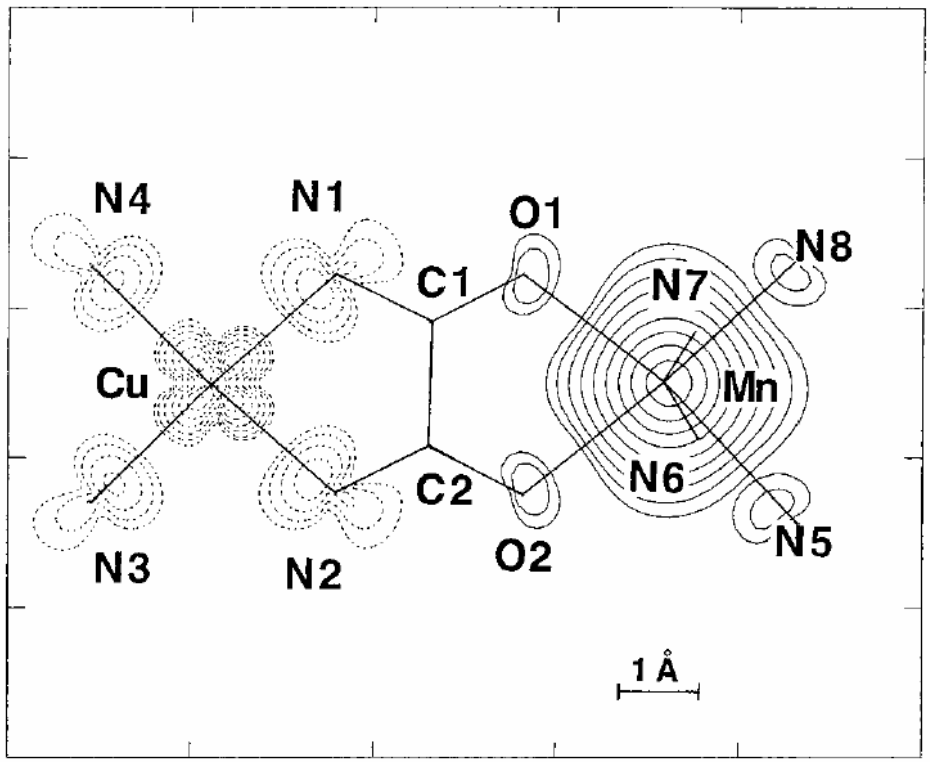
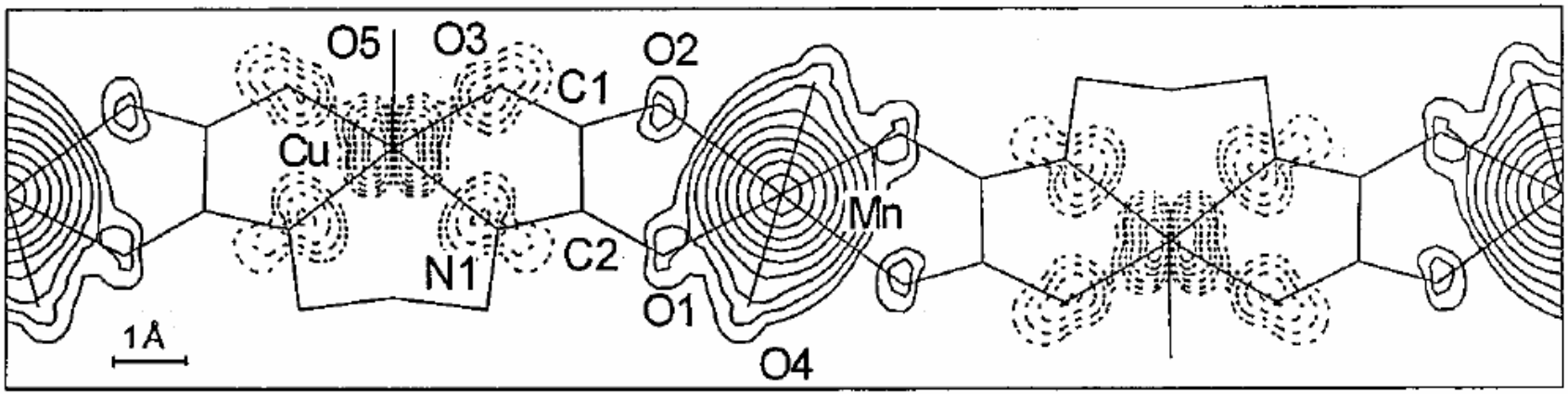


Figure 7. Calculated spin-density map for the broken symmetry (BS) state of the model compound **4** in projection along the perpendicular to the oxamido mean plane. The contours are the same as in Figure 3, so that those two figures may be compared.

MAGMA Net
NETWORK OF EXCELLENCE

Cu-Mn chains



DFT calculations agree with experimental results

Gd-NITR: ferro

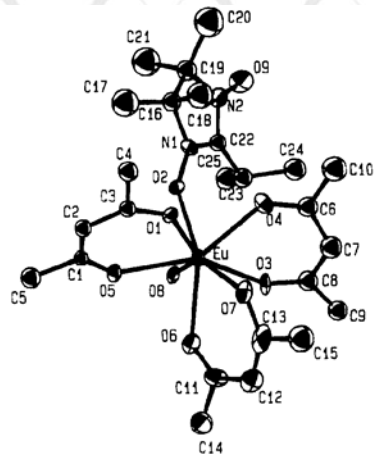


Figure 1. ORTEP drawing of the asymmetric unit of $Eu(hfac)_3(NITiPr)(H_2O)$.

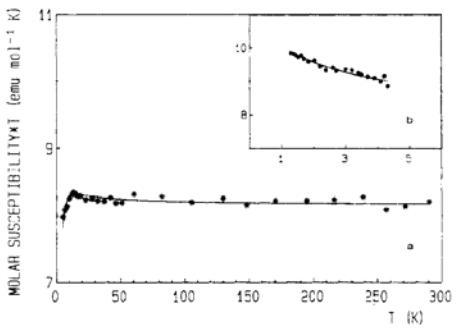
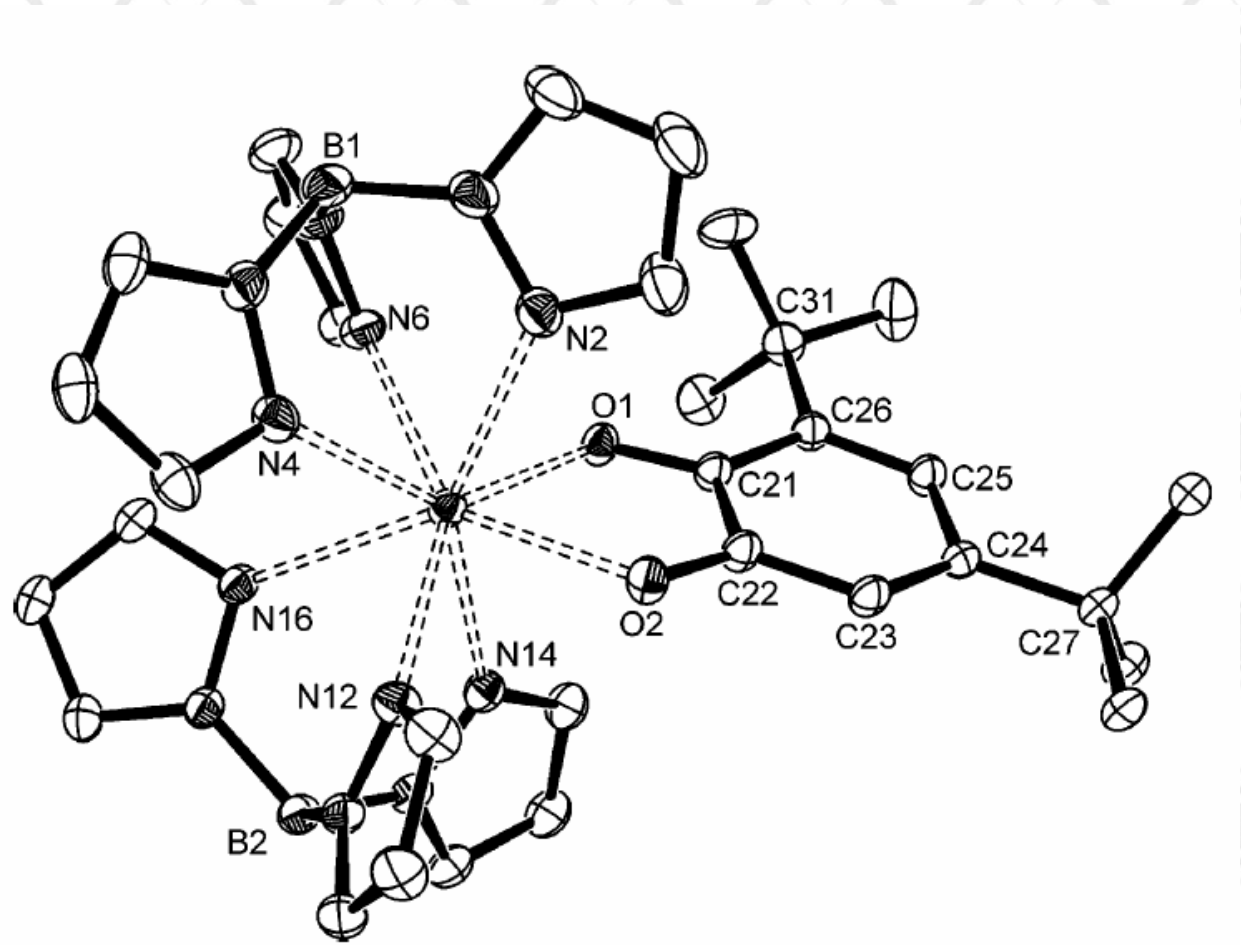


Figure 2. Temperature dependence of the χT product of $Gd(hfac)_3(NITiPr)(H_2O)$: (a) high-temperature data, the curve representing the best fit obtained for $J = -0.83$ cm^{-1} and $g = 1.99$. (b) low-temperature data, best fit parameters of $J = -0.65$ cm^{-1} and $g = 2.00$.

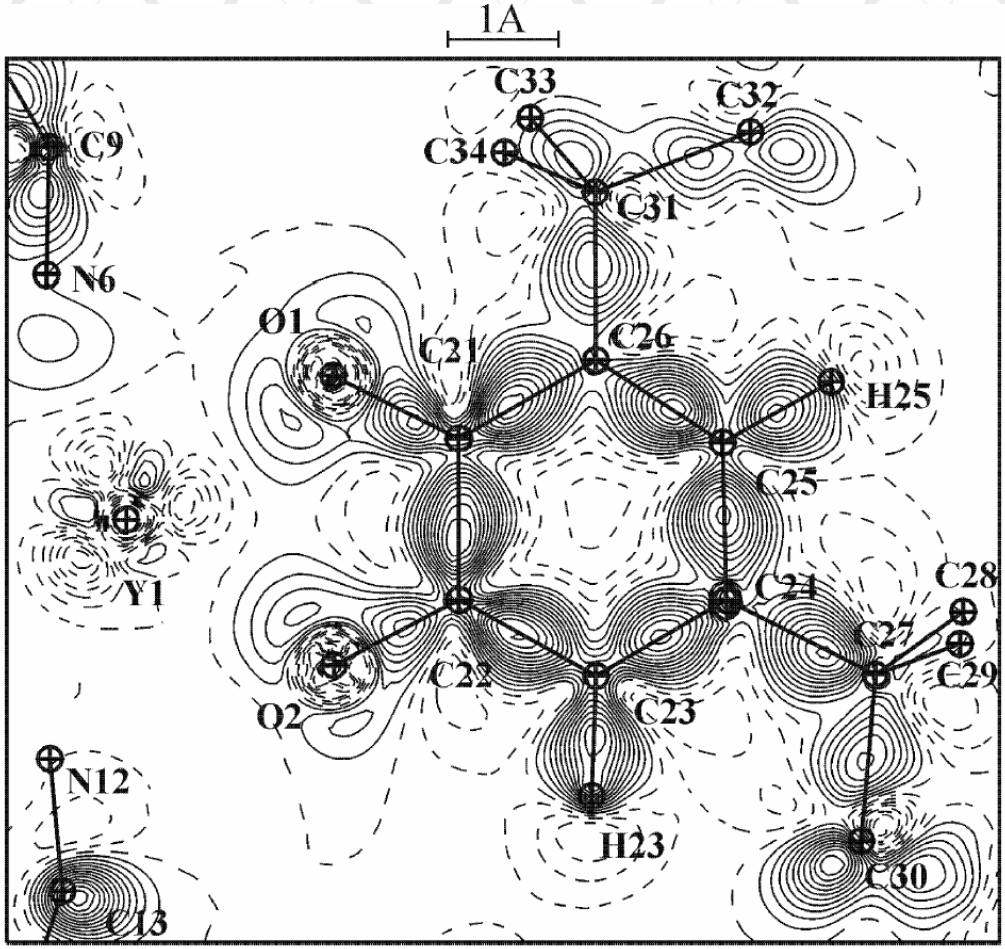
Benelli et al Inorg Chem 1990

MAGMA Net
NETWORK OF EXCELLENCE

Gd-SQ: AF

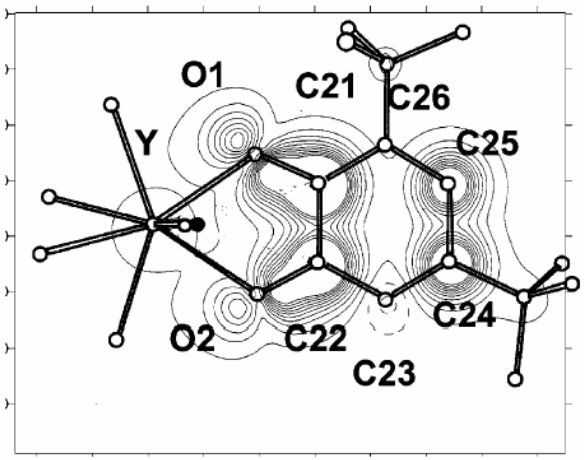


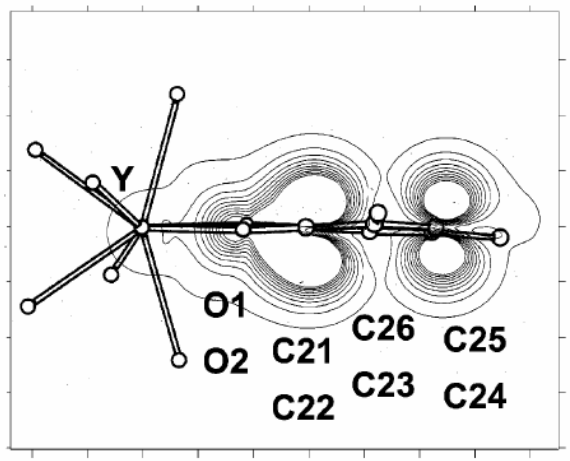
Static deformation map of Y-SQ



Claiser et al JPhysChemB 2005

Spin density map of Y-SQ

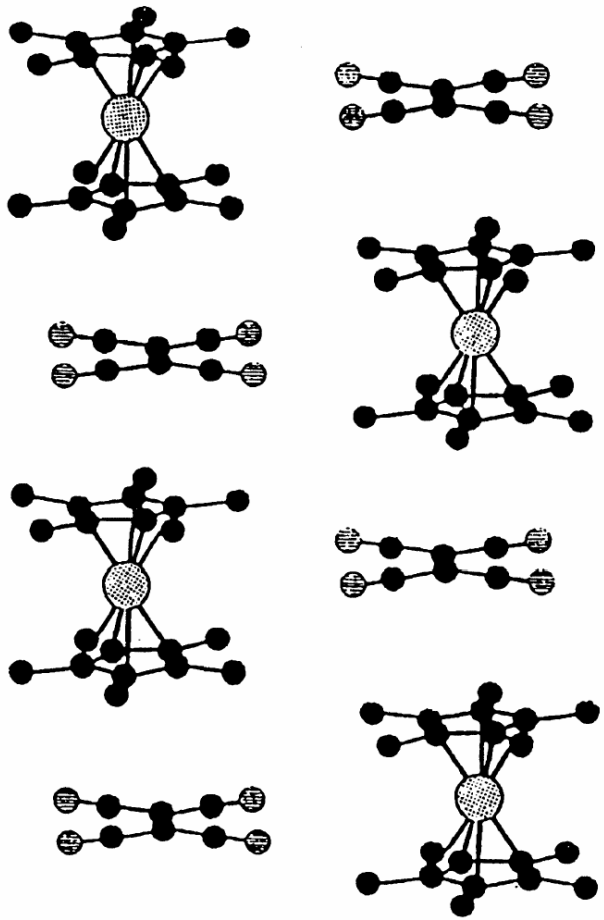




A molecular ferromagnet

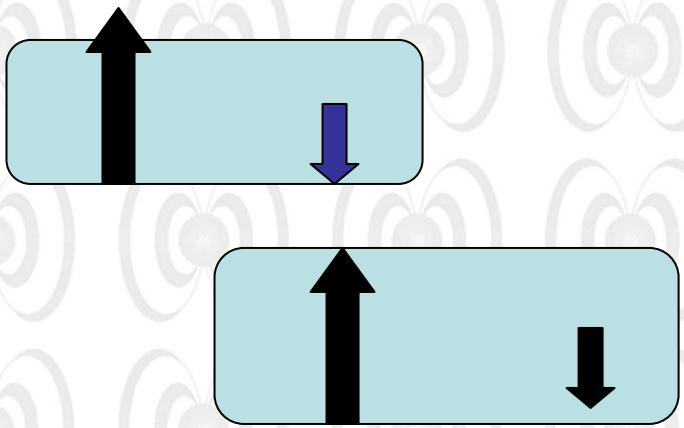
[Fe(cp)2]+

TCNE-



MAGMA Net
NETWORK OF EXCELLENCE

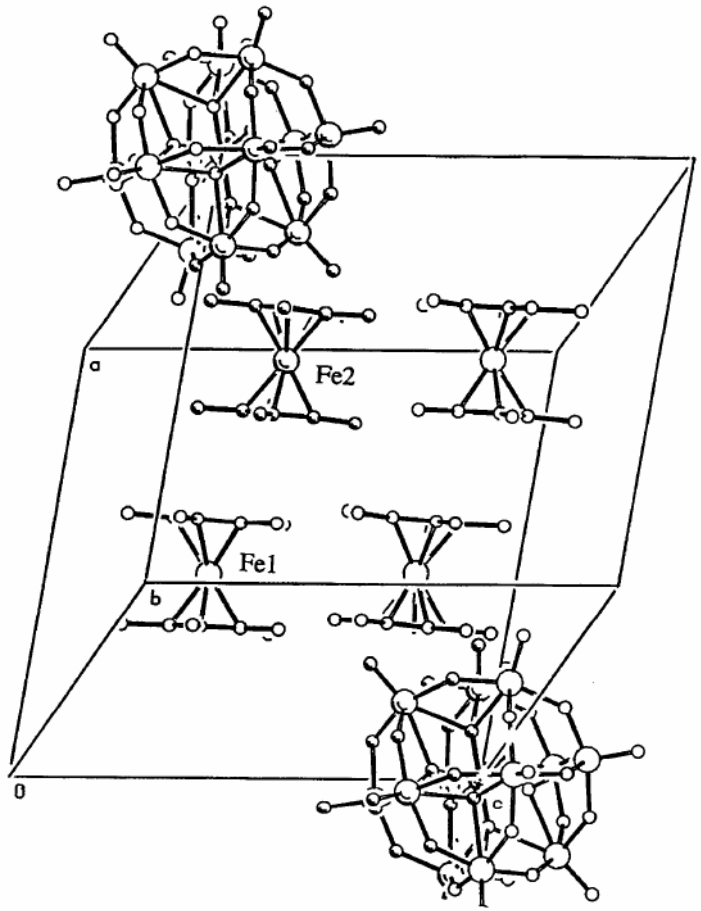
Scheme of the interaction



The AF coupling between the positive spin density on one molecule and the negative one on the other gives rise to ferromagnetic coupling

MAGMA Net
NETWORK OF EXCELLENCE

$[Fe(cp)_2]$ An



MAGMA Net
NETWORK OF EXCELLENCE

Magnetization density

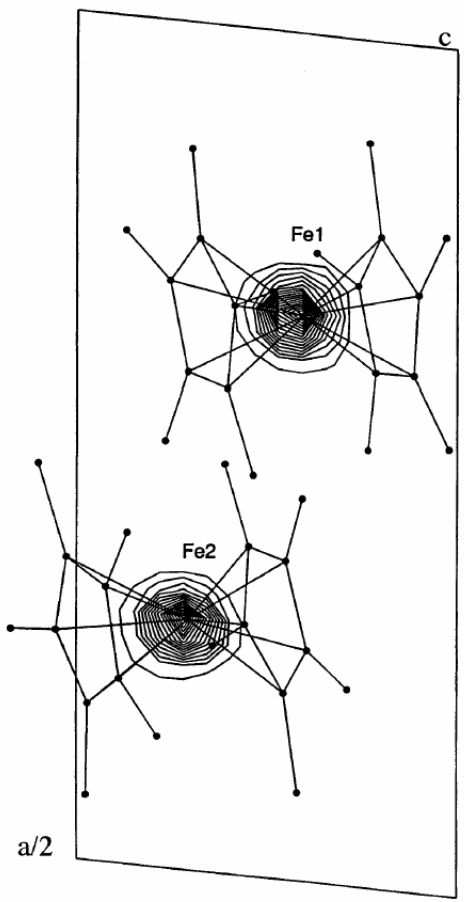


Table 1
Atomic spin populations (moments) in $[FeCp^*_2]^{\bullet+}$

Atom	m_i
Fe1 (spin + orbit)	1.932(18)
Fe2 (spin + orbit)	2.024(18)
Ccp	−0.005(1)
Cme	0.008(1)
Σm_i	8.03(8)
Magnetization	8.11(5)

Spin density in TCNE-

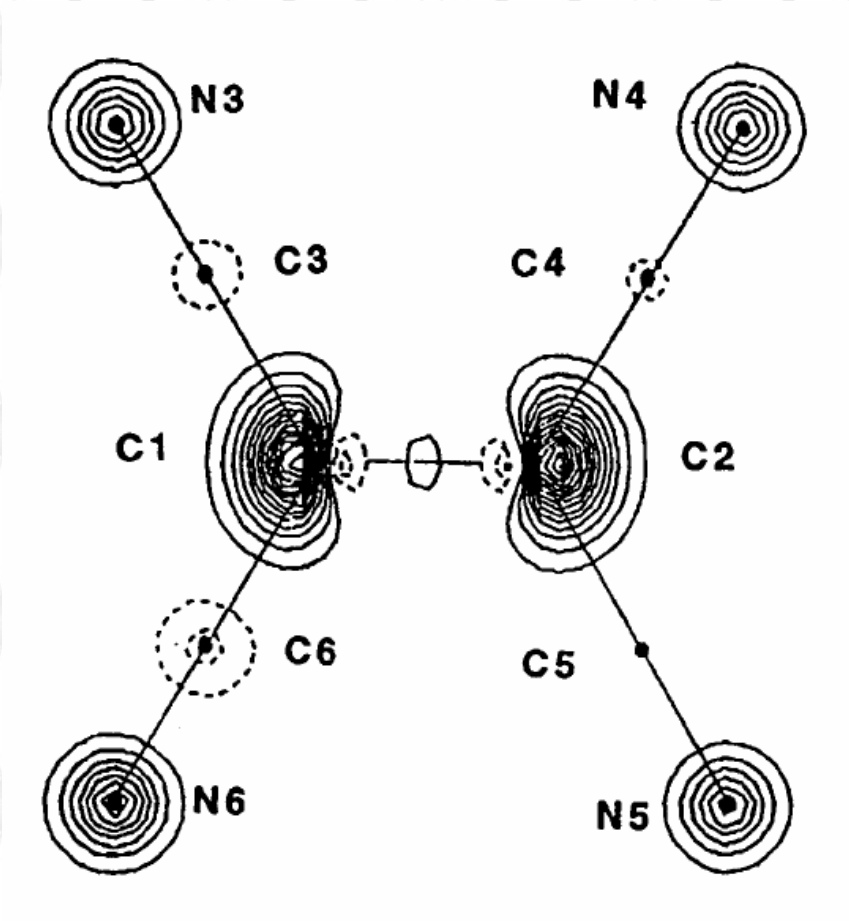
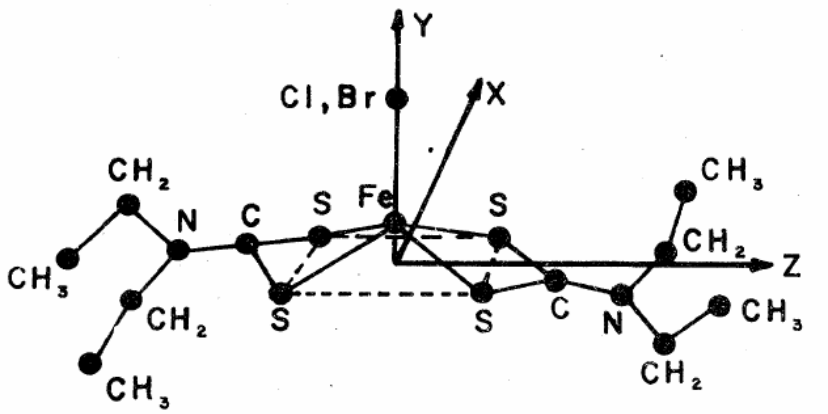


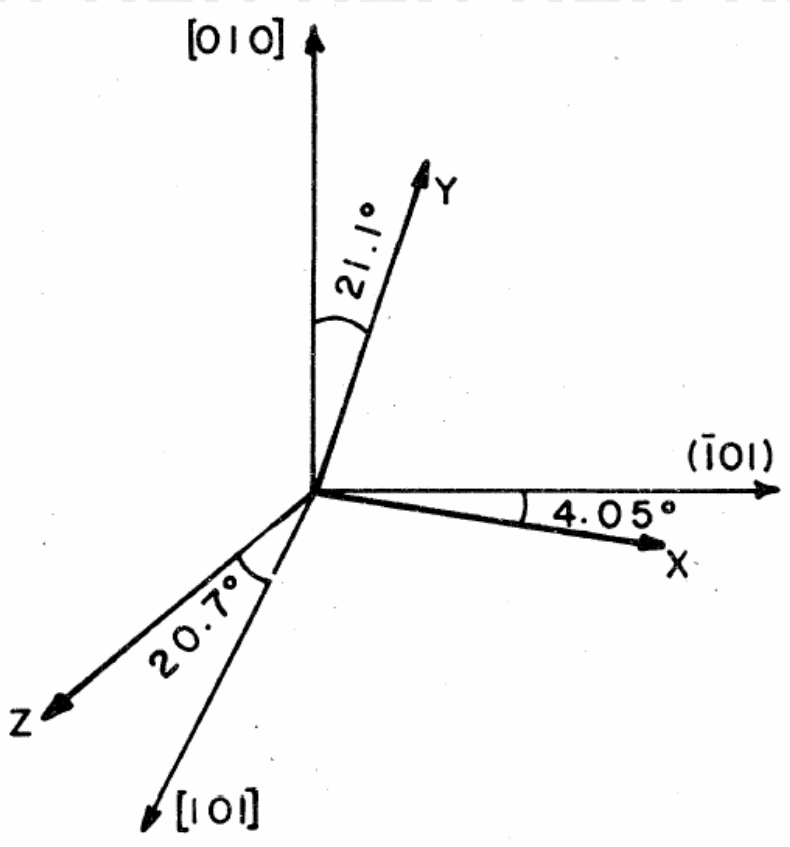
Table 2
Atomic spin populations in $[TCNE]^{\bullet -}$

Atom	Spin population
C1	0.33
C2	0.33
C3	−0.05
C4	−0.04
C5	−0.03
C6	−0.08
N3	0.12
N4	0.12
N5	0.13
N6	0.16

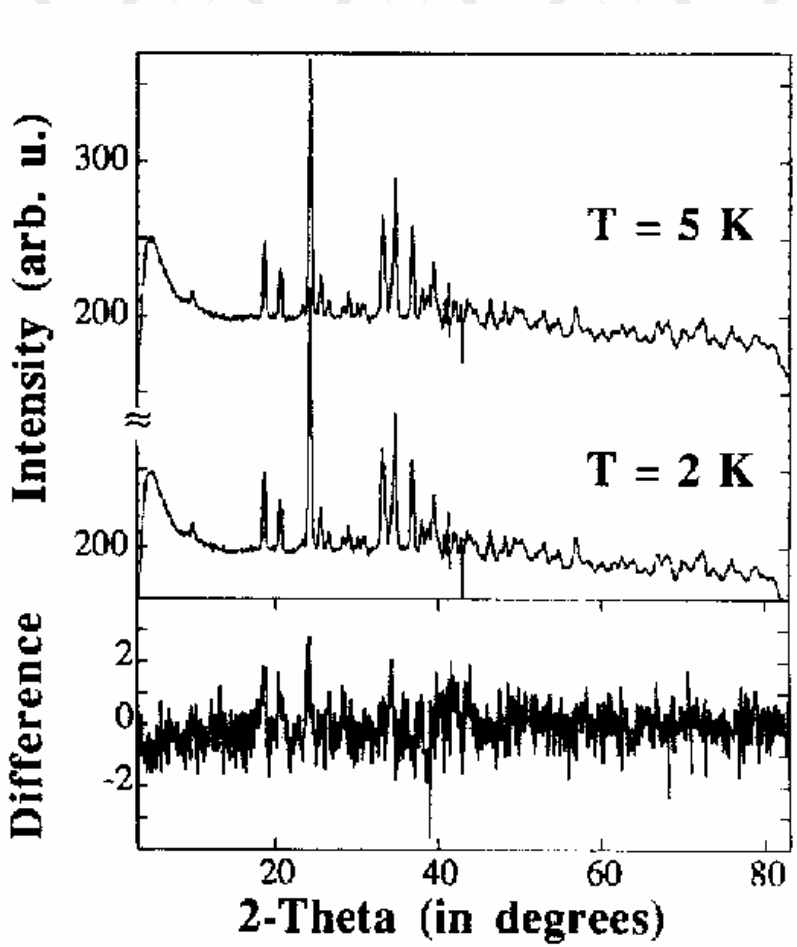
MAGMA Net
NETWORK OF EXCELLENCE

[Fe(dtc)2]Cl



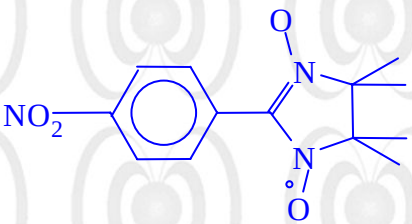


Neutron diffraction of powders

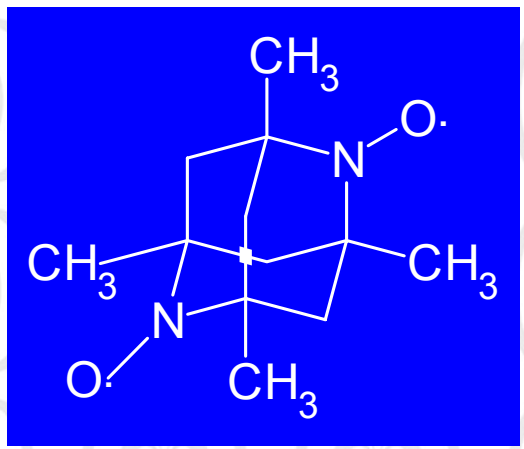


Non-collinear ferromagnet

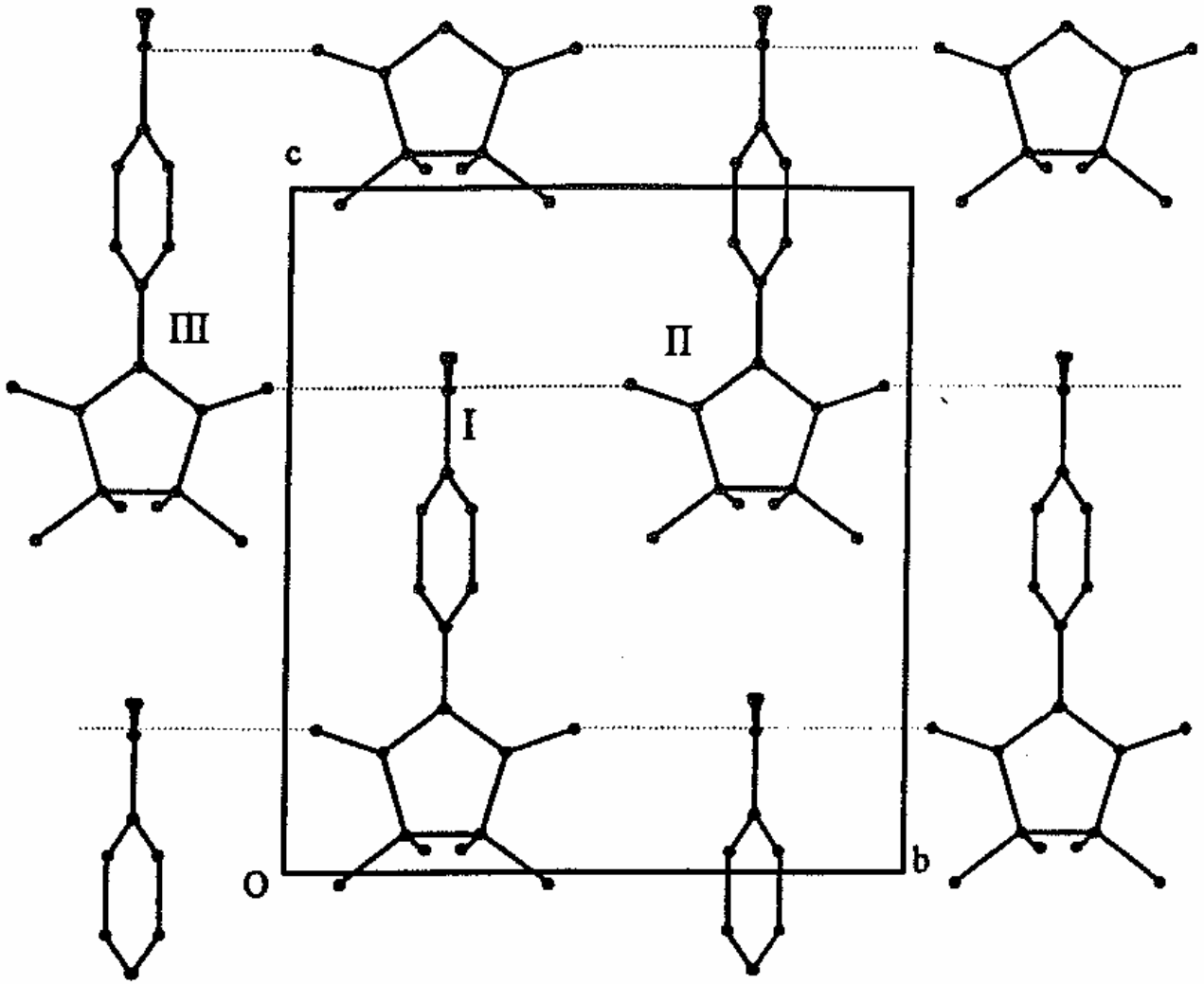
Nitroxides

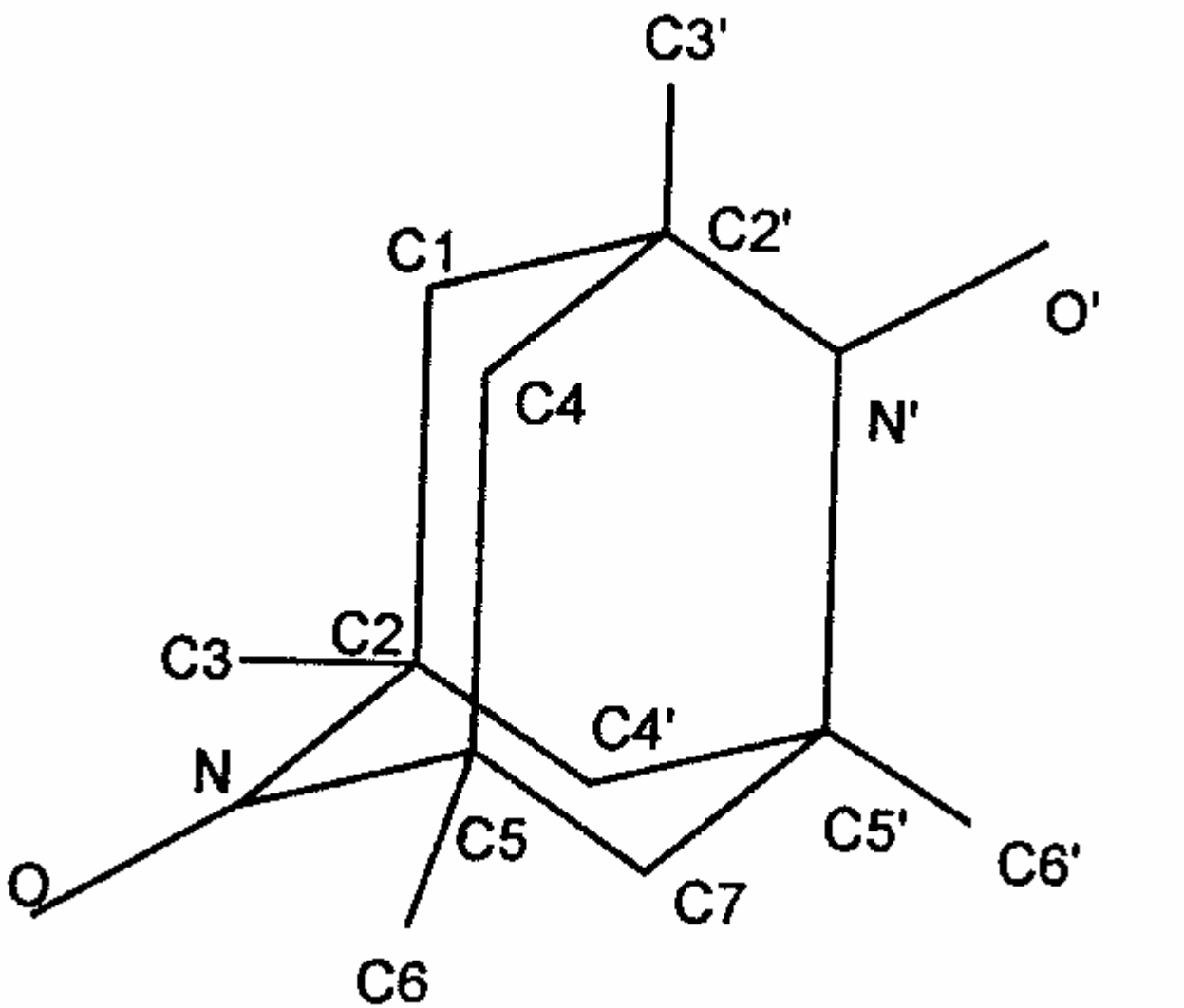


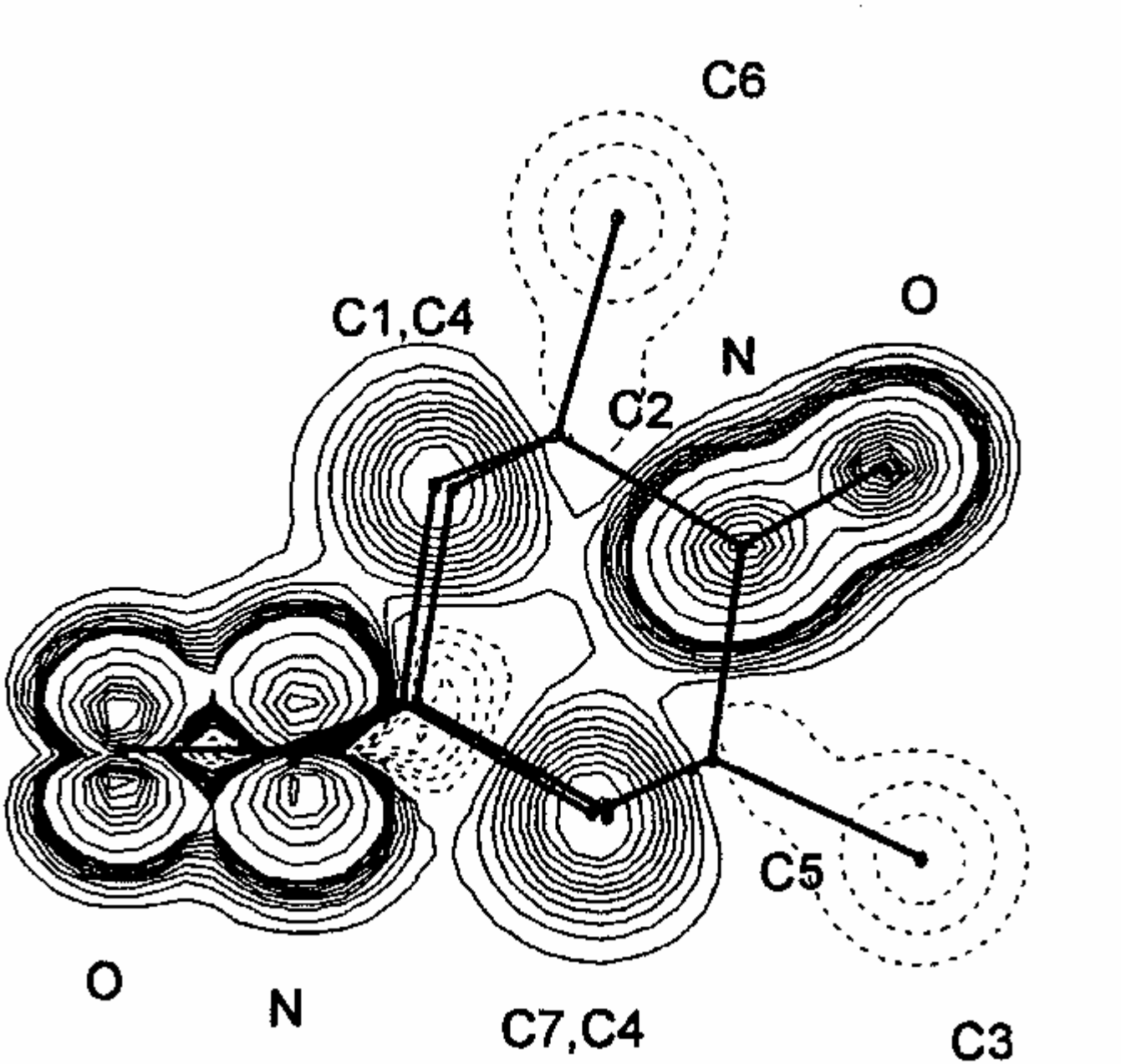
$T_c = 0.6$ K



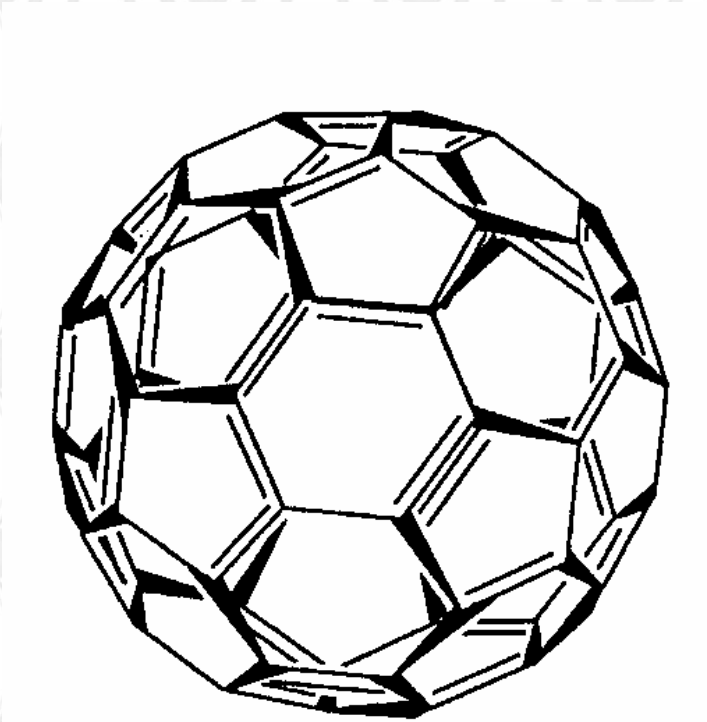
$T_C = 1.5$ K


c
III
II
I
O
b


C3'
C1
C2'
O'
C4
N'
C3
C2
C4'
N
C5
C5'
C6'
O
C7
C6


C6
C1,C4
O
N
C2
C5
O
N
C7,C4
C3

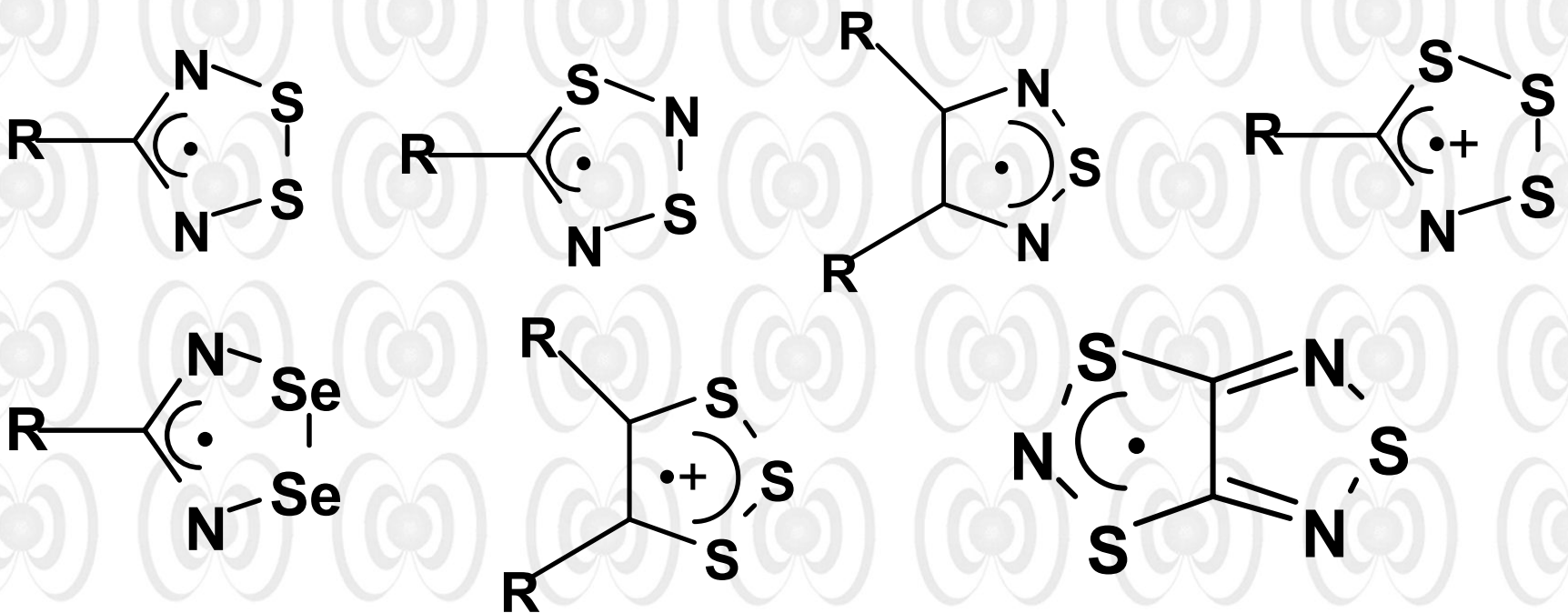
Fullerene



T_C= 16 K

Alternatives for increasing T_c

To use atoms with more diffuse orbitals, such as S or Se



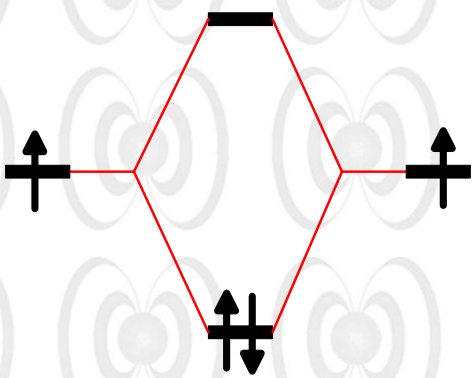
Strong tendency to dimerization

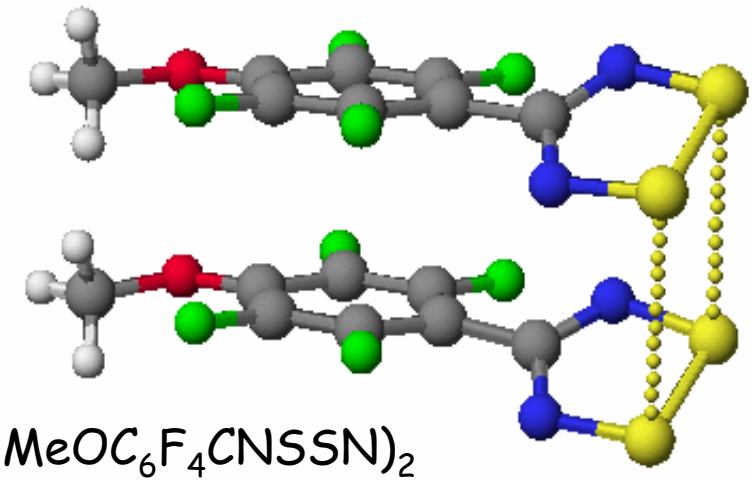
e.g., dithiadiazolyls

Most exist as dimers in the solid state.

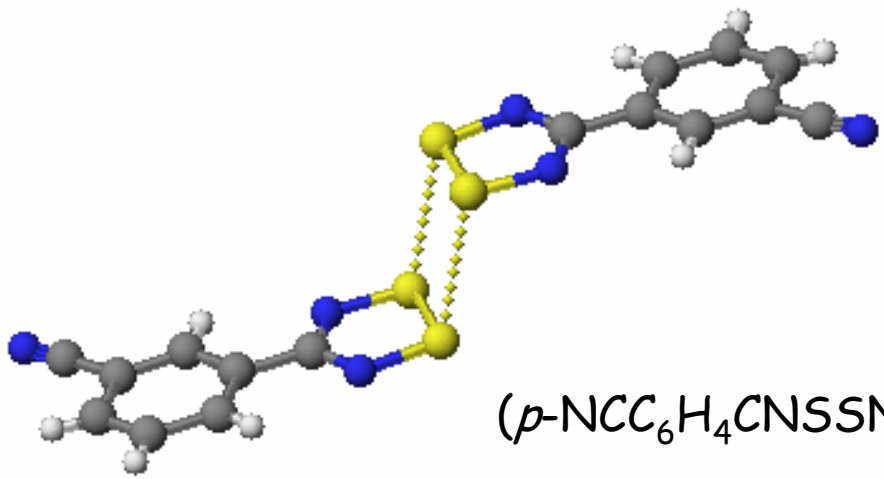
S…S separation ~ 3.0Å

Association via a π*-π* interaction



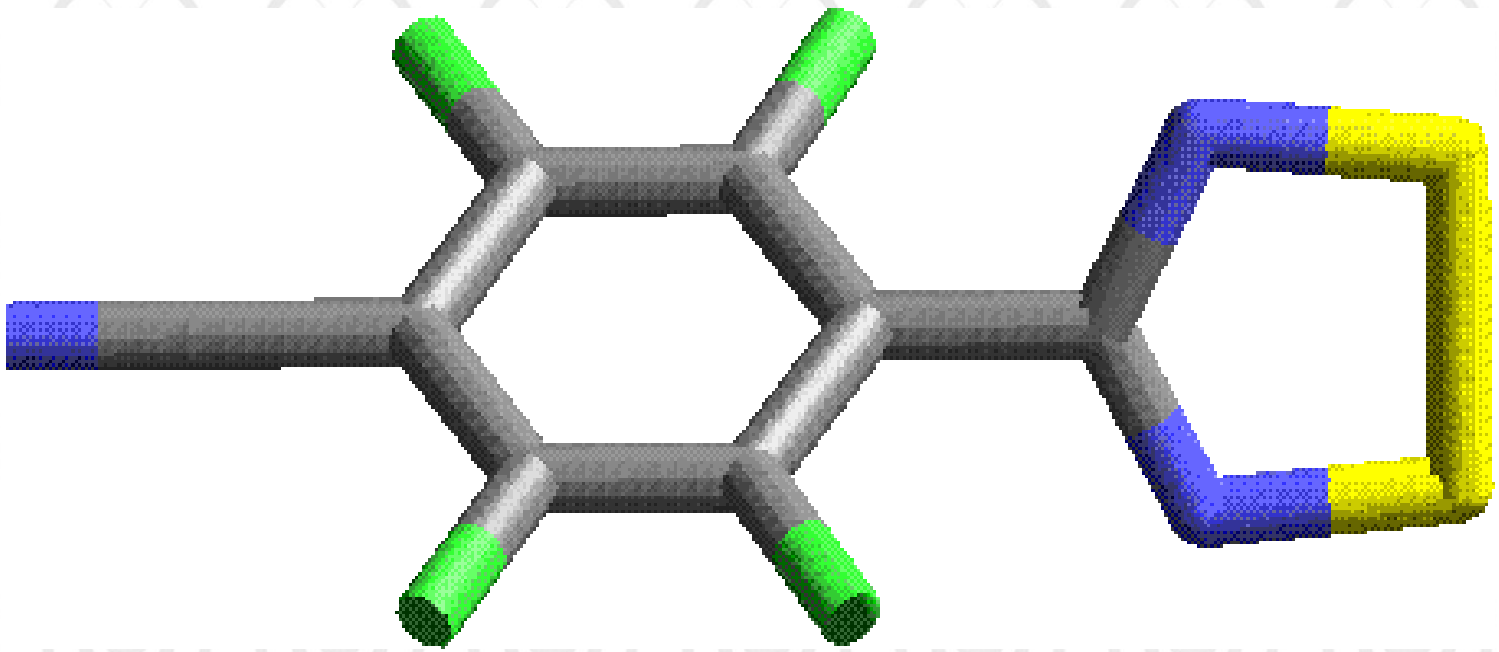


(*p*-$MeOC_6F_4CNSSN)_2$



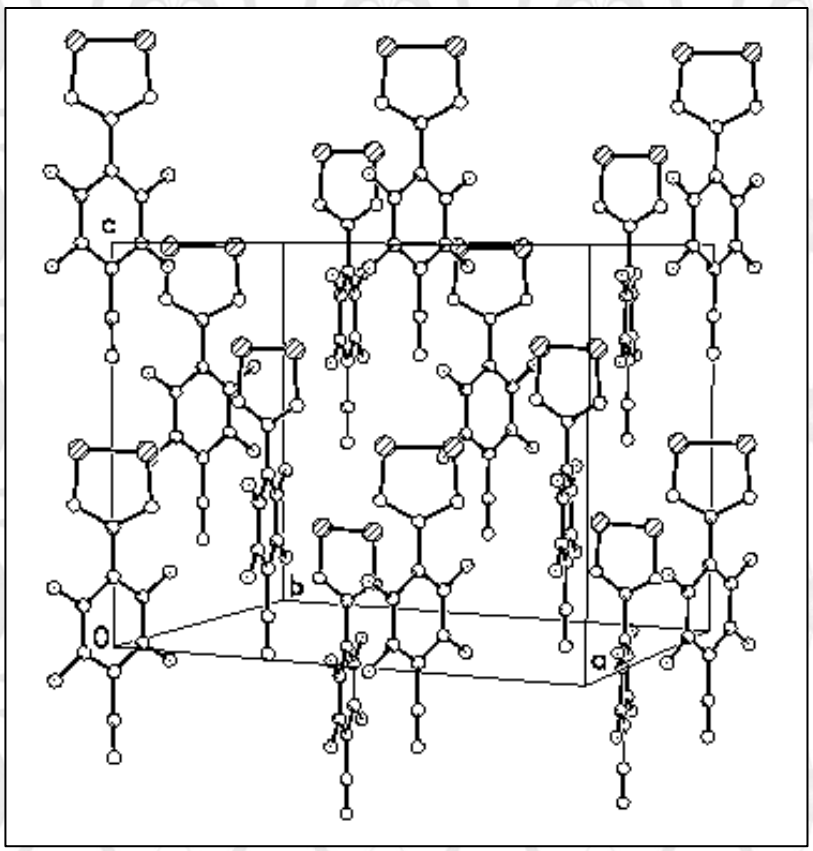
(*p*-$NCC_6H_4CNSSN)_2$

p-NC-C_6F_4-CNSSN$^{\cdot}$: a monomeric S-based radical



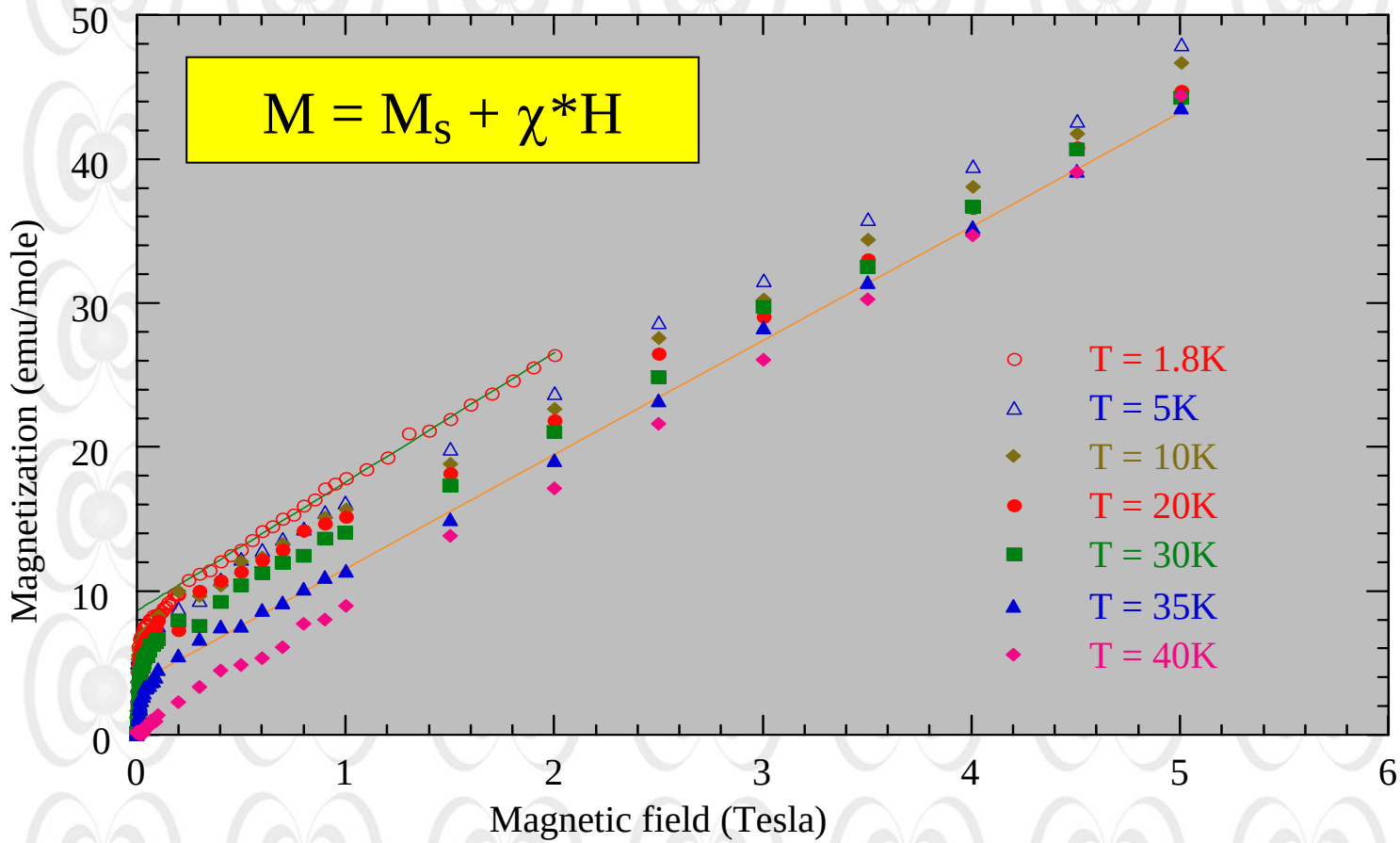
Crystal structure of the β-phase of p-CN·C$_6$F$_4$·CNSSN·

A.J. Banister, N. Bricklebank, I. Lavender, J.M. Rawson, C.I. Gregory, B.K. Tanner, W. Clegg, M.R.J. Elsegood and F. Palacio, *Angew. Chem. Int. Ed. Engl.*, **35**, 2533-5 (1996)



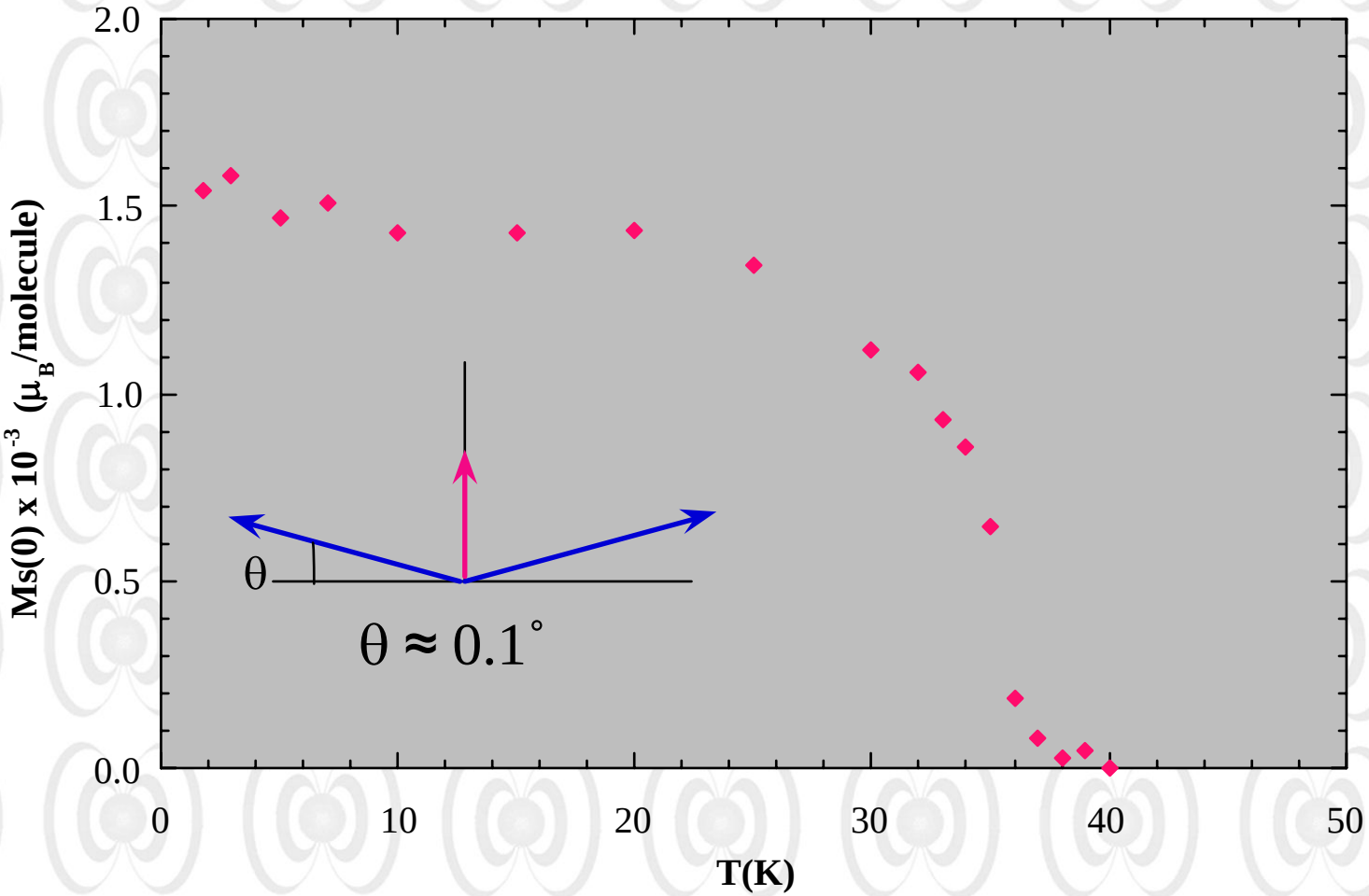
- *Fdd2* space group
- Eight molecules per unit cell
- Non centrosymmetric

Magnetization isotherms

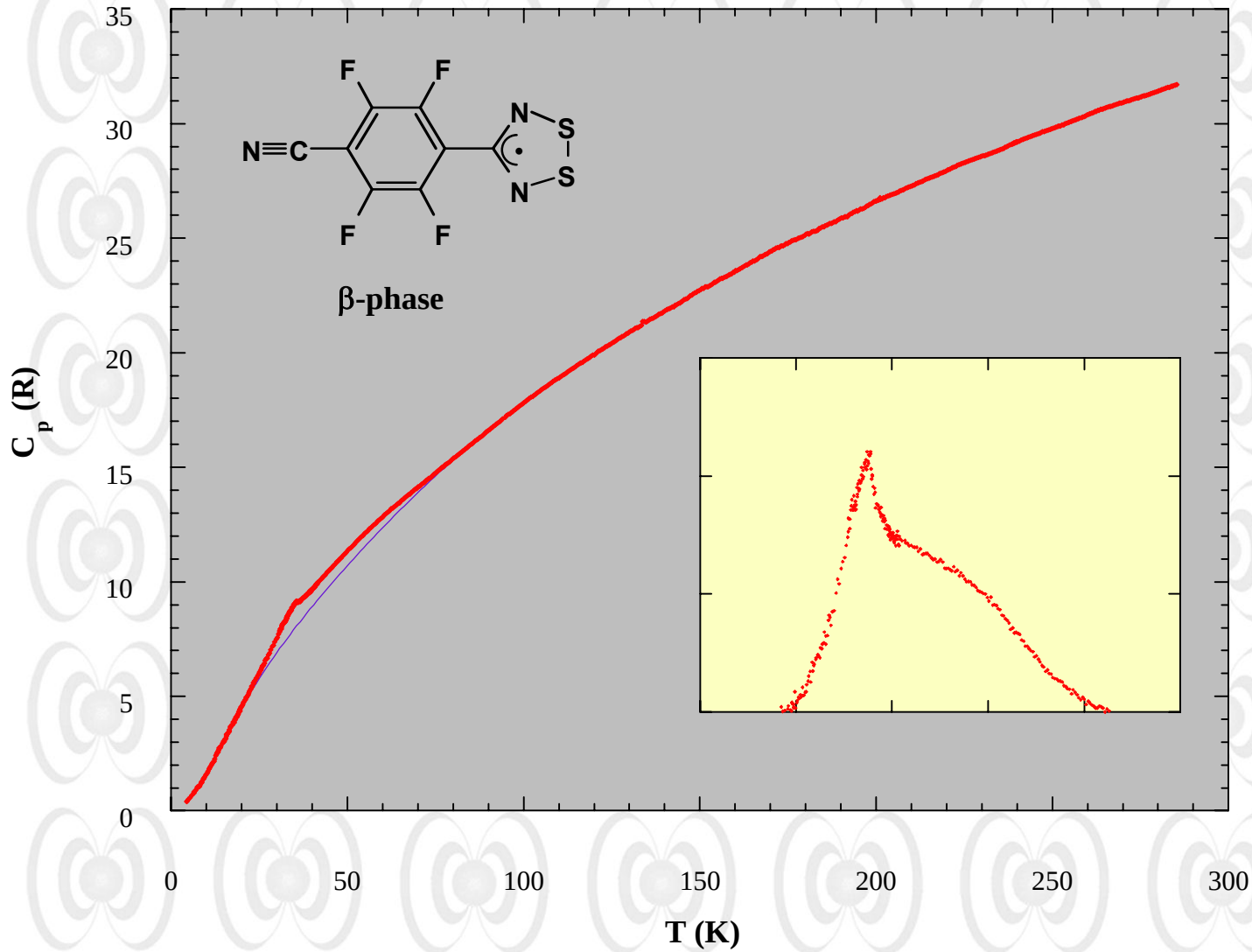


Saturation magnetization

F. Palacio, G. Antorrena, M. Castro, R. Burriel, J.M. Rawson, J.N.B. Smith, N. Bricklebank, J. Novoa and C. Ritter, *Phys. Rev. Lett.* **79**, 2336-9 (1997)

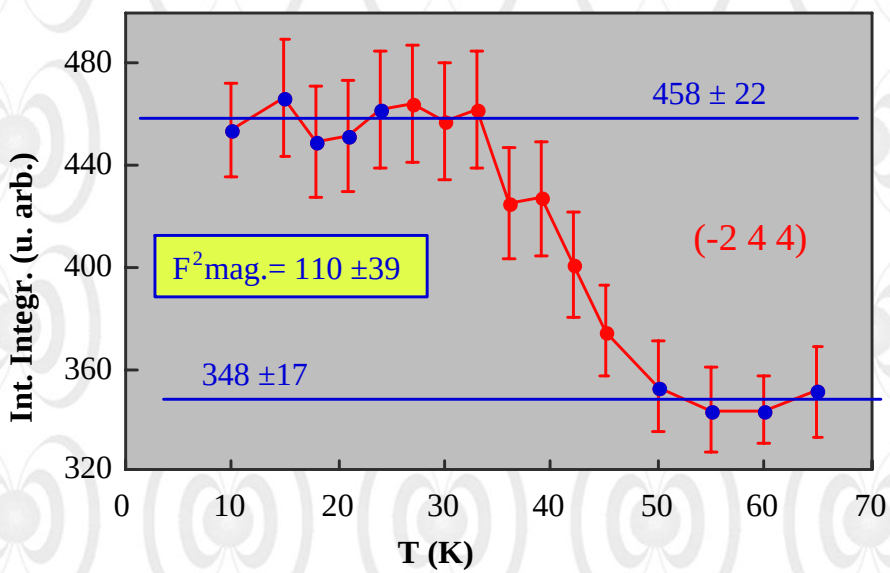


Heat capacity

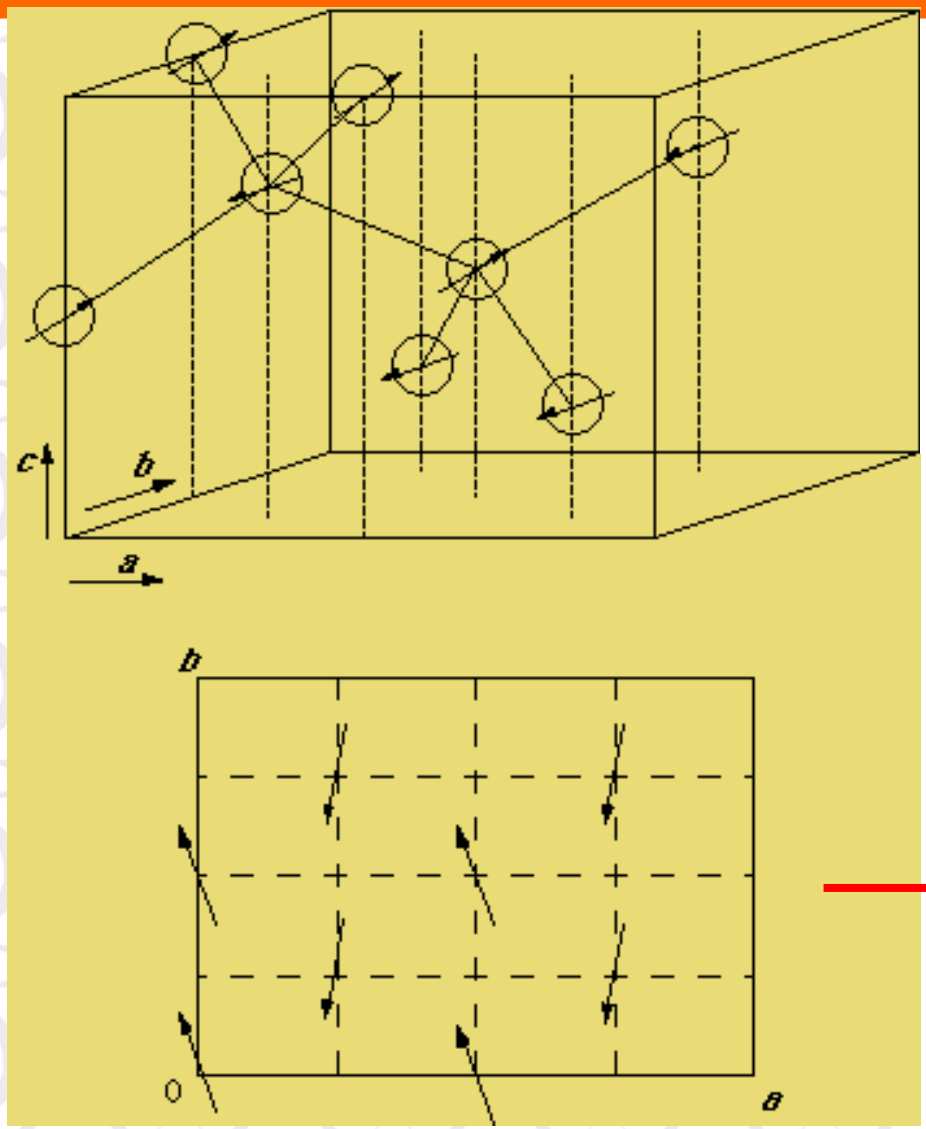


Magnetic structure

- Experiments made in powder (D1B, ILL) and in single crystal (SXD, ISIS) samples
- A cut of a 2x2x30 mm^3 crystal was used
- For each reflection, magnetic form factor is calculated as $F^2_{mag} = F^2_{l.t.} - F^2_{h.t.}$, where $F^2_{h.t.}$ is the nuclear form factor and $F^2_{l.t.}$ is the sum of the nuclear and magnetic form factors averaged over several temperatures



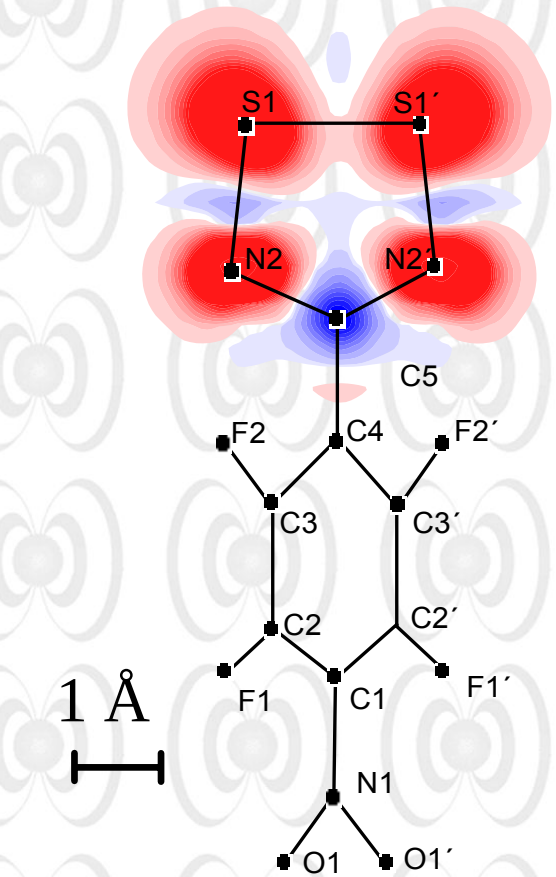
Magnetic structure

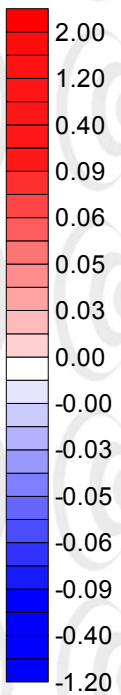


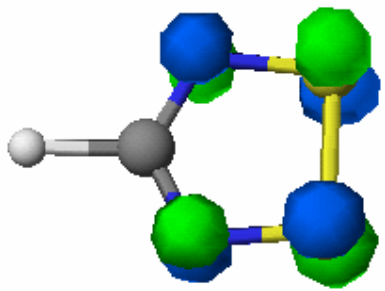
Net moment parallel to **a**

Spin density distribution

PND





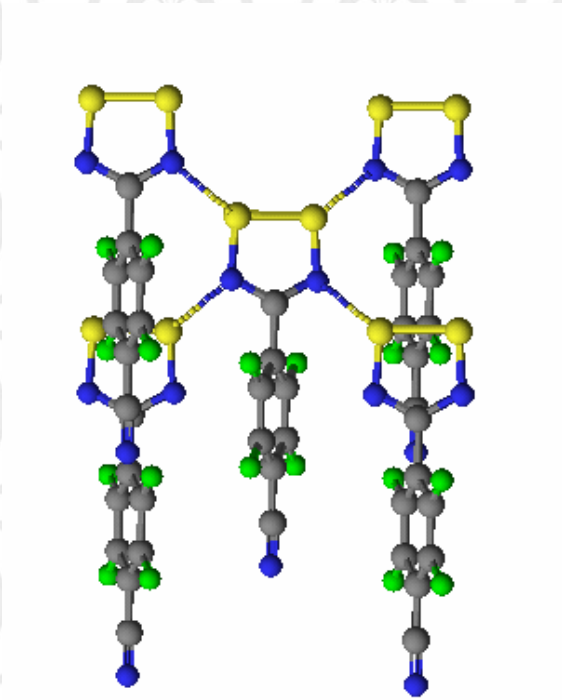


π* orbital

Spin density basically in the π* molecular orbital
Polarization of a negative density in the carbon atom

Magnetic interactions

Exchange pathways



J_1: inter-ring N ··· S = 3.488Å
J_2: C-N ··· S = 2.986Å
J_3: mF ··· S = 3.345 Å
J_4: mF ··· S = 3.325 Å

DFT calculations, B3LYP funct.

6-31G basis set**

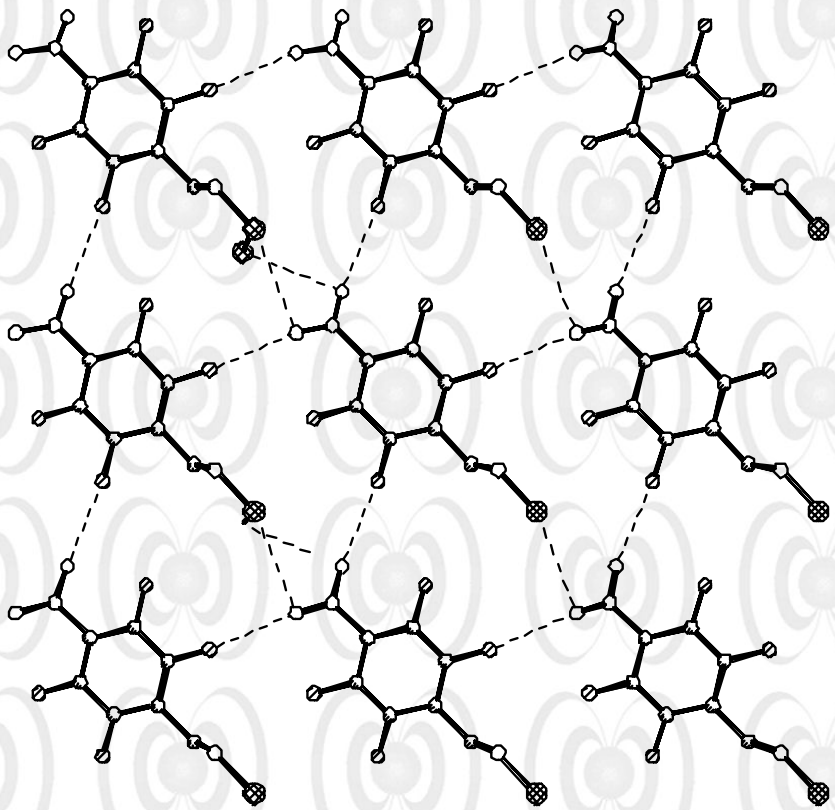
J1: -32.58320 cm-1 ==> -46.88231 K
J2: -0.03073 cm-1 ==> -0.04421 K
J3: -0.00658 cm-1 ==> -0.00947 K
J4: 0.00438 cm-1 ==> 0.00632 K

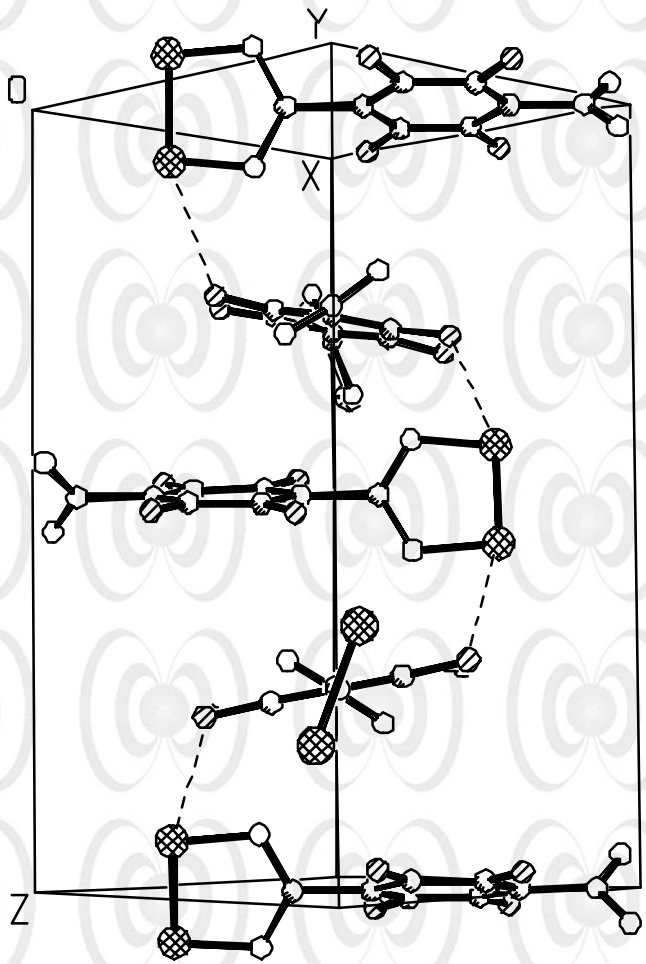
6-311G basis set**

J1: -31.38048 cm-1 ==> -45.15177 K
J2: -0.03512 cm-1 ==> -0.05053 K
J3: -0.00658 cm-1 ==> -0.00947 K
J4: 0.00219 cm-1 ==> 0.00316 K

Efforts to find new high T_c examples

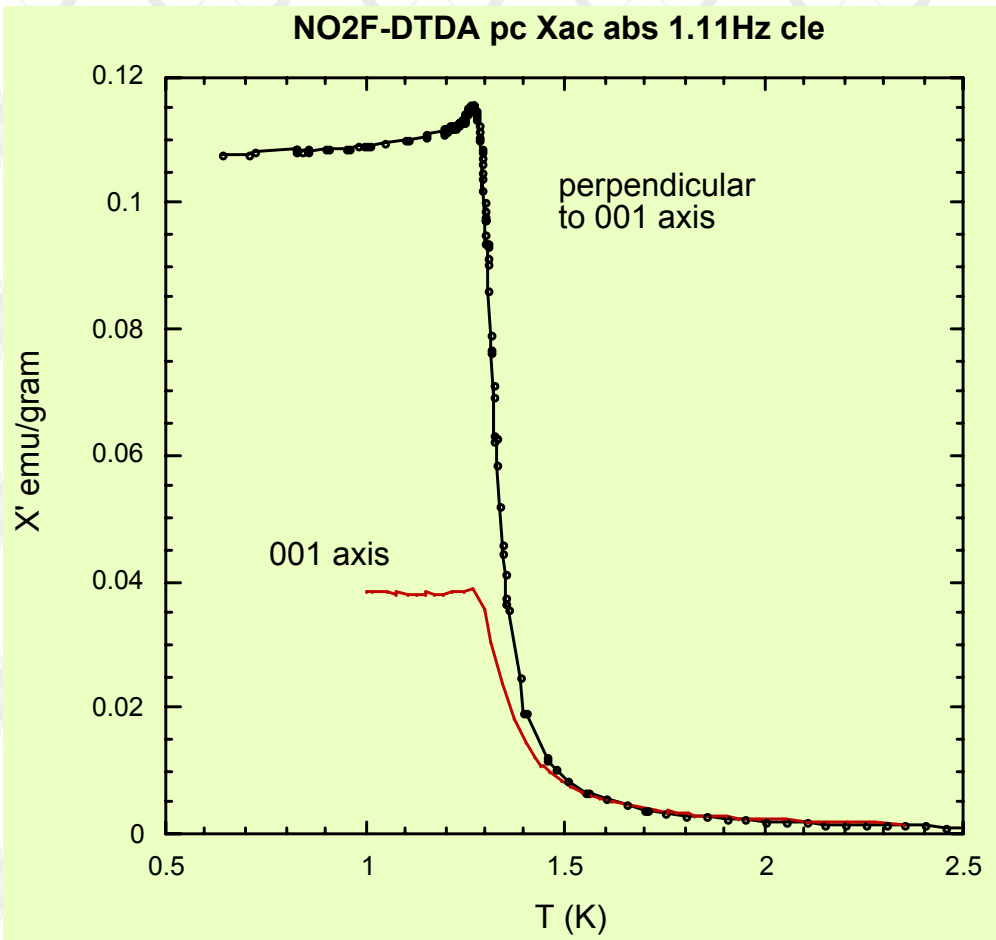
p-NO_2-C_6F_4-CNSSN$^{\bullet}$





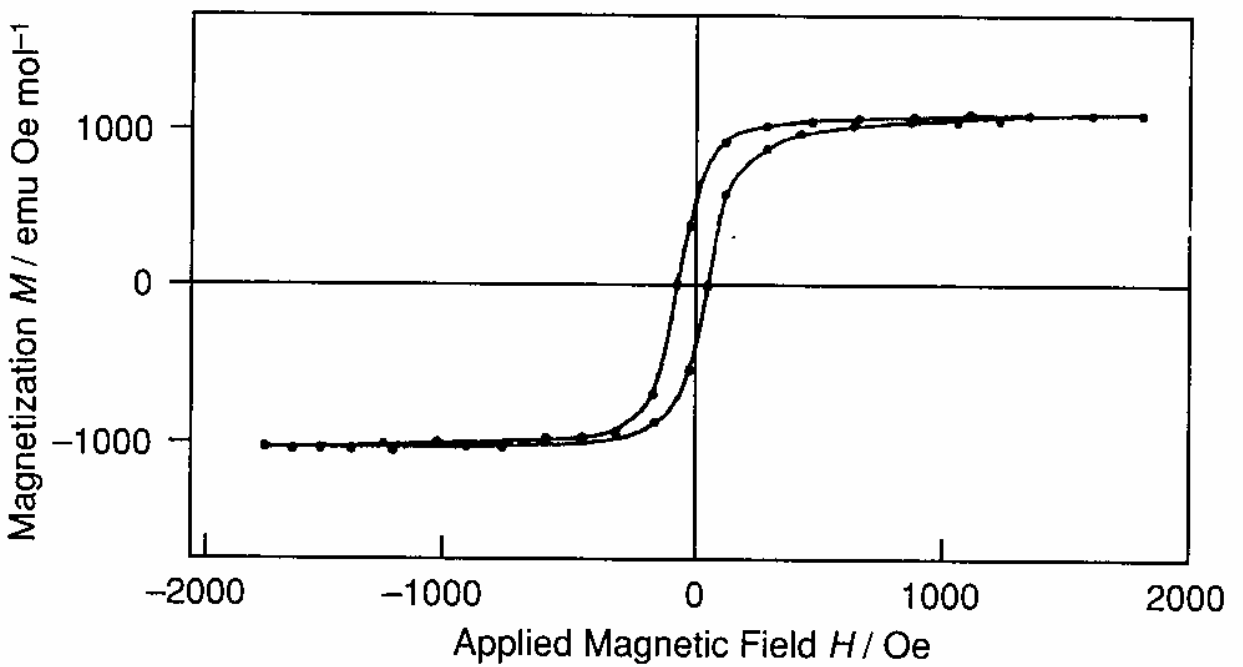
p-NO_2-C_6F_4-CNSSN$^{\cdot}$: an Organic Ferromagnet with Tc > 1K

A. Alberola, R.J. Less, C.M. Pask, J.M. Rawson, F. Palacio, P. Oliete, C. Paulsen, A. Yamaguchi and R.D. Farley. Angew. Chem. Int. Ed. (2003, in press)



Tc = 1.32 K

$V(TCNE)_2$



$V(TCNE)_2$ becomes a disordered ferrimagnet below 350 K

MAGMA Net
NETWORK OF EXCELLENCE

Photomagnetic Effects

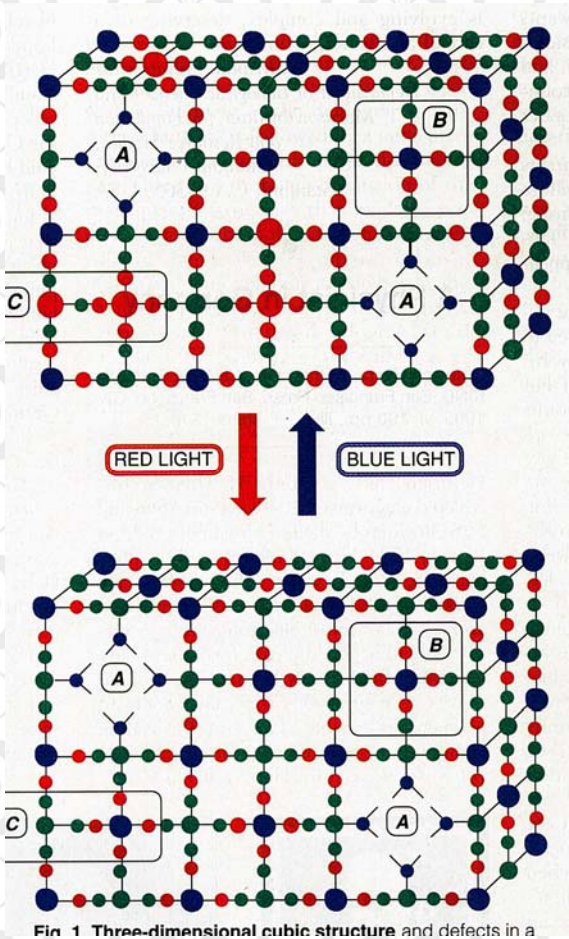
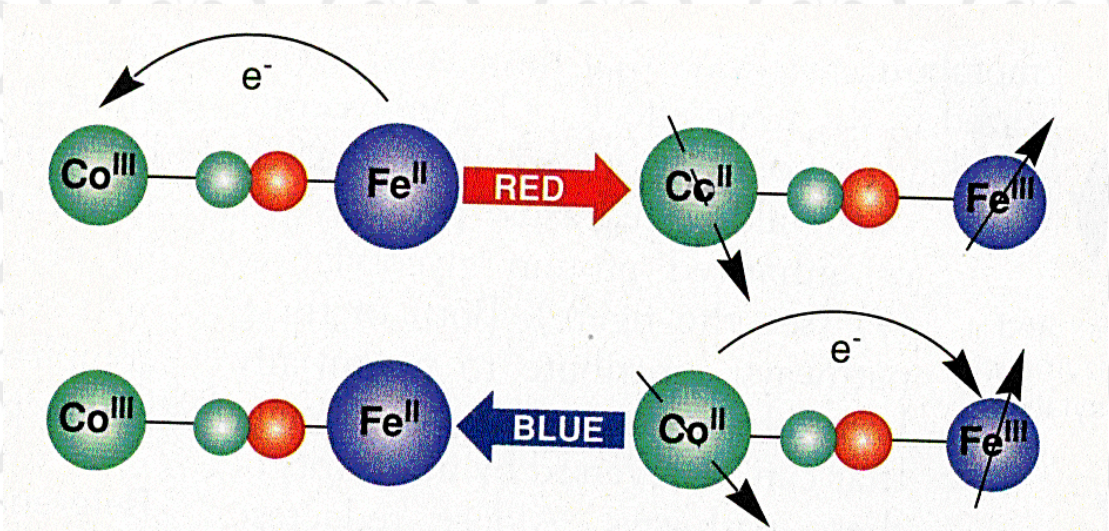
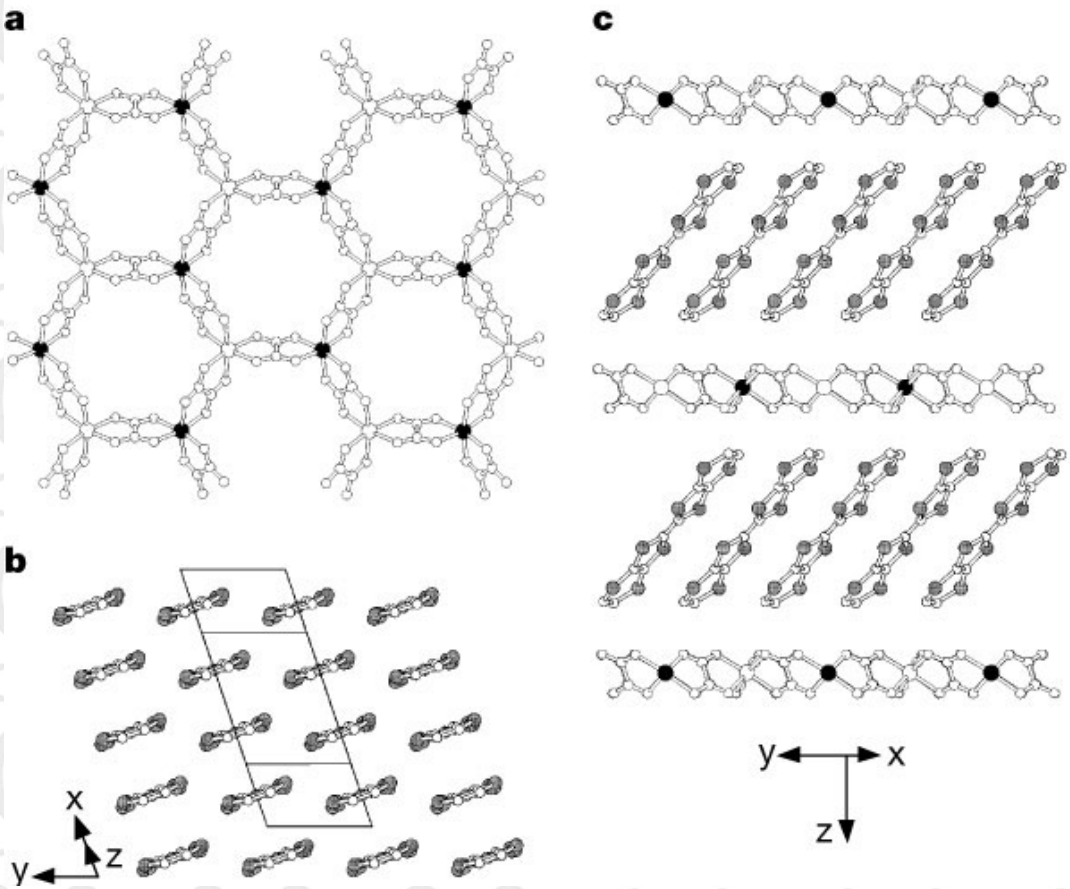


Fig. 1. Three-dimensional cubic structure and defects in a



Hashimoto; Verdaguer

A Ferromagnetic Conductor



The inorganic moiety is ferromagnetic

The organic moiety is a conductor

Separation between the magnetic and conducting electrons

Coronado et al Nature 2001

MAGMA Net
NETWORK OF EXCELLENCE

Molecular Nanomagnets

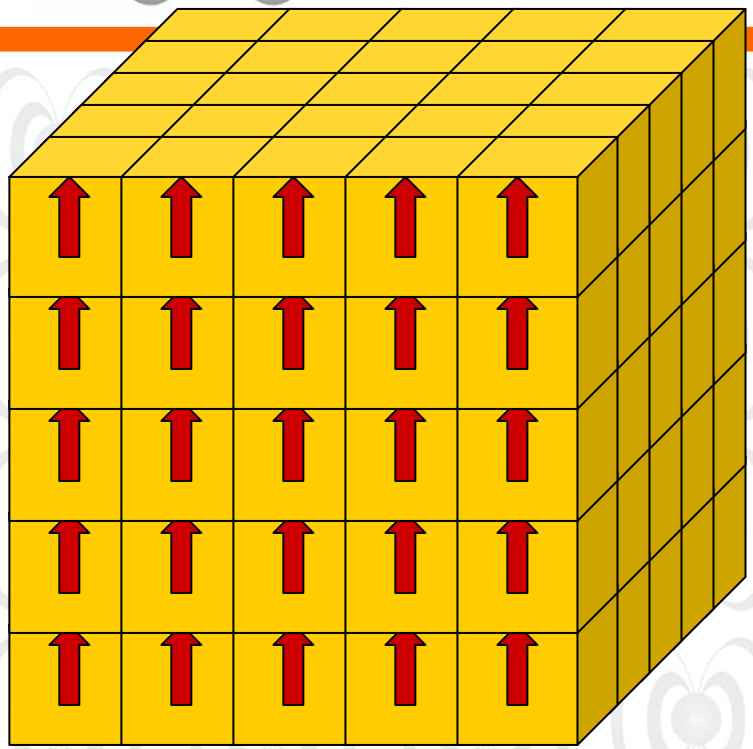
Single Molecule Magnets

Why Nanomagnets?

- Potential applications
- Minimum size of a memory element
- Coexistence of classical and quantum effects
- "Hardware" for quantum computing
- Magnetocaloric effect
- Models for biological magnets
- Contrast agents for MRI
- Magnetic drug delivery

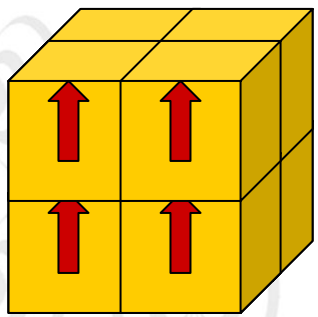
MAGMA Net
NETWORK OF EXCELLENCE

Reducing the size



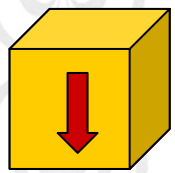
magnet

Classical physics



super paramagnet

??????????



paramagnet

Quantum mechanics

MAGMA Net
NETWORK OF EXCELLENCE

Top-down vs. Bottom -up

MAGMA Net
NETWORK OF EXCELLENCE

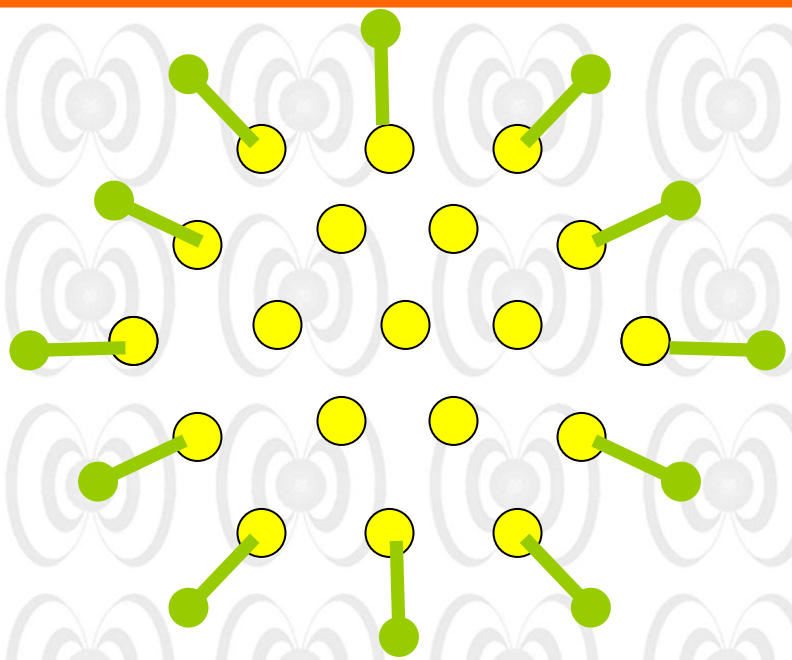
Sculpture: top-down

MAGMA Net

NETWORK OF EXCEL

MAGMA Net
NETWORK OF EXCELLENCE

Mosaic: bottom up

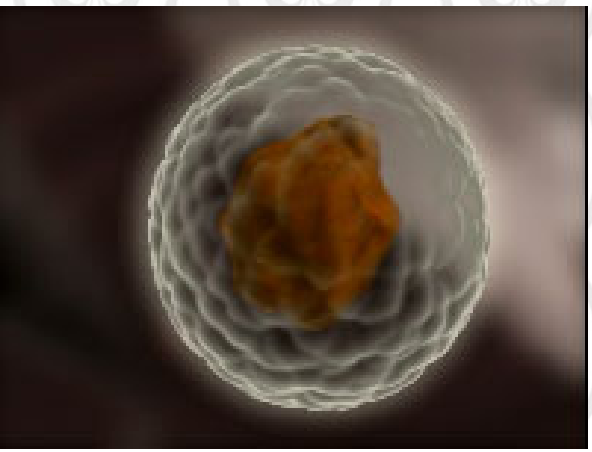


Natural Nanomagnets

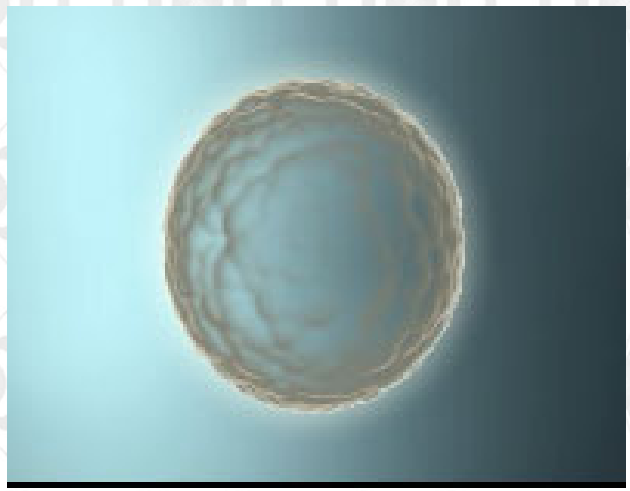
- Ferritin
- Magnetosomes

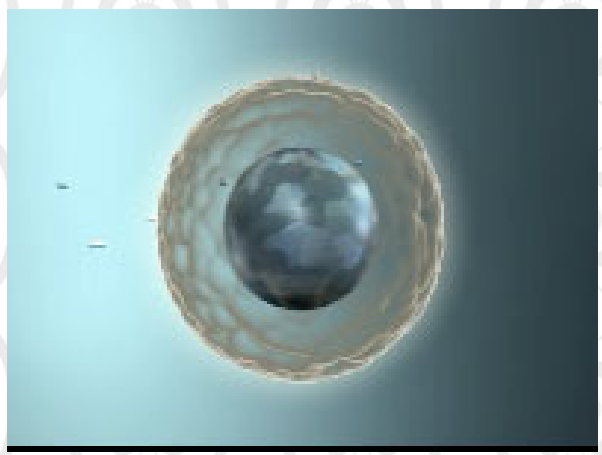
MAGMA Net
NETWORK OF EXCELLENCE

Variations on a Natural Theme



- rust





+ CoPt

Even viruses!!

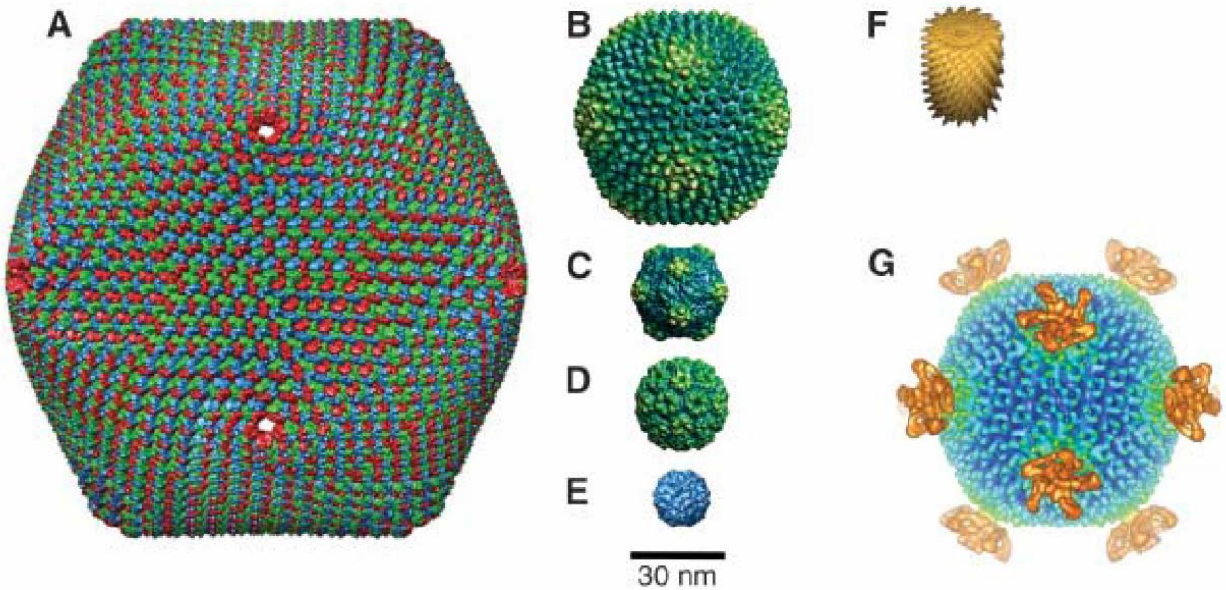
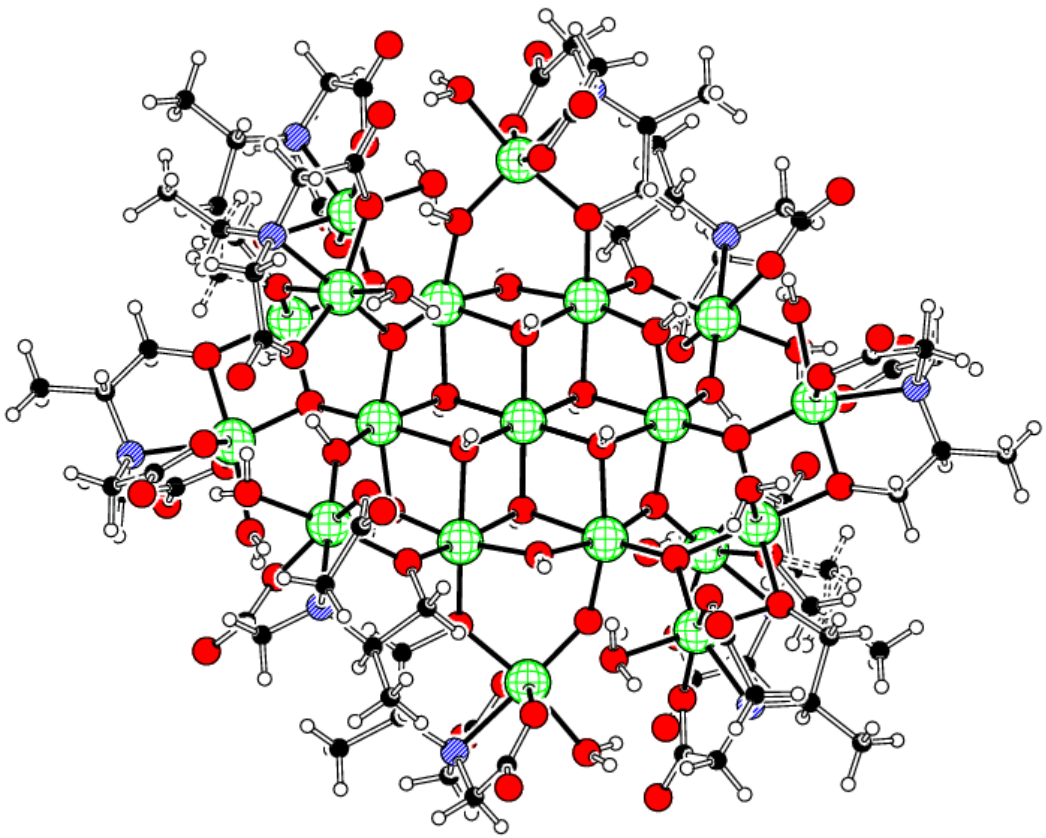


Fig. 2. Cryo–electron micrograph and image reconstructions of a library of viral capsids, including both icosahedral (*2*) and helical viruses (*3*). (**A**) *Paramecium bursaria* Chlorella virus type 1 (PCB-1), 170-nm diameter. (**B**) Murine polyoma virus, 51-nm diameter. (**C**) Cowpea mosaic virus, 31-nm diameter. (**D**) CCMV, 28-nm diameter. (**E**) Satellite tobacco mosaic virus, 18-nm diameter. (**F**) A small section of the rod-shaped TMV, which measures 18 by 300 nm. (**G**) Sulfolobus turreted icosahedral virus isolated from a boiling, acid environment in Yellowstone National Park (*30*).

Dougas t al. Science 312, 2006

MAGMA Net
NETWORK OF EXCELLENCE

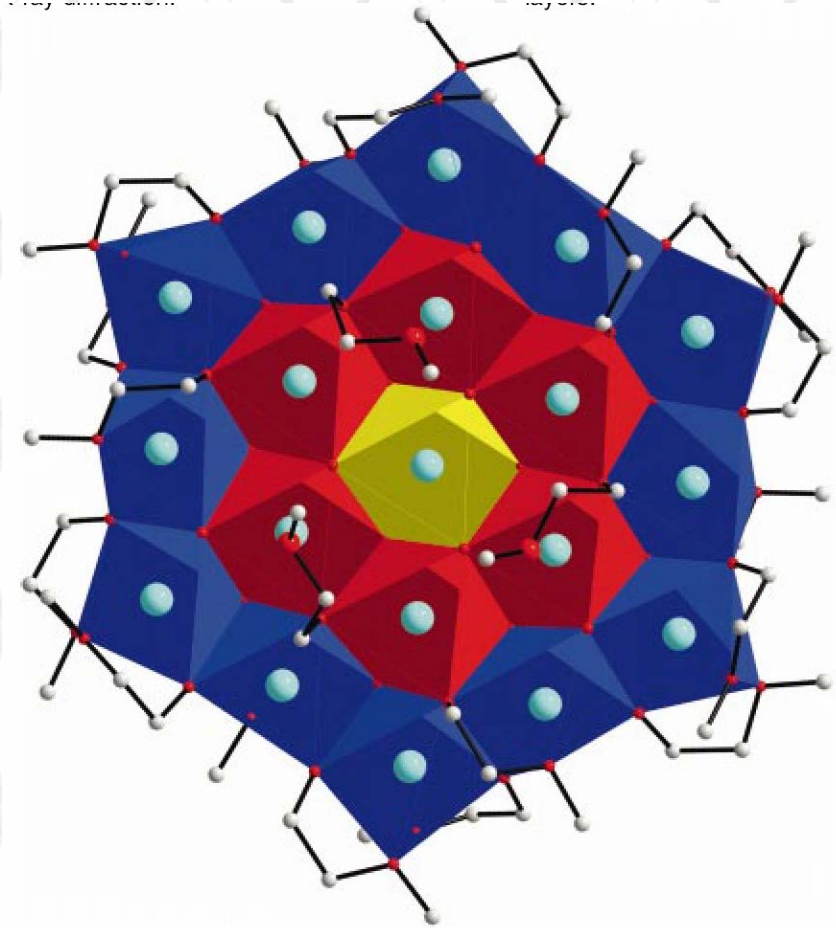
A model of the ferritin core

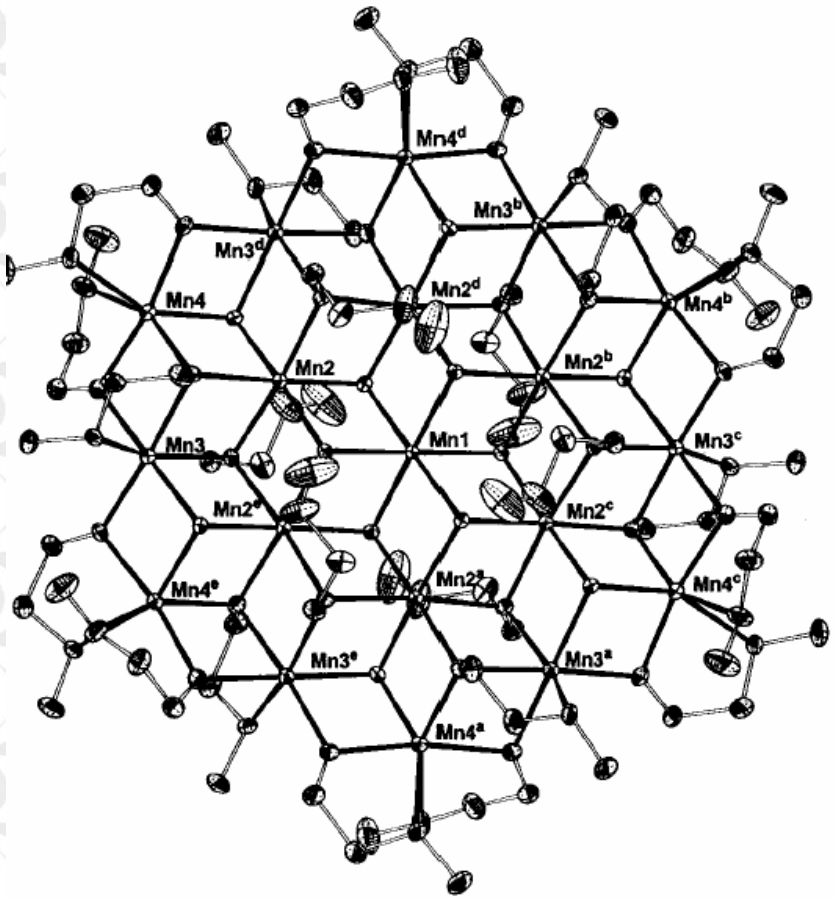


Powell et al.

MAGMA Net
NETWORK OF EXCELLENCE

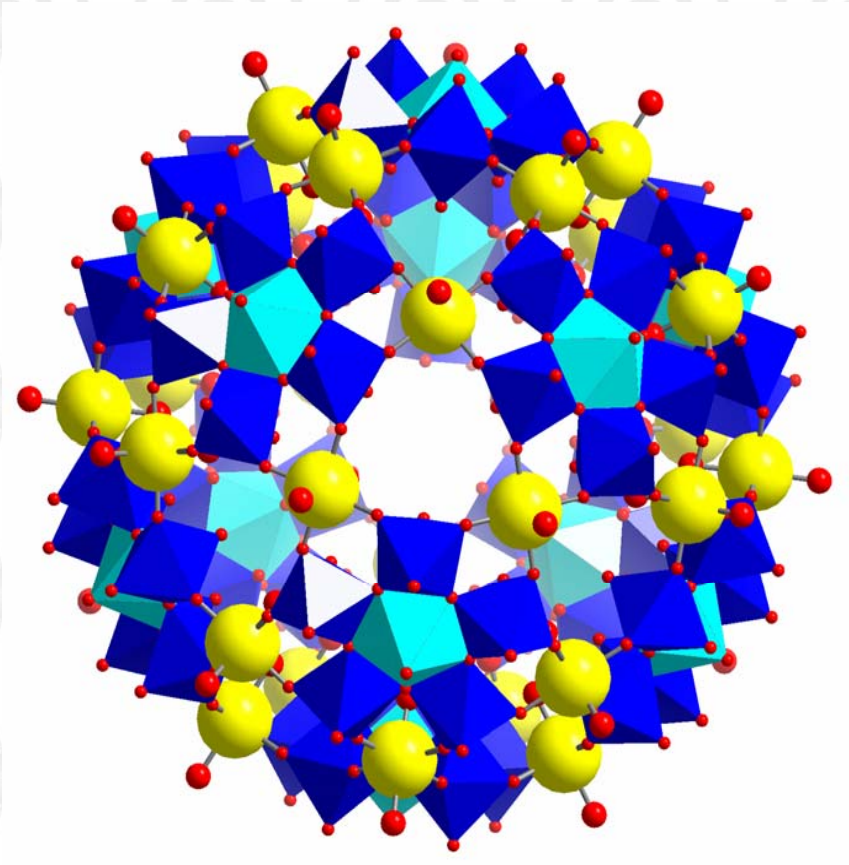
Mn19



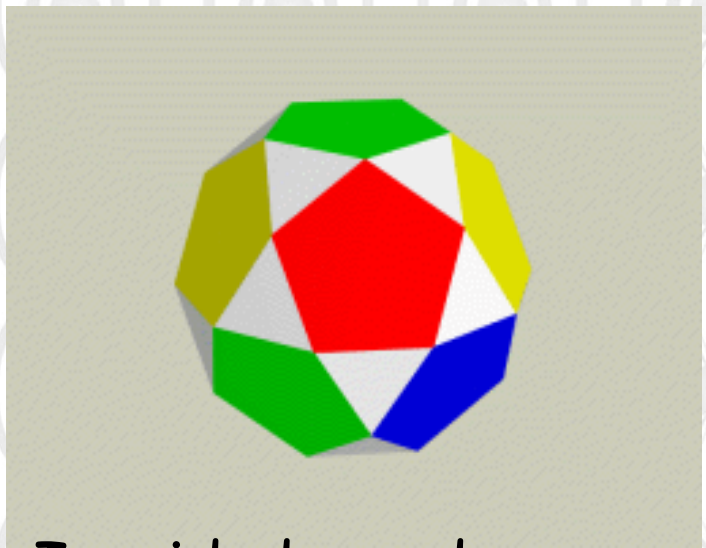


Westin et al.

Giant Molecular Antiferromagnets: Fe30



A. Müller, M. Luban



Icosidodecaedro

DG1

Diapositiva 93

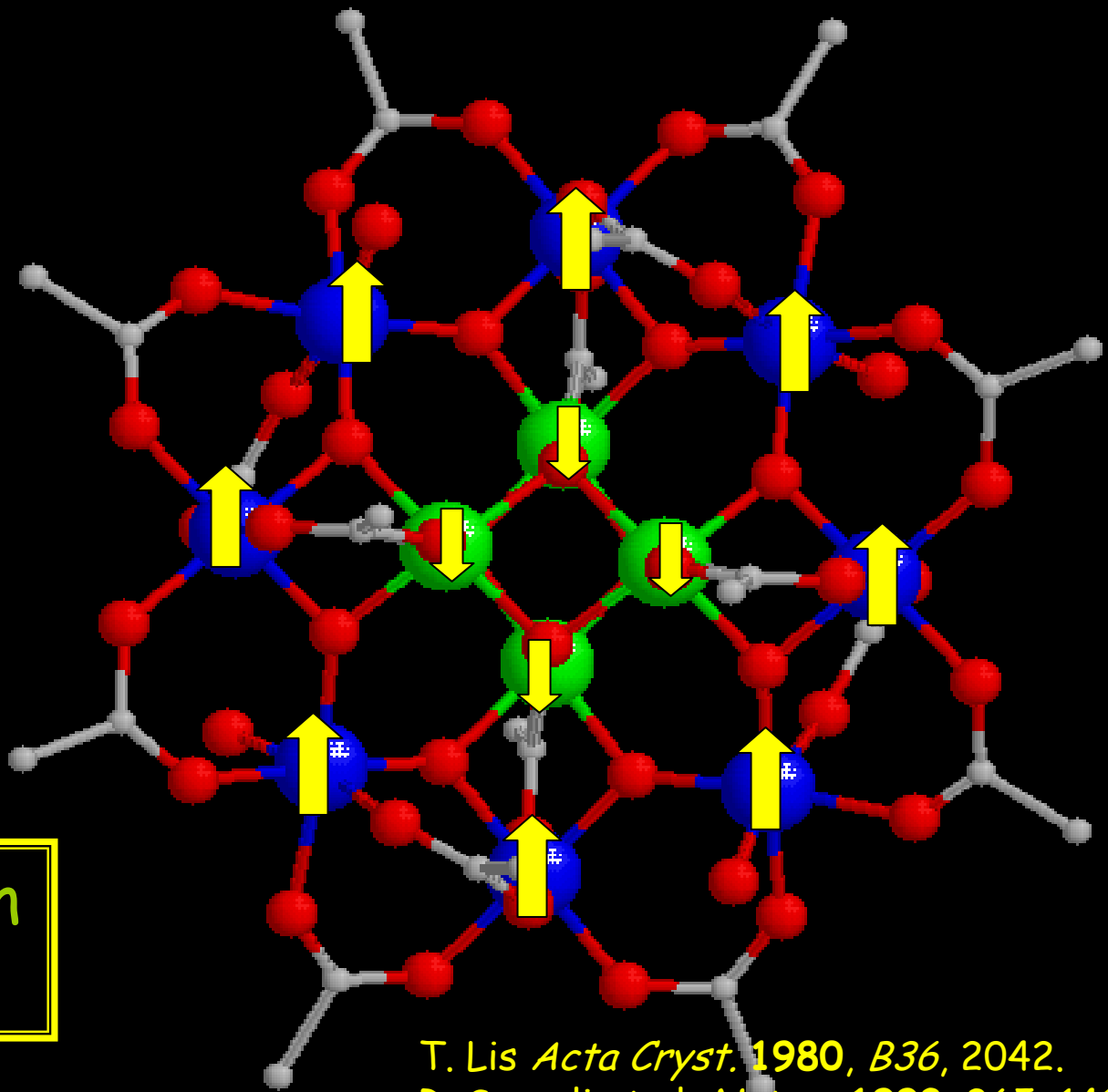
DG1 Dante Gatteschi; 25/06/2003

Mn12acetato

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

Mn(III)
S=2

Mn(IV)
S=3/2



Total Spin
S=10

T. Lis *Acta Cryst.* **1980**, *B36*, 2042.
R. Sessoli et al. *Nature* **1993**, 365, 141.

Neutrons confirm

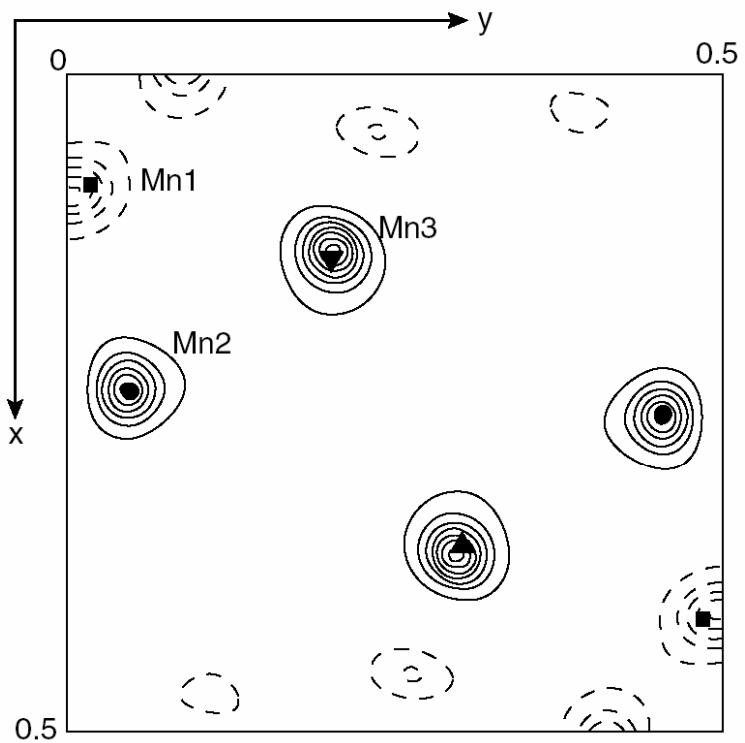


Figure 2. Maximum-entropy projection onto the (001) tetragonal basal plane of the magnetization density in Mn_{12} acetate at 1.7 K and 4.6 T. The contours are drawn at equal intervals of 1 μ_B Å^{-2}. Negative contours are shown as dashed lines. The molecule centres are at (0, 0, 0) and (0.5, 0.5, 0.5).

MAGMA Net
NETWORK OF EXCELLENCE

Spectroscopy too

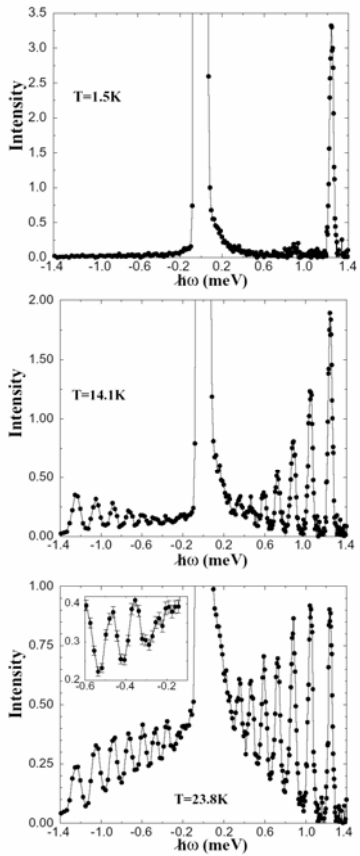


FIG. 1. Energy spectra at three temperatures (raw data). The intensity units are the same but the scales are different for all spectra. In the inset, the low-energy range on the sample energy loss side.

The spin Hamiltonian

$$H = D[S_z^2 - 1/3S(S+1)] + B_4^0 O_4^0 + B_4^4 O_4^4, \quad (2)$$

with $O_4^0 = 35S_z^4 - [30S(S+1) - 25]S_z^2 - 6S(S+1) + 3S^2(S+1)^2$ and $O_4^4 = 1/2(S_+^4 + S_-^4)$.

MAGMA Net
NETWORK OF EXCELLENCE

The analysis

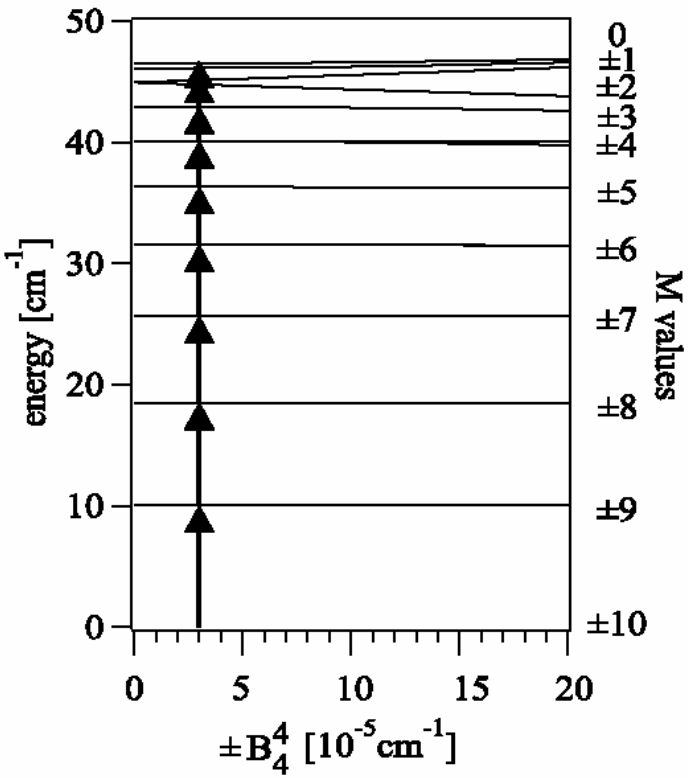
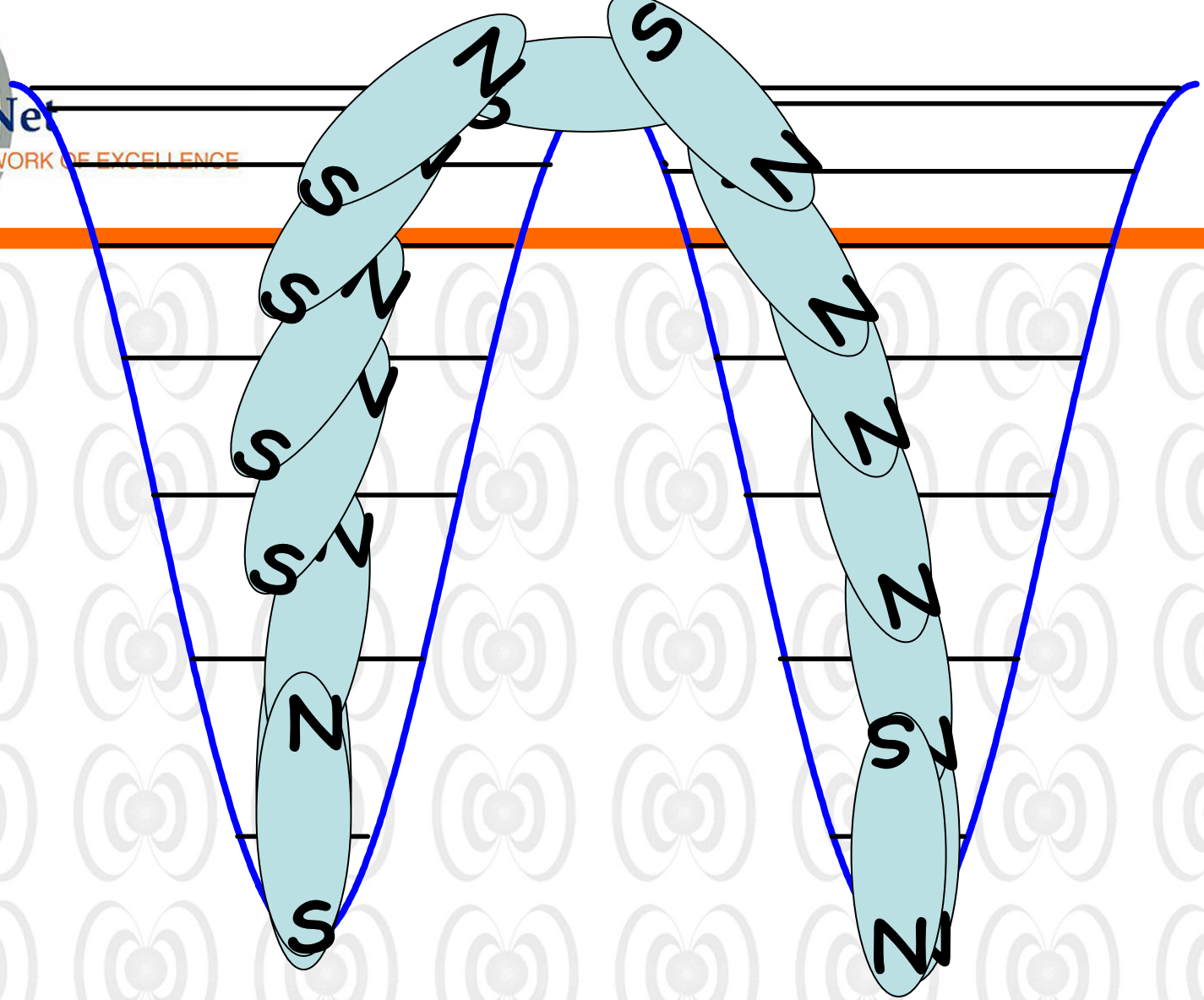
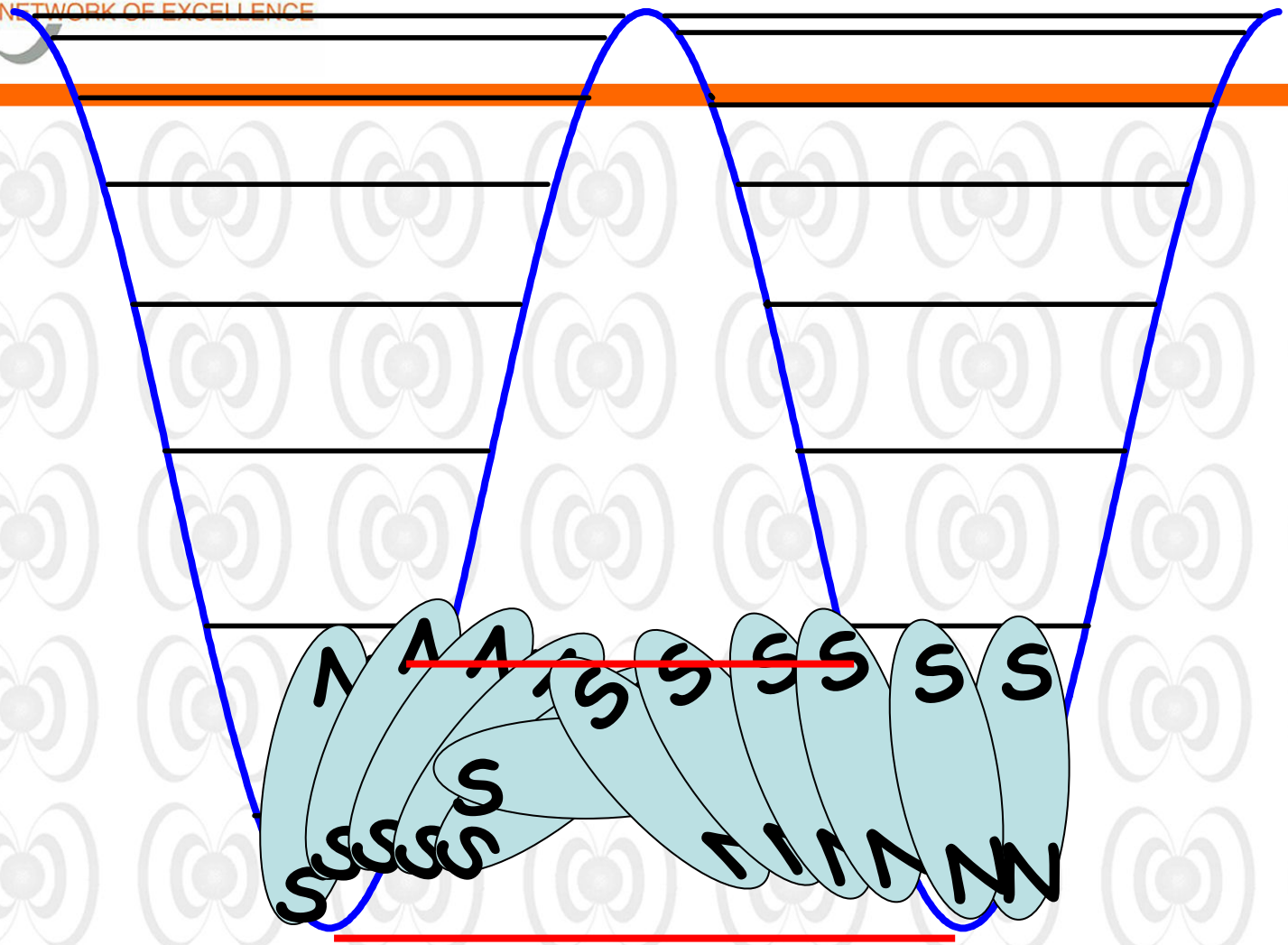


FIG. 2. Energy sublevels of the $S = 10$ ground state versus B_4^4, as calculated for $D = -0.457$ cm^{-1}, $B_4^0 = -2.33 \times 10^{-5}$ cm^{-1}.



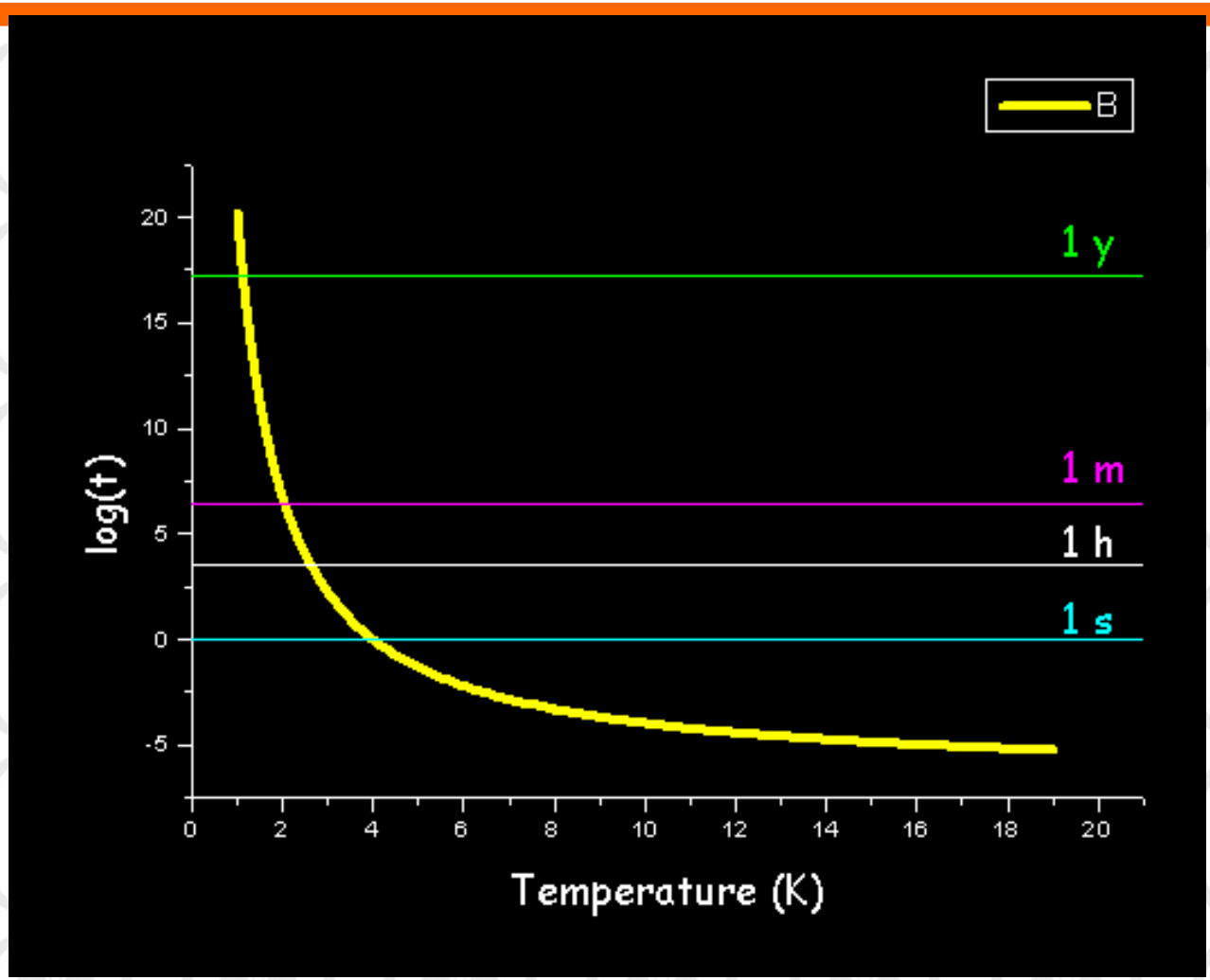
Relaxation of magnetization: classic



Relaxation of magnetization: quantum

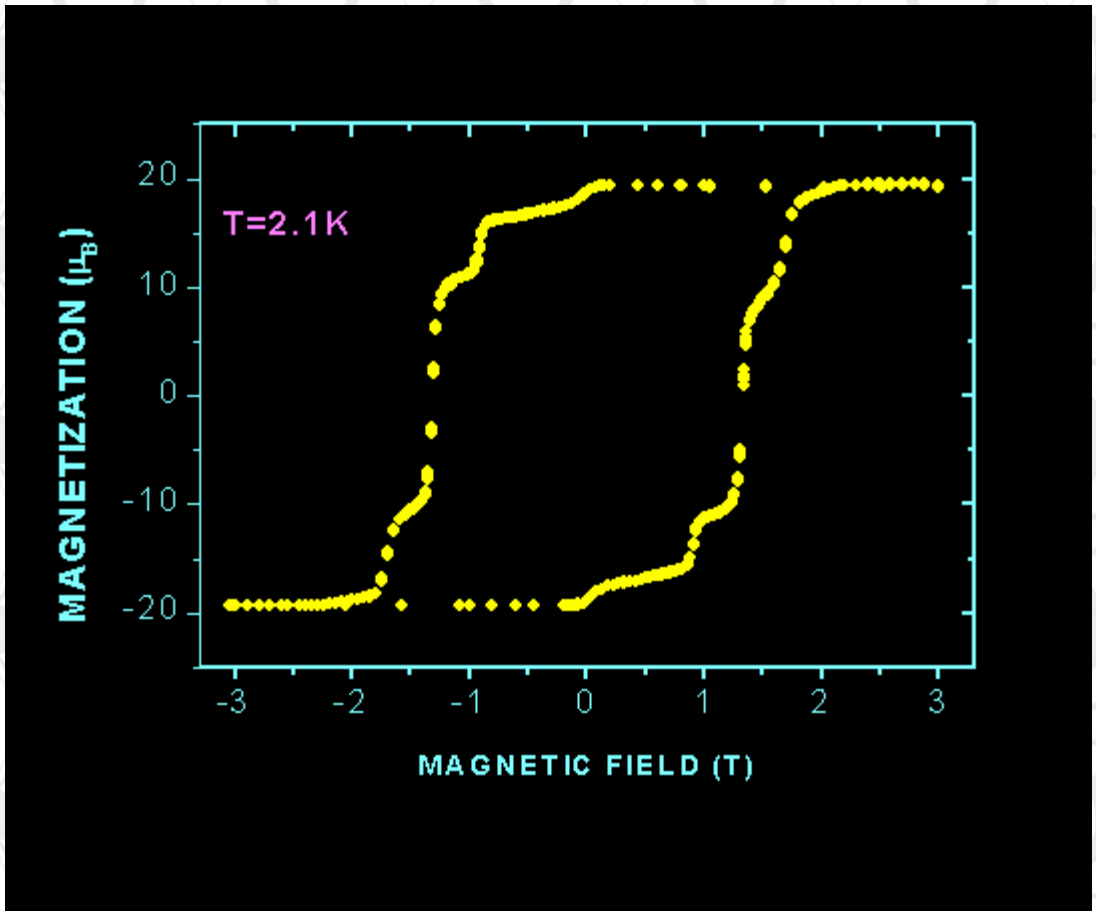
MAGMA Net
NETWORK OF EXCELLENCE

Mn12 is a magnet at low T



MAGMA Net
NETWORK OF EXCELLENCE

Mn12 Magnetic Hysteresis



MAGMA Net
NETWORK OF EXCELLENCE

Why stepped hysteresis?

- Two mechanisms of relaxation: thermally activated and tunnel
- tunnel is different from zero only at given values of the magnetic field
- At those fields the two mechanisms enhance the relaxation

Back to the origins

Acta Cryst. (1980). B36, 2042–2046

Preparation, Structure, and Magnetic Properties of a Dodecanuclear Mixed-Valen… Manganese Carboxylate

BY T. LIS

Instytut Chemii Uniwersytetu Wrocławskiego, 50-383 *Wrocław, ul. Joliot-Curie* 14, *Poland*

(*Received* 29 *January* 1980; *accepted* 17 *March* 1980)

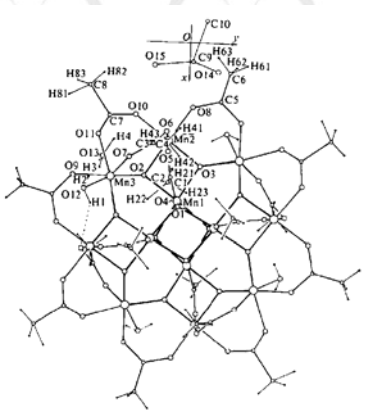


Fig. 1. The crystal structure of $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].2CH_3COOH.4H_2O$: projection on the (001) plane.

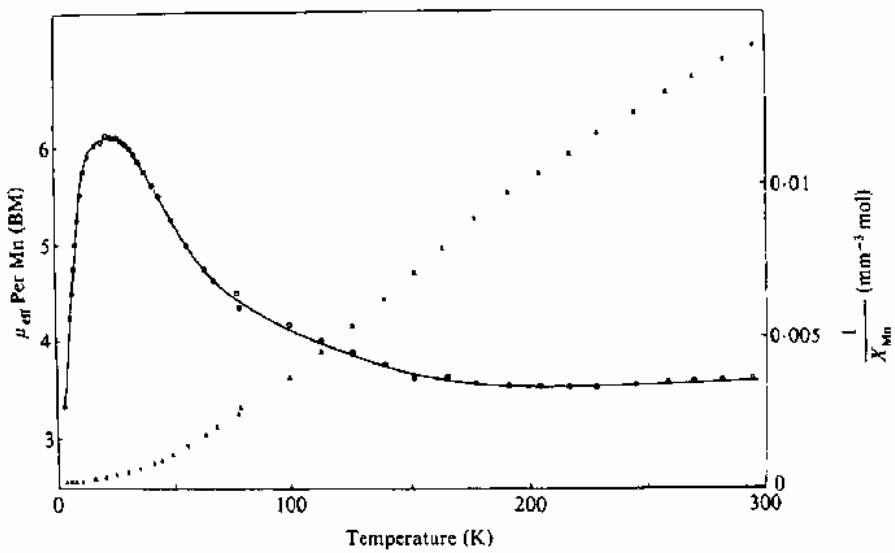


Fig. 2. Magnetic moment (continuous curve) and inverse of the magnetic susceptibility (broken curve) (both per one Mn atom) for $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}].2CH_3COOH.4H_2O$. [1 BM ≡ $9{\cdot}27 \times 10^{-24}$ J T^{-1}.]

A deeper structural insight: neutrons and 20 K

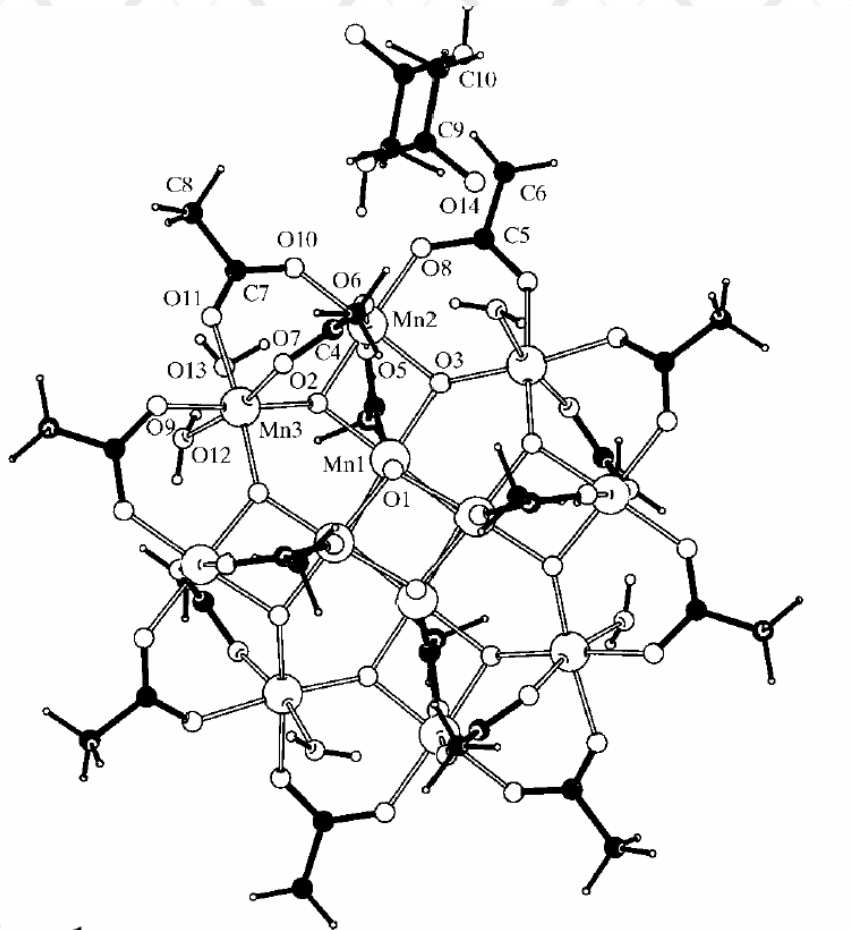
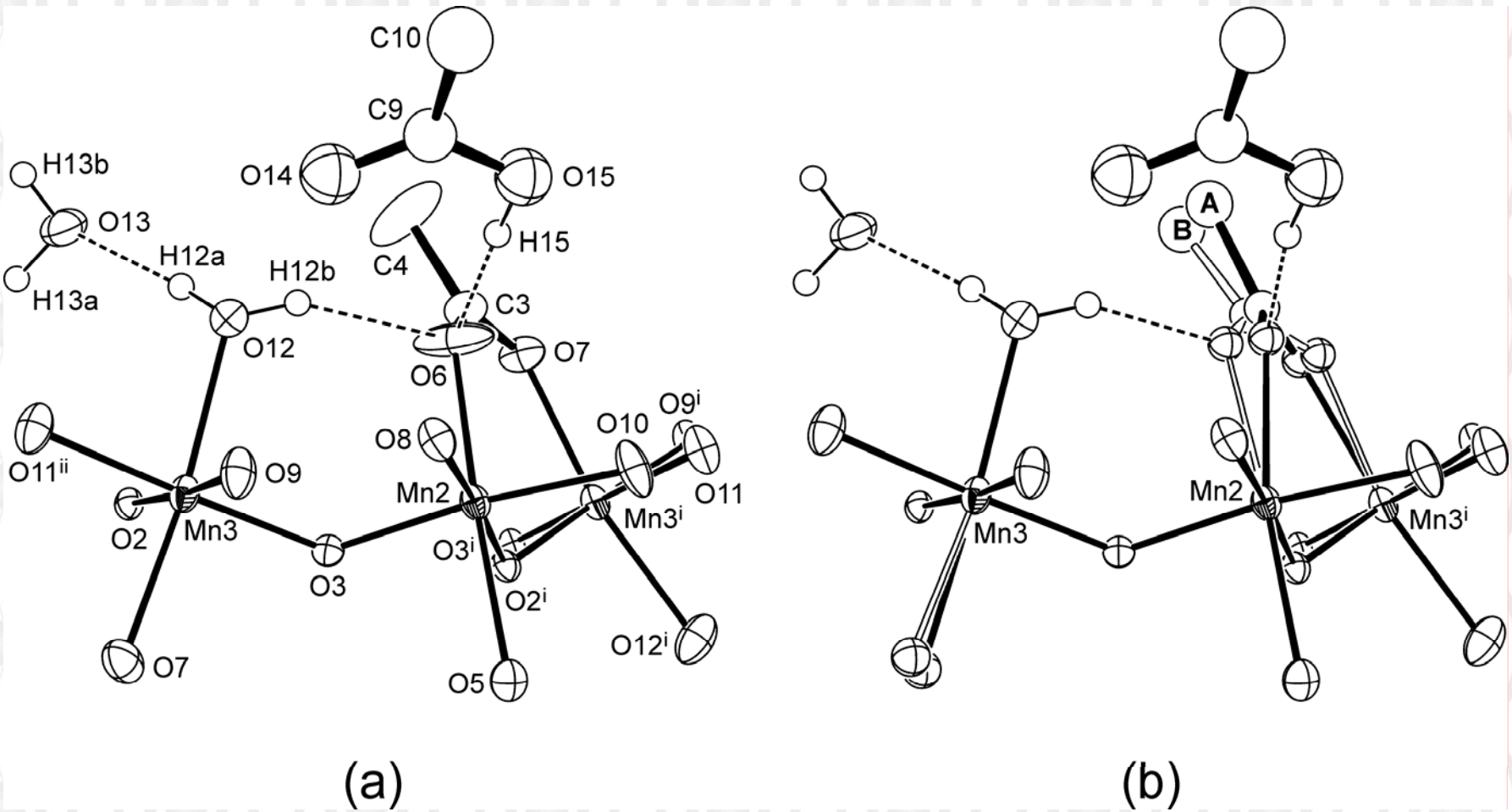
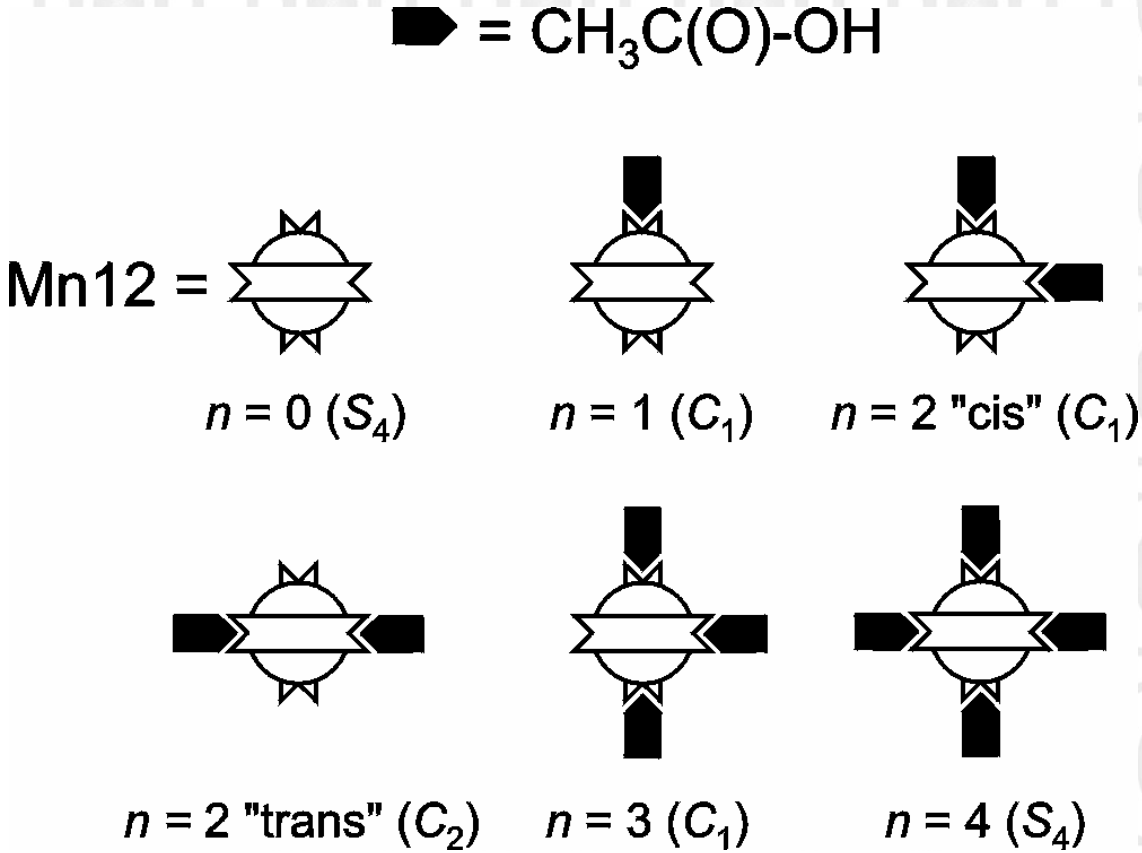


Figure 1

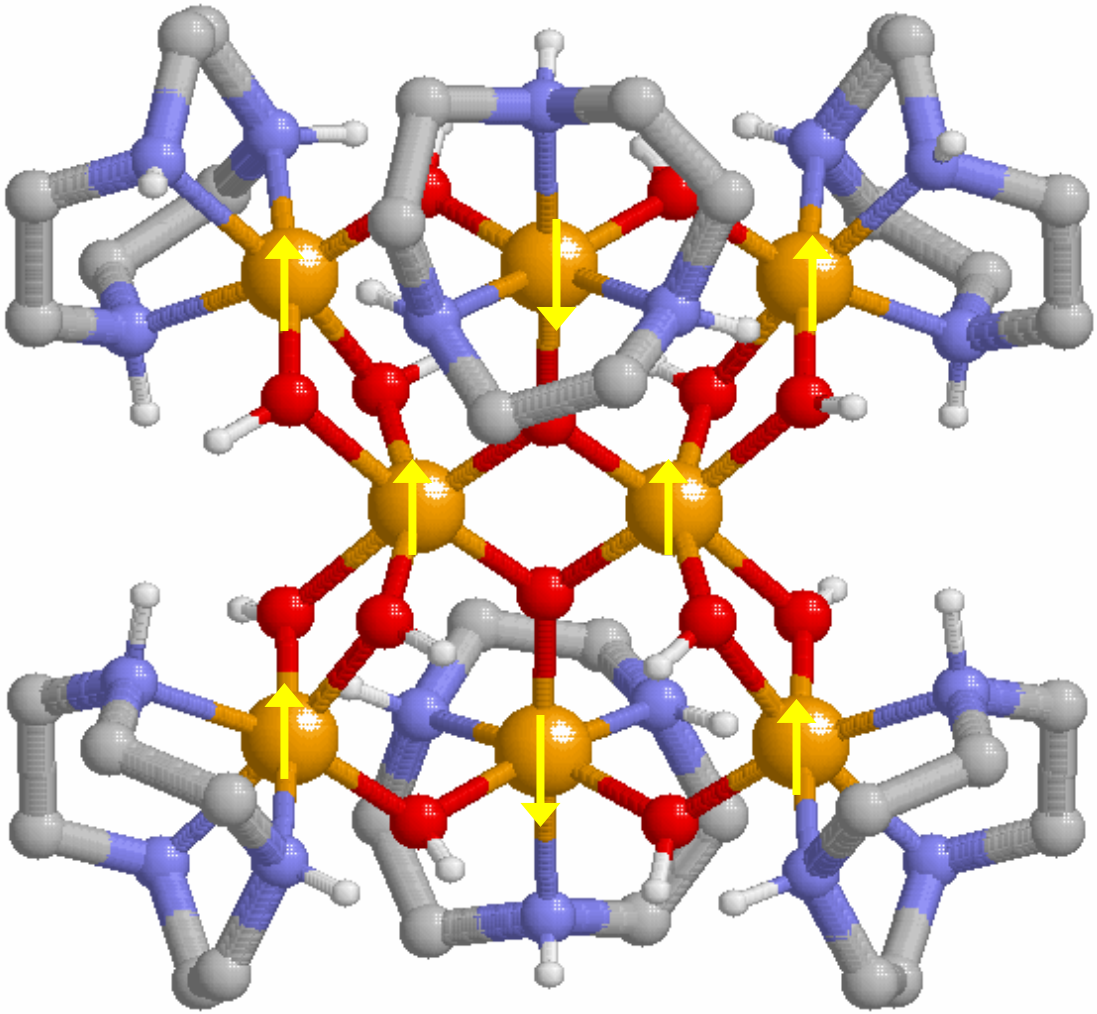
Hydrogen bonds are the key



Many isomers, but only two are tetragonal!



$[Fe_8O_2(OH)_{12}(tacn)_6]Br_8 \cdot 9H_2O$



K. Wieghardt et al. 1984

Fe^{3+}

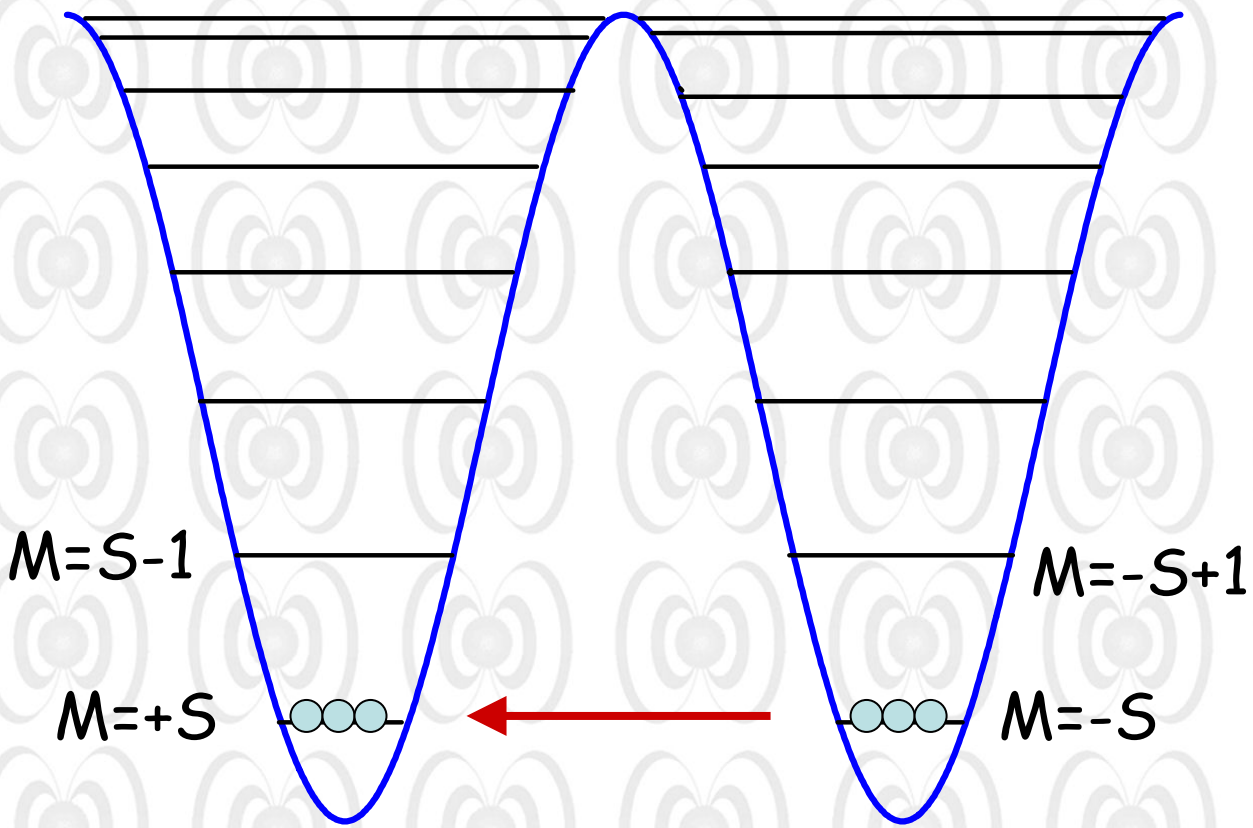
S=5/2

S=10

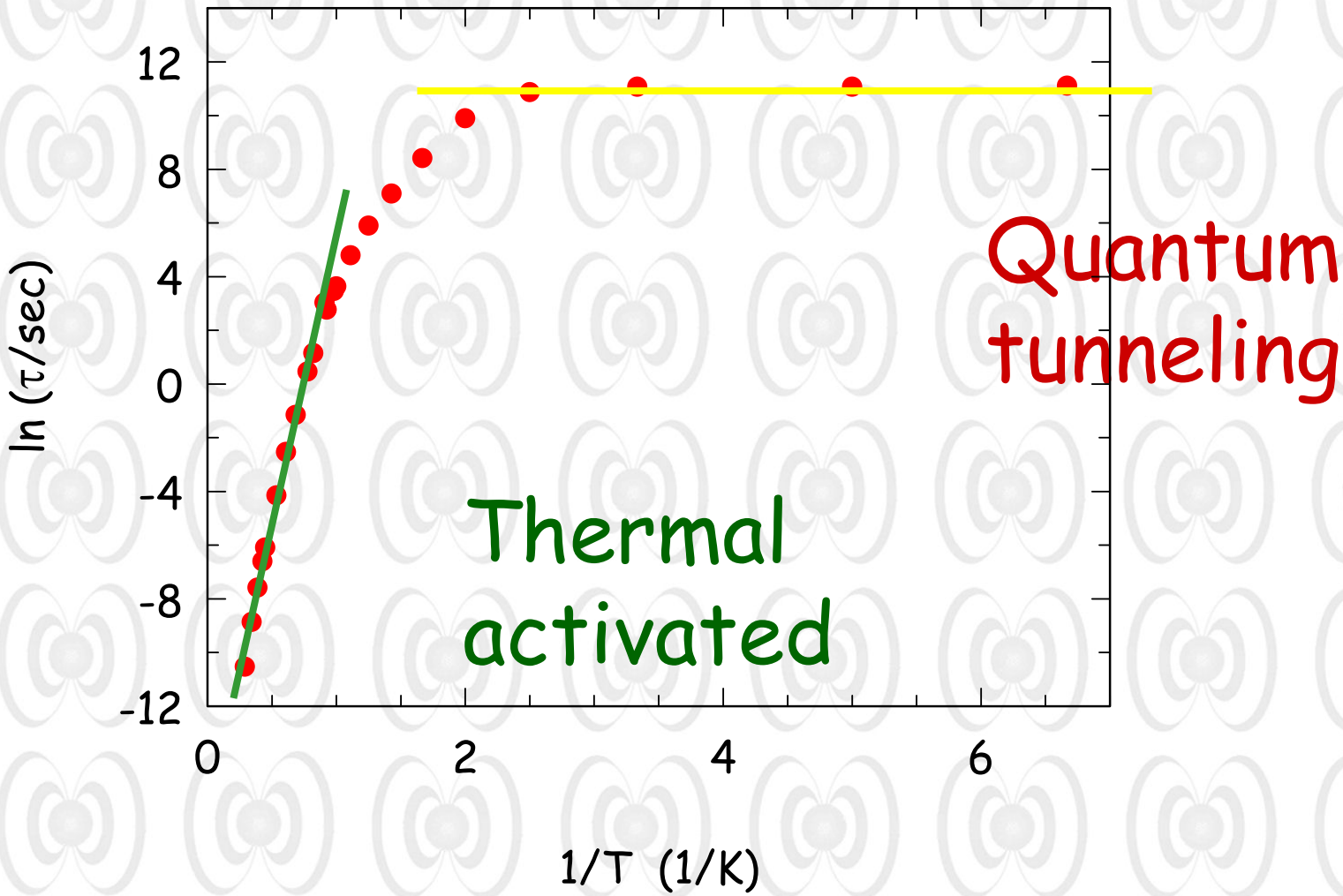
The relaxation time of the magnetization becomes independent of T

The cross-over from thermally activated to tunneling occurs at 300 mK

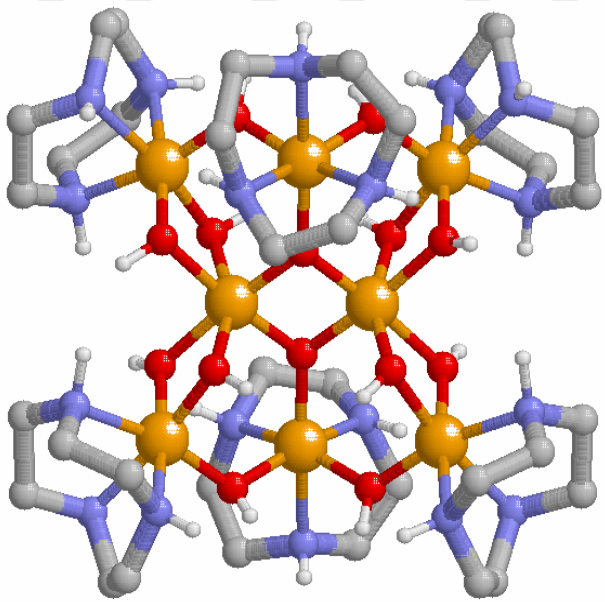
H=0



Temperature dependence of the relaxation time τ in Fe8



Fe8: the origin of the magnetic ground state

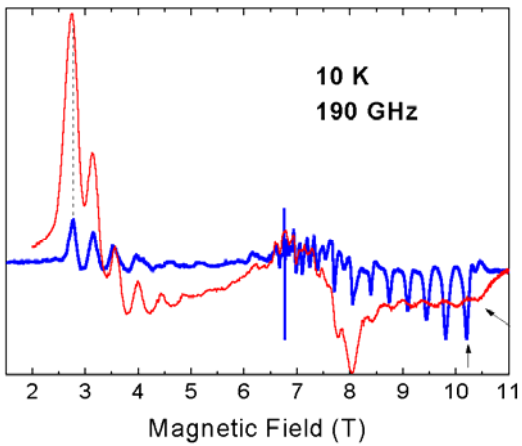


- Fe8 has a ground S= 10 state
- the iron(III) ions are antiferromagnetically coupled
- spin frustration is operative
- which is the spin density map?

Polarized Neutron Spin Density of Fe8

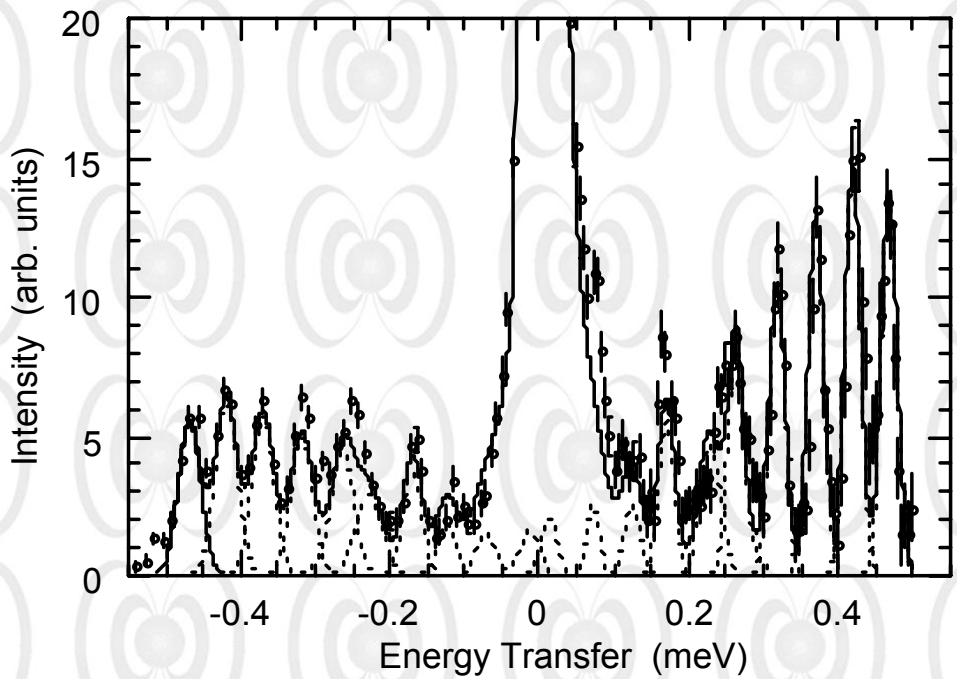
- PNSD data showed the two iron ions whose magnetisation is reversed compared to that of the others
- the spin density does not correspond to simple “up-down” models

HF-EPR of Fe8Br and Fe8PCl

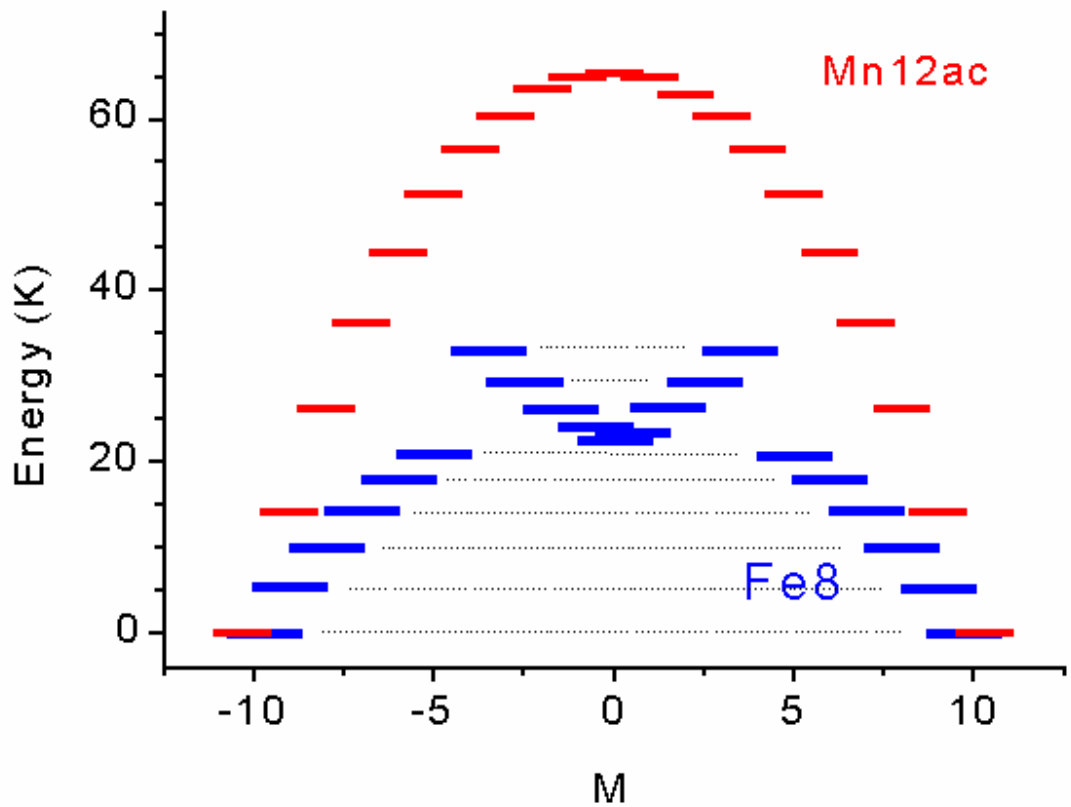


- The HF-EPR spectra of the two compounds are very similar
- the transverse anisotropy is slightly larger for Fe8PCl

The split levels of S= 10 can be observed through Inelastic Neutron Scattering

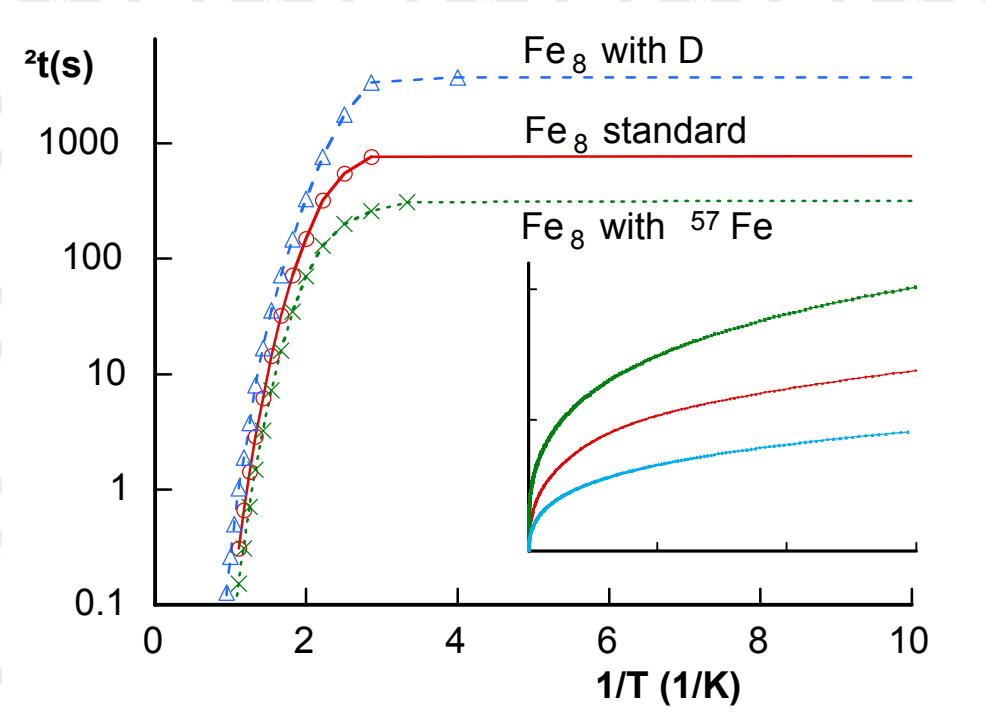


Zero field splitting of the ground S= 10 state of Mn12Ac and Fe8



The relaxation times depend on the magnetic isotopes

Below 300 mK the relaxation is independent of T: tunnel mechanism



If ^{57}Fe (I=1/2) replaces ^{56}Fe (I=0) the relaxation time decreases

If ^{2}H replaces ^{1}H the relaxation time increases

Where to go?

- Larger clusters
- Larger spins
- Antiferromagnetic rings

MAGMA Net
NETWORK OF EXCELLENCE

Angewandte Chemie

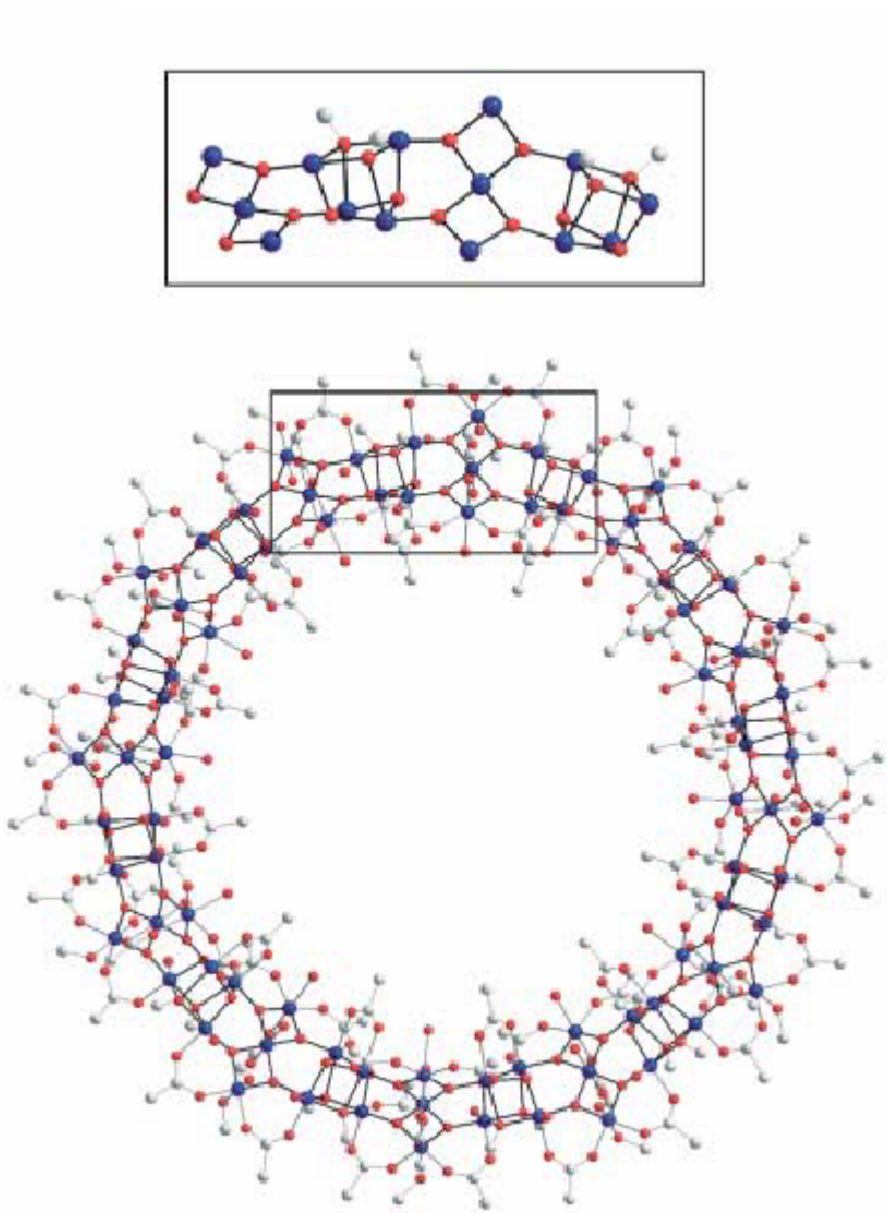
Cluster Compounds

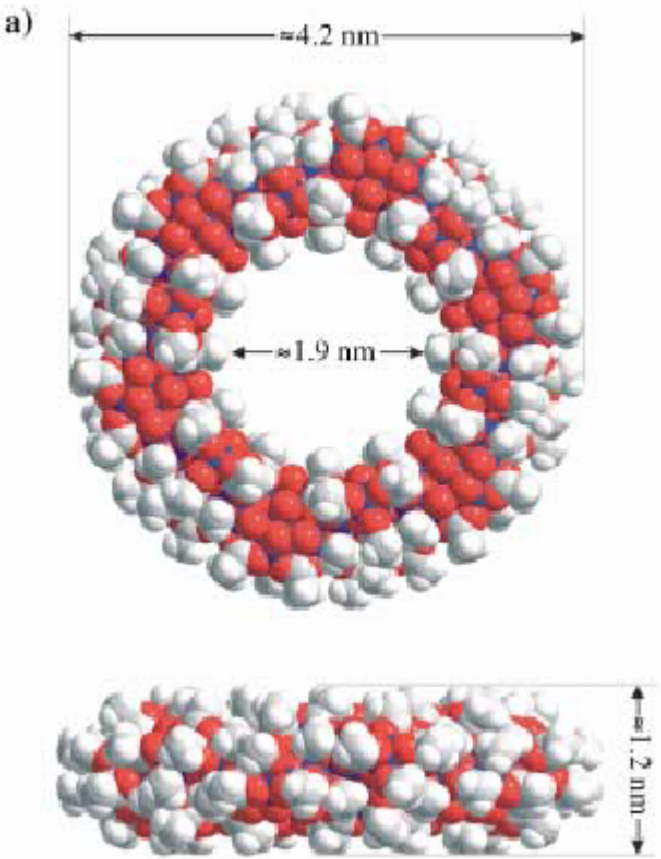
VIP

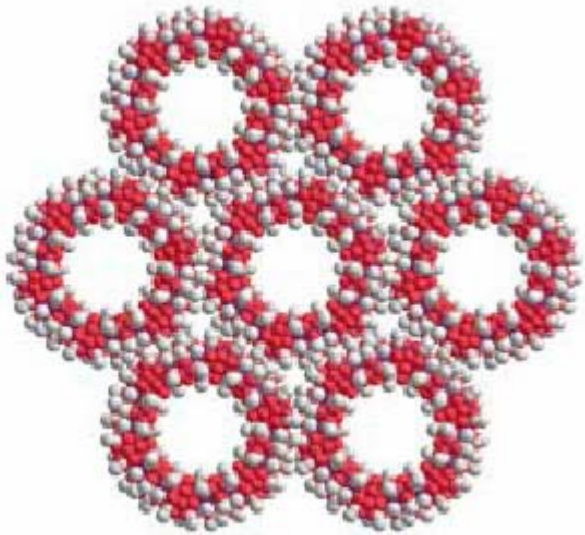
Giant Single-Molecule Magnets: A $\{Mn_{84}\}$ Torus and Its Supramolecular Nanotubes**

*Anastasios J. Tasiopoulos, Alina Vinslava, Wolfgang Wernsdorfer, Khalil A. Abboud, and George Christou**

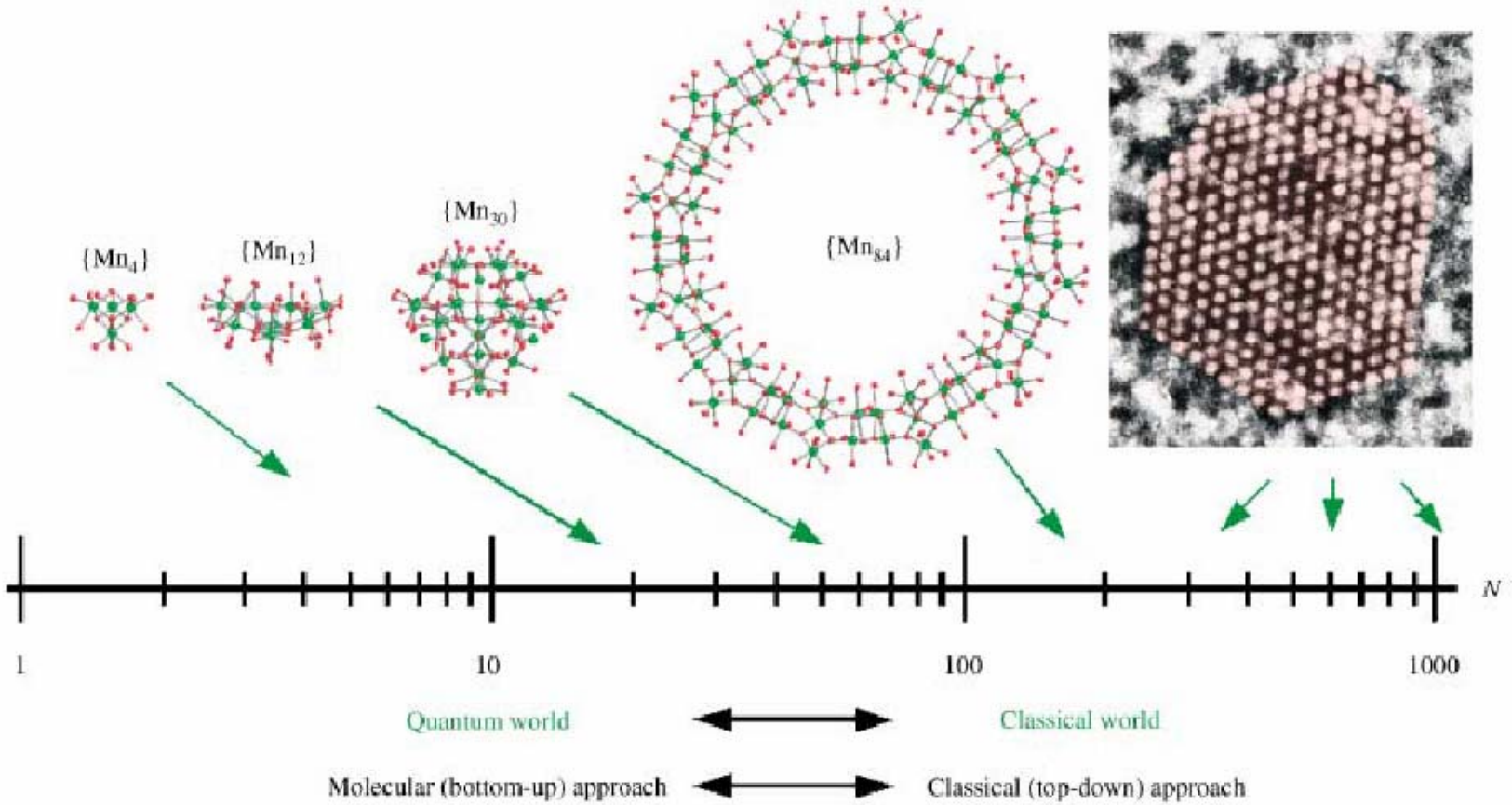
MAGMA Net
NETWORK OF




a)
≈4.2 nm
≈1.9 nm
≈1.2 nm


c)

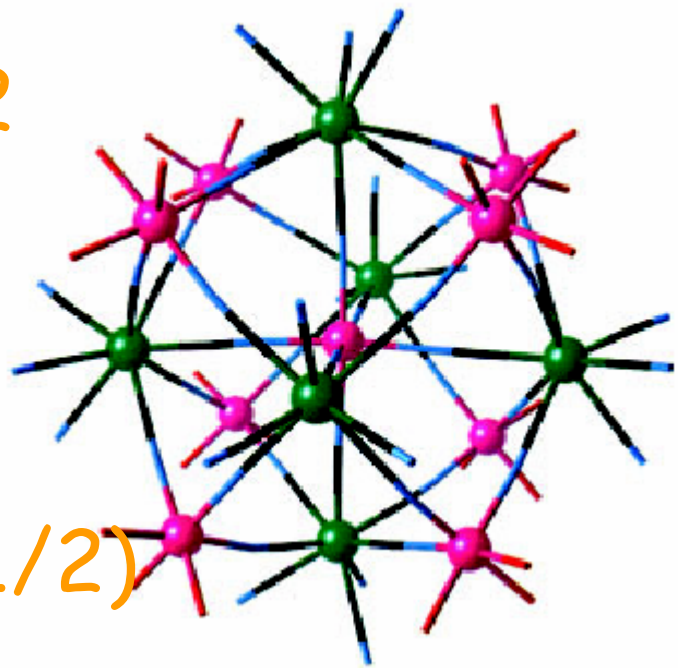

b)


{Mn4}
{Mn12}
{Mn30}
{Mn84}
N
1
10
100
1000
Quantum world
Classical world
Molecular (bottom-up) approach
Classical (top-down) approach

Mn_9Mo_6: S= 51/2?

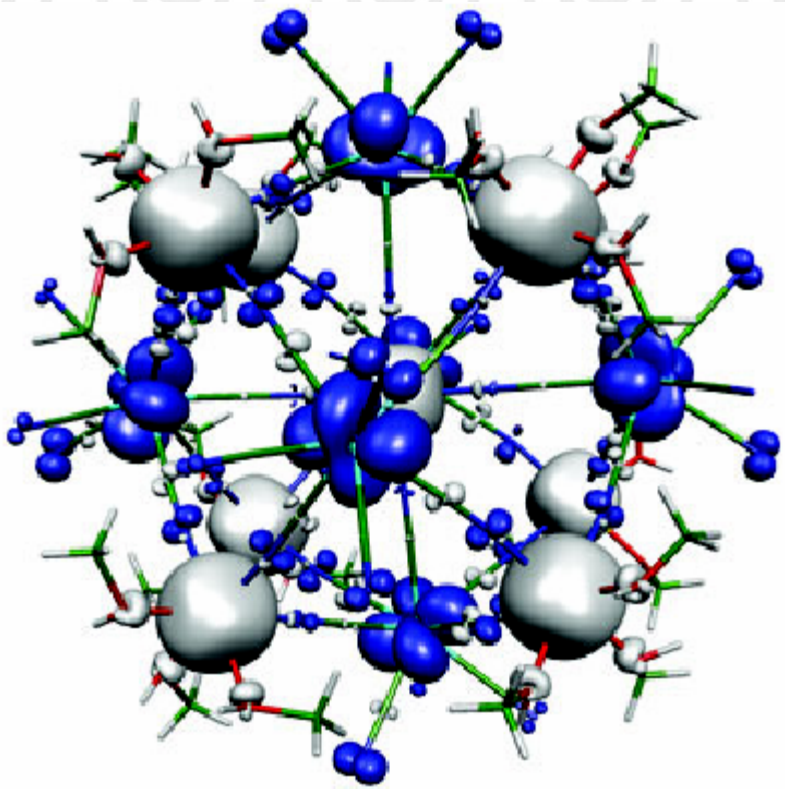
Mn^{2+}, S= 5/2

Mo^{5+}, S= $\frac{1}{2}$



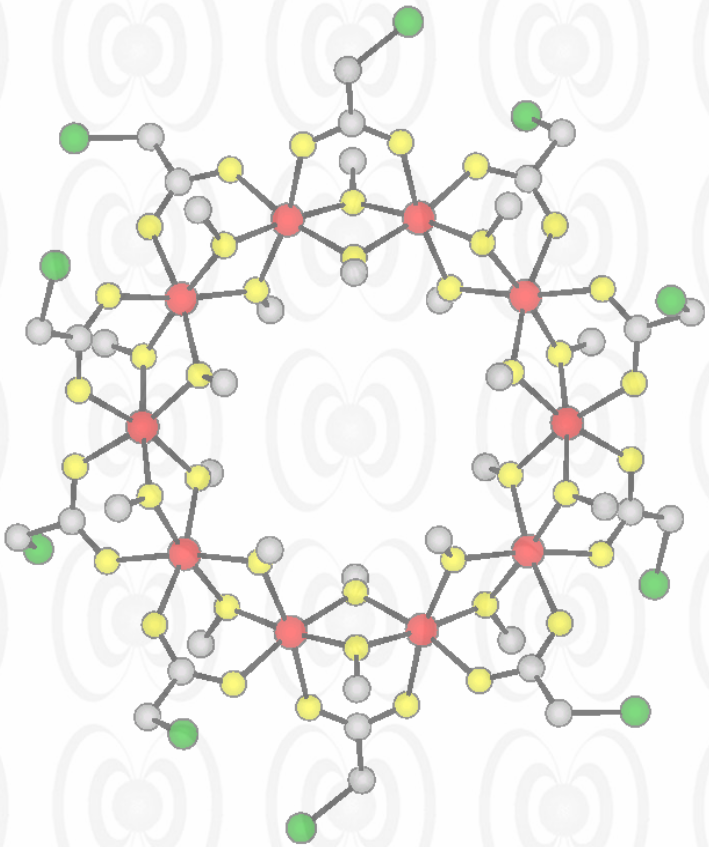
9 (5/3) ± 6 (1/2)

Spin density: S= 39/2



MAGMA Net
NETWORK OF EXCELLENCE

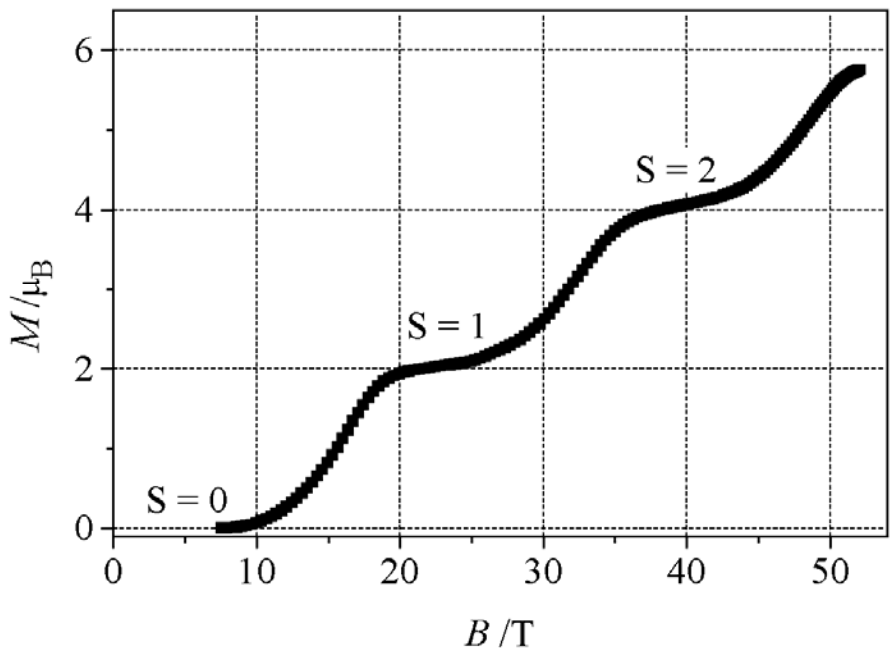
Antiferromagnetic Rings



Ferric Wheel

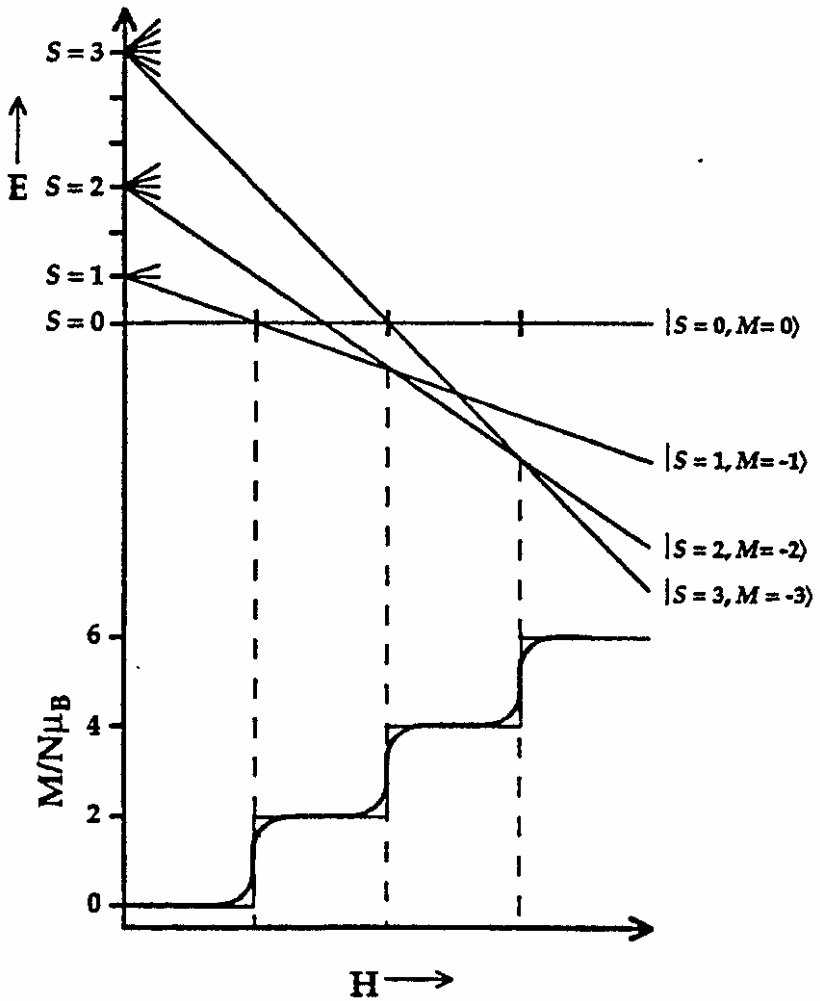
Ferris Wheel

Stepped Magnetization is an evidence of quantum size effects

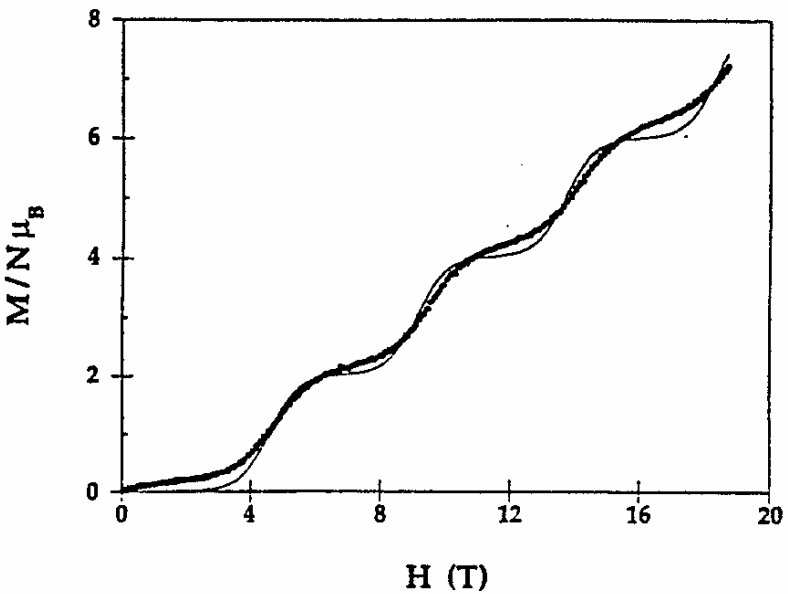


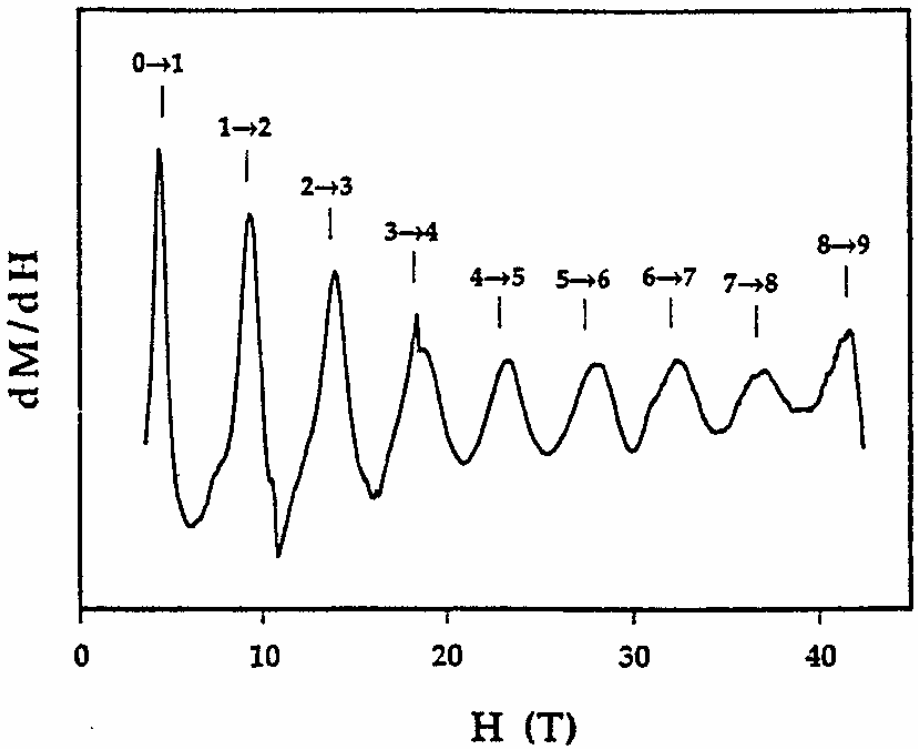
Magnetization of NaFe6 at 1.5 K

The steps measure the energies of the excited spin states with S>0



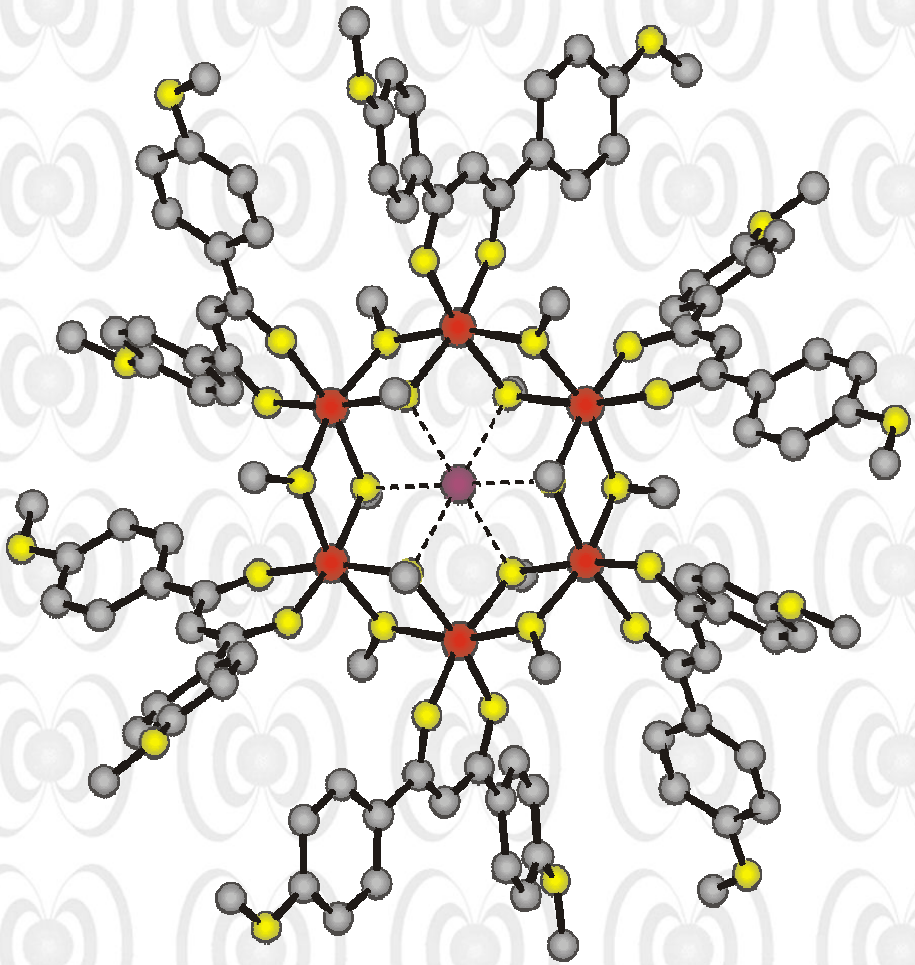
Stepped magnetization in the ferric wheel





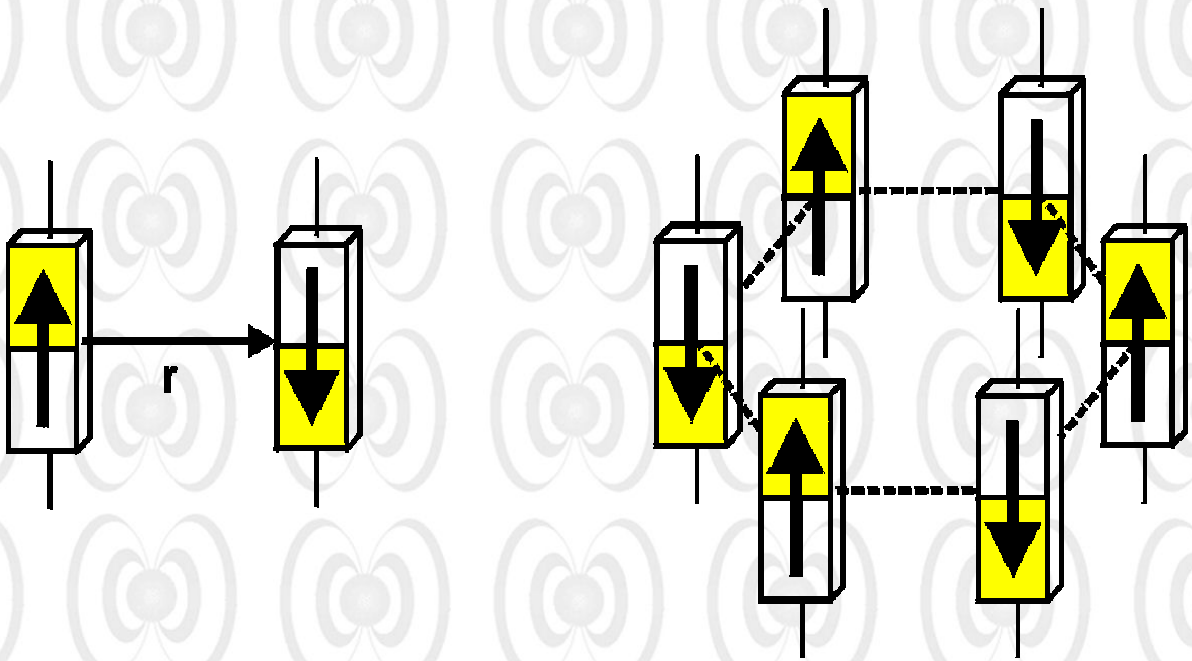
MAGMA Net
NETWORK OF EXCELLENCE

$[NaFe_6(OCH_3)_{12}(pmdbm)_6]ClO_4$

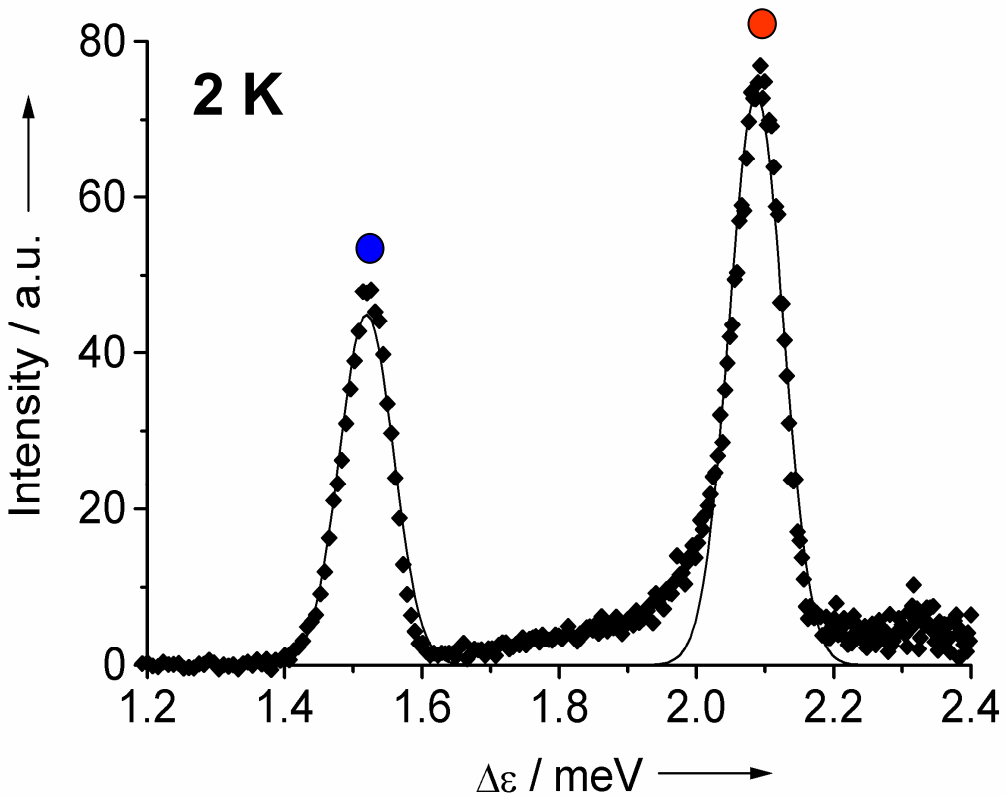


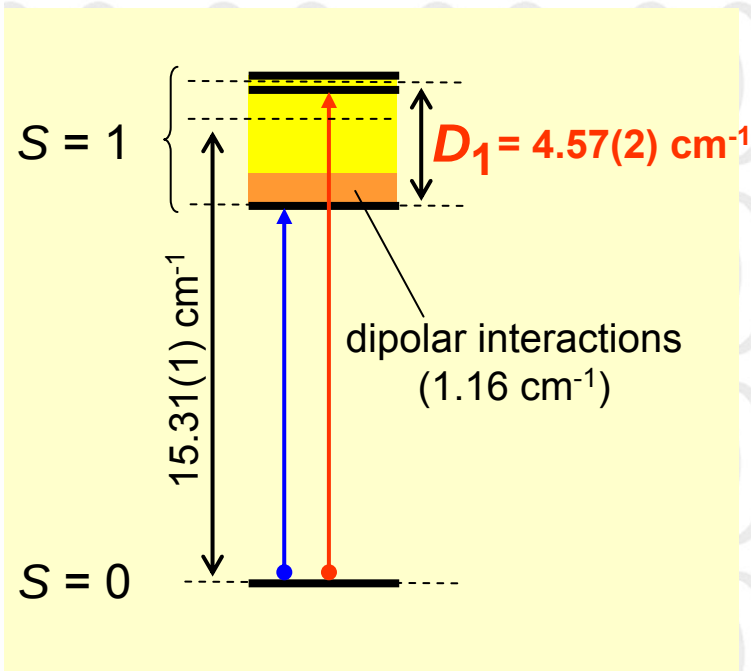
MAGMA Net
NETWORK OF EXCELLENCE

Dipolar Interactions

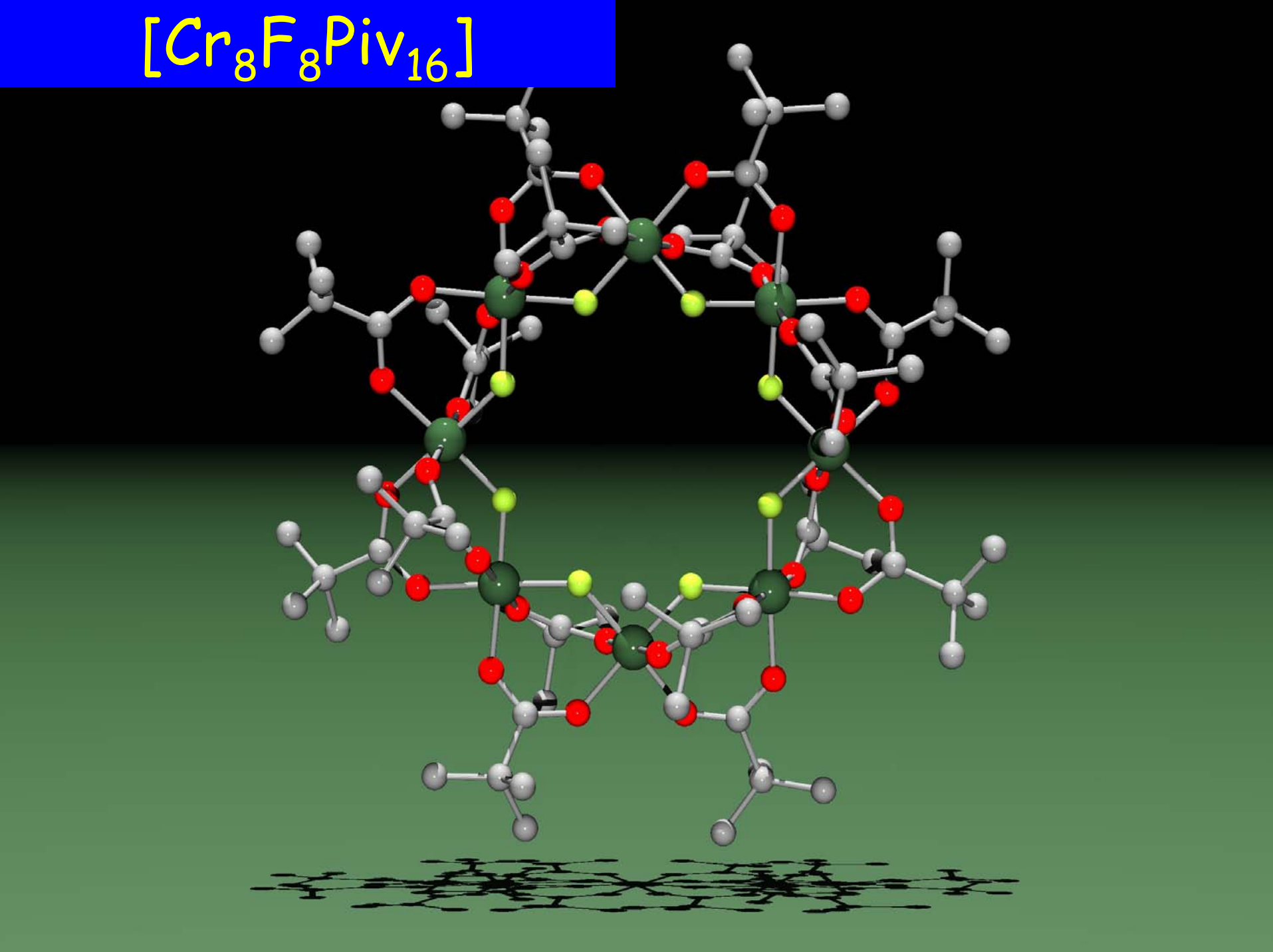


Inelastic Neutron Scattering

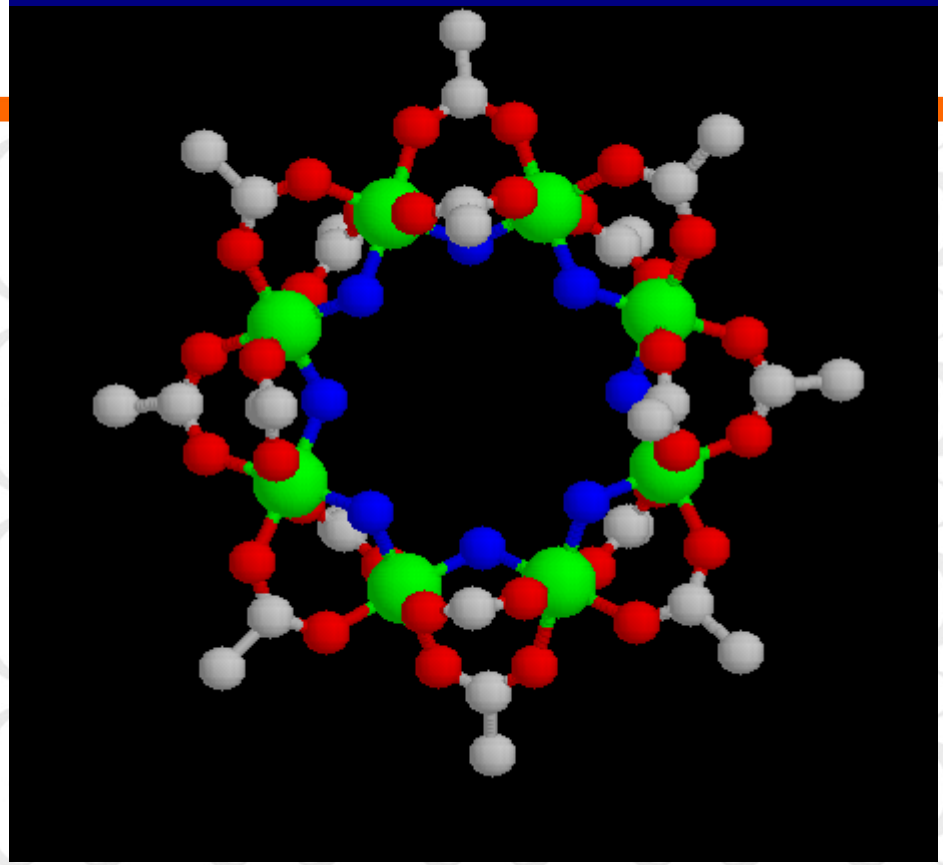




$[Cr_8F_8Piv_{16}]$

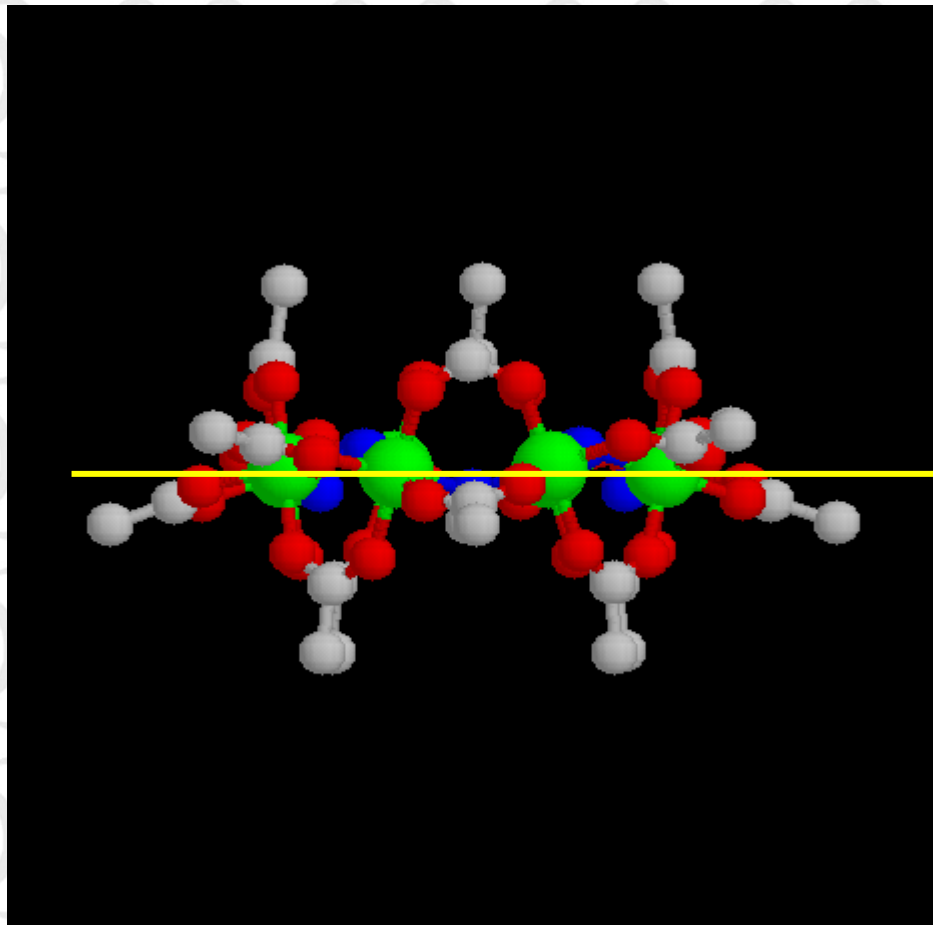


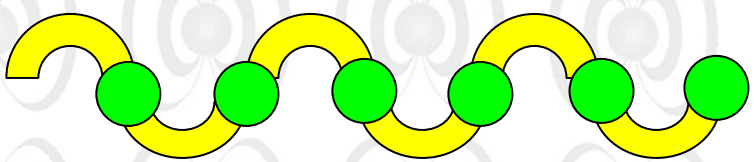
$[Cr_8F_8Piv_{16}]$



The metal ions lie on a plane but the ligands are alternating **above** and **below** this plane

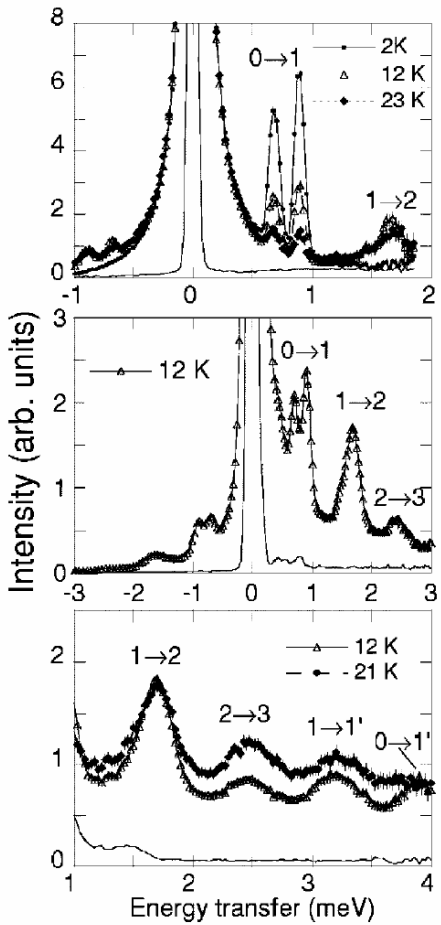
Odd-member rings cannot have this structure

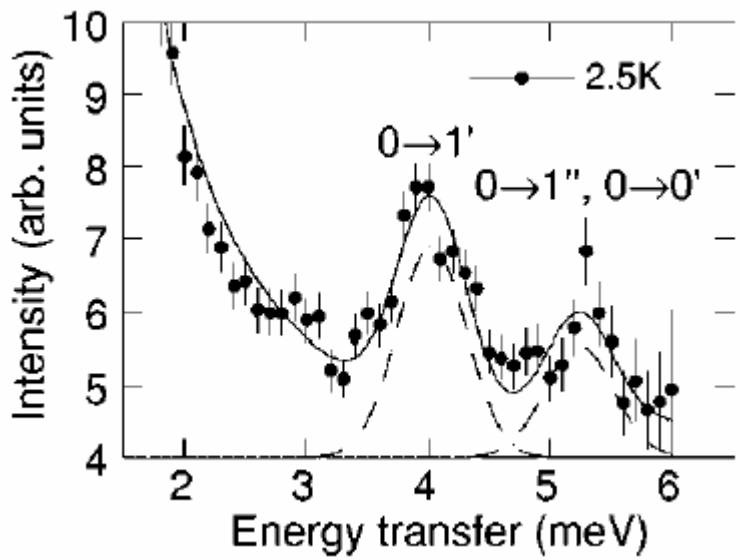




MAGMA Net
NETWORK OF EXCELLENCE

INS of Cr8





Lowest energy levels

S. CARRETTA *et al.*

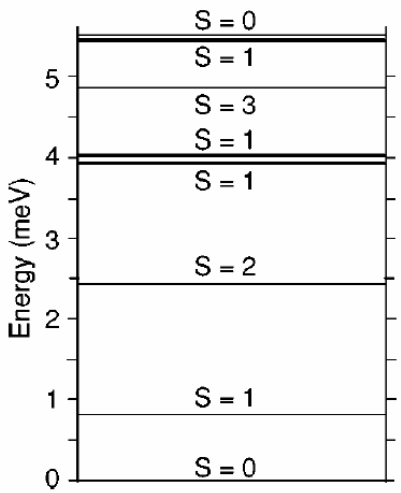


FIG. 4. Lowest energy spin multiplets calculated for tetragonal Cr_8 assuming isotropic exchange interactions only, with parameters corresponding to the best fit of INS spectra ($J = J' = 1.46$ meV). Thick lines indicate twofold degenerate S levels.

TABLE II. Lowest eigenvalues (in meV) and main contributions to the eigenvectors of Cr_8 evaluated with the best-fit parameters given in the text.

Energy (meV)	S-mixing eigenvectors $\Sigma_i c_i \lvert S,M\rangle_i$
0	$0.9981\lvert 0,0\rangle + 0.0606\lvert 2,0\rangle$
0.69	$0.9995\lvert 1,0\rangle + 0.03\lvert 3,0\rangle$
0.86	$0.7069(\lvert 1,1\rangle + \lvert 1,-1\rangle) + 0.0171(\lvert 3,1\rangle + \lvert 3,-1\rangle)$
0.90	$0.7068(\lvert 1,1\rangle - \lvert 1,-1\rangle) + 0.0192(\lvert 3,1\rangle - \lvert 3,-1\rangle)$
2.36	$0.9929\lvert 2,0\rangle + 0.073(\lvert 2,2\rangle + \lvert 2,-2\rangle) - 0.0592\lvert 0,0\rangle$
2.38	$0.7071(\lvert 2,1\rangle + \lvert 2,-1\rangle)$
2.41	$0.7071(\lvert 2,1\rangle - \lvert 2,-1\rangle)$
2.53	$0.7071(\lvert 2,-2\rangle - \lvert 2,2\rangle)$
2.53	$0.7033(\lvert 2,2\rangle + \lvert 2,-2\rangle) - 0.1025\lvert 2,0\rangle + 0.0165\lvert 0,0\rangle$

TABLE I. Single-ion and spin-spin projection coefficients and zero-field splitting parameters, in meV, for excited spin states S with exchange parameters given in the text. $D^{(n)}*$ and $E^{(n)}*$ are the ZFS parameters determined in Ref. 19.

S,n	$d_i^{(n)}$	$d_{i,i+1}^{(n)}$	$d_{i,i+2}^{(n)}$	$D^{(n)}$	$E^{(n)}$	$D^{(n)}*$	$E^{(n)}*$
1	−0.62	0.85	−0.99	0.188	0.02	0.20	0.004
2	−0.14	0.21	−0.22	0.044	0.005	0.046	0.001
3	−0.06	0.11	−0.091	0.0196	0.002		

MAGMA Net
NETWORK OF EXCELLENCE

MAGMANet

Molecular Approach to Nanomagnets and Multifunctional Materials

Coord.: Dante Gatteschi (INSTM)

The entire range of expertise necessary for carrying out research in molecular magnetism is involved, from theoretical and solid state physics, to synthetic organic and inorganic chemistry.

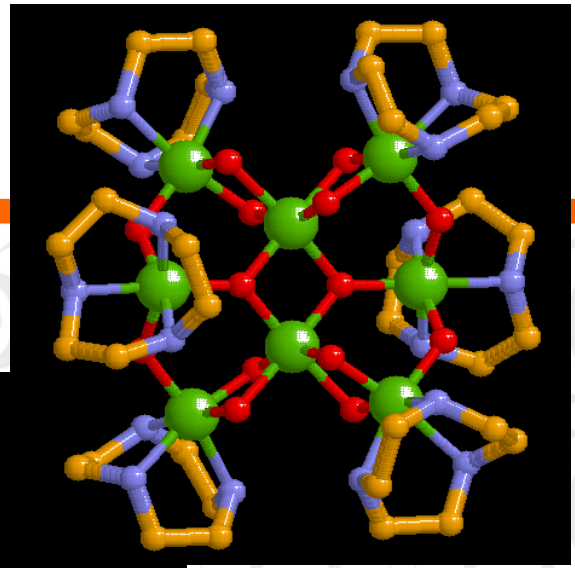
MAGMANet Geography

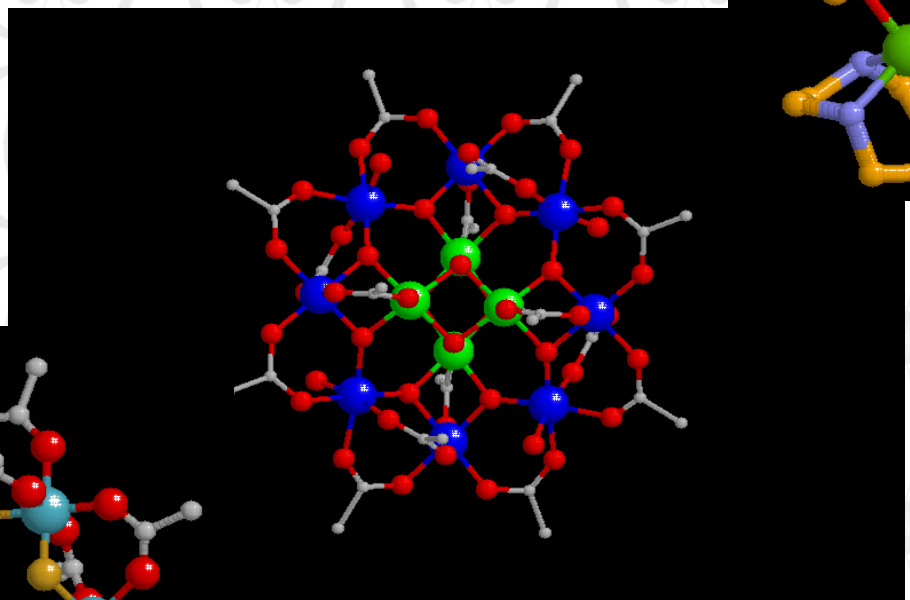
21 leading nodes (28 teams) in the field from 10 countries.

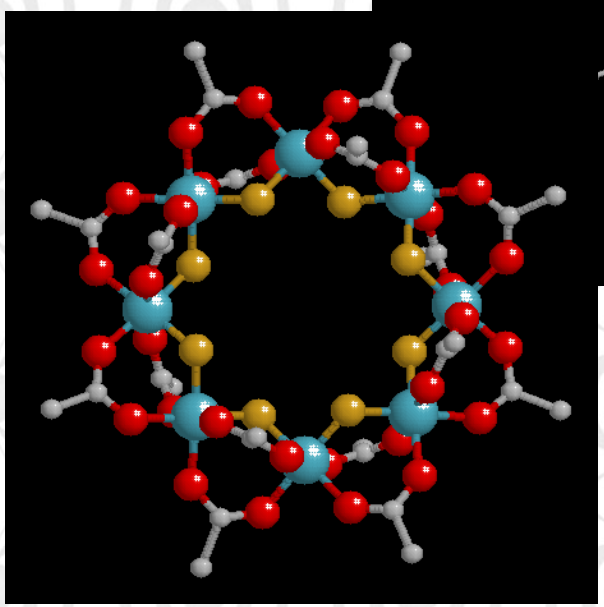
143 researchers and 81 PhD students integrated at Network start

MAGMA Net
NETWORK OF EXCELLENCE

...thank







you