

MOLECULE-BASED MAGNETS: Concept and design



I. Molecular magnetism:

- Concept
- Rules and tools
- Rational design of a magnet

II. Polyfunctional Magnets

- Photo-triggered magnets, Chiral magnets, Porous magnets, conducting magnets ...



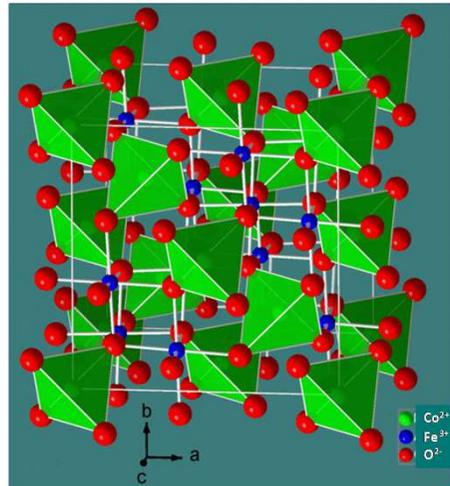
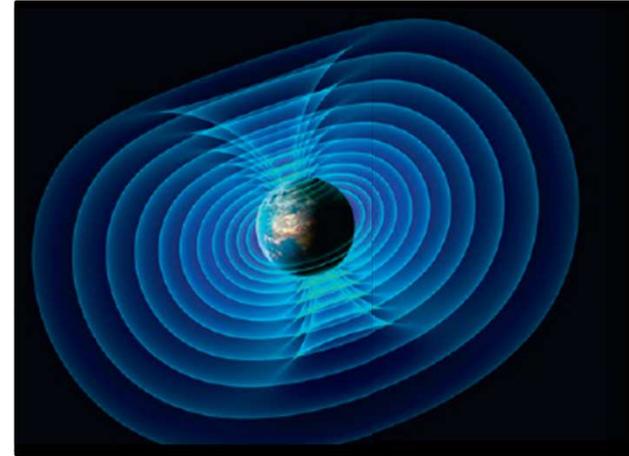
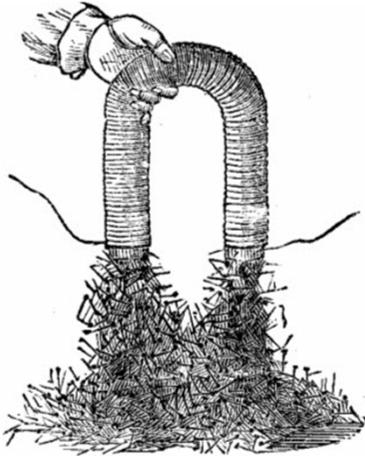
School on “Magnetism of Molecules”, Bangalore, November 2018

Jean-Pascal SUTTER, Coordination Chemistry Laboratory of CNRS, Toulouse (France)



I. Molecular Magnetism: Concept

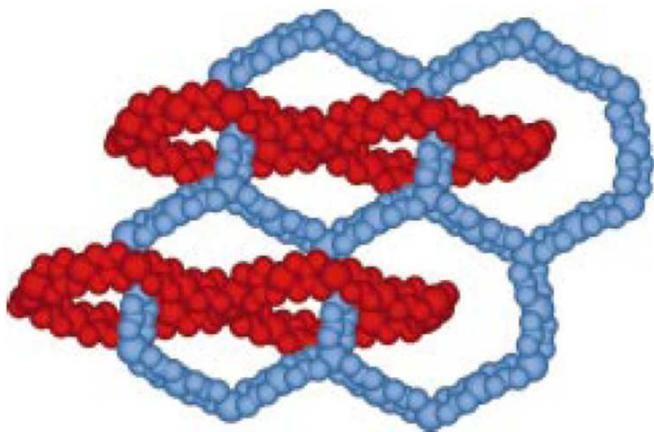
Traditional magnets: metals (iron), metal oxides (ferrite), ...



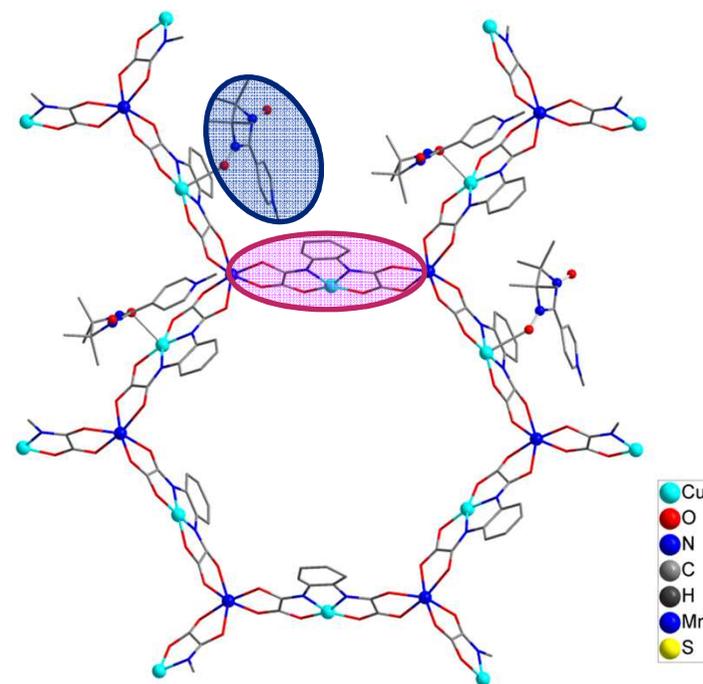
Crystal structure of Cobalt ferrite
 CoFeO_4 ($\text{CoO-Fe}_2\text{O}_3$)

I. Molecular Magnetism: Concept

Molecule-based magnets: The structural **building blocks are molecular** in nature. These building blocks are either purely **organic molecules**, **coordination compounds** or a **combination of both**.



Ref: O. Kahn et al. *Chem. Eur. J.* **1999**, **5**, 1486

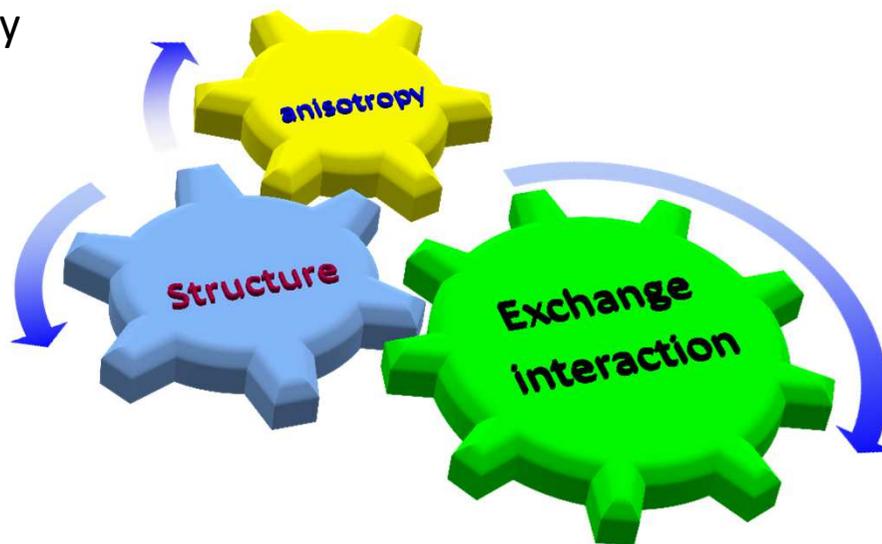


I. Molecular Magnetism: Concept

Molecule-based magnets: The structural **building blocks are molecular** in nature. These building blocks are either purely **organic molecules**, **coordination compounds** or a **combination of both**.

The observed magnetic behavior is determined by chemical and physical parameters:

- chemical scaffold,
- Paramagnetic centers,
- the exchange interaction between them,
- and the magnetic anisotropy



I. Molecular Magnetism: Concept

Main approach: coordination polymers

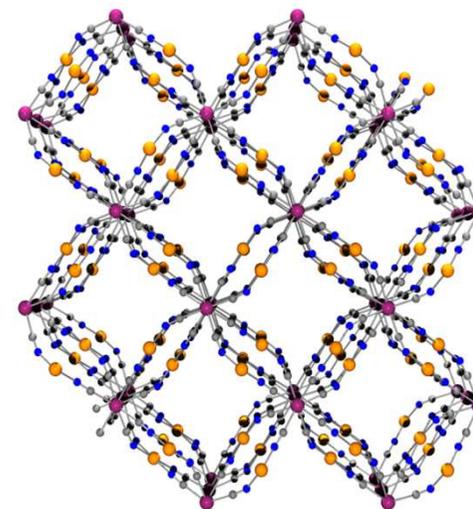
- chemical architecture formed by paramagnetic metal ions linked by bridging ligands (diamagnetic or paramagnetic)
- **exchange interactions** take place between the paramagnetic centers
- the macroscopic property is the result of a **collective behavior** and not the sum of individual behaviors



molecules

At the molecular level...

- ↪ pre-defined structural features
- ↪ seat of the elementary property



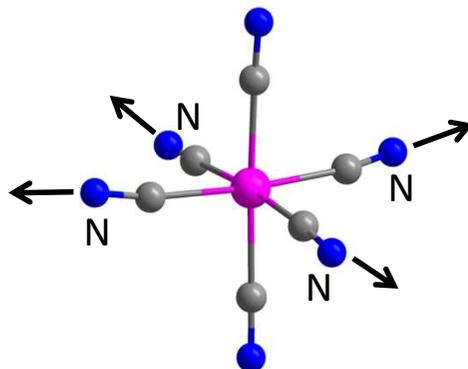
material

Collective properties

I. Molecular Magnetism: Rules and tools

=> The rational design of a magnet has to take into account the construction of the chemical architecture and of its function (property)

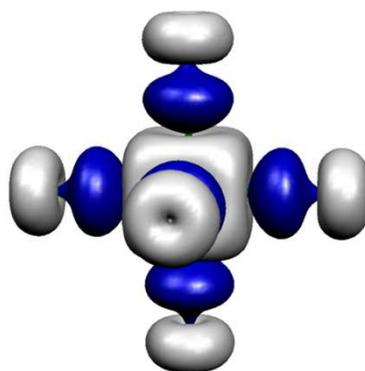
The building unit ...



from the angle of

chemical construction

↪ supramolecular chemistry



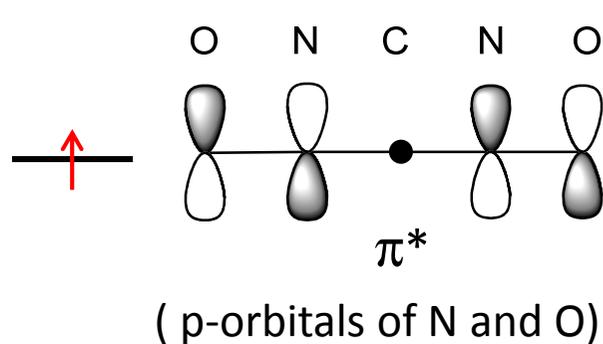
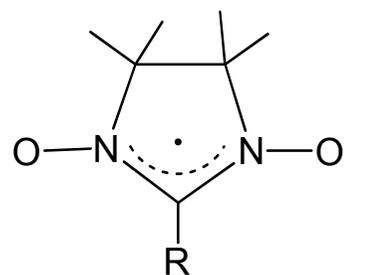
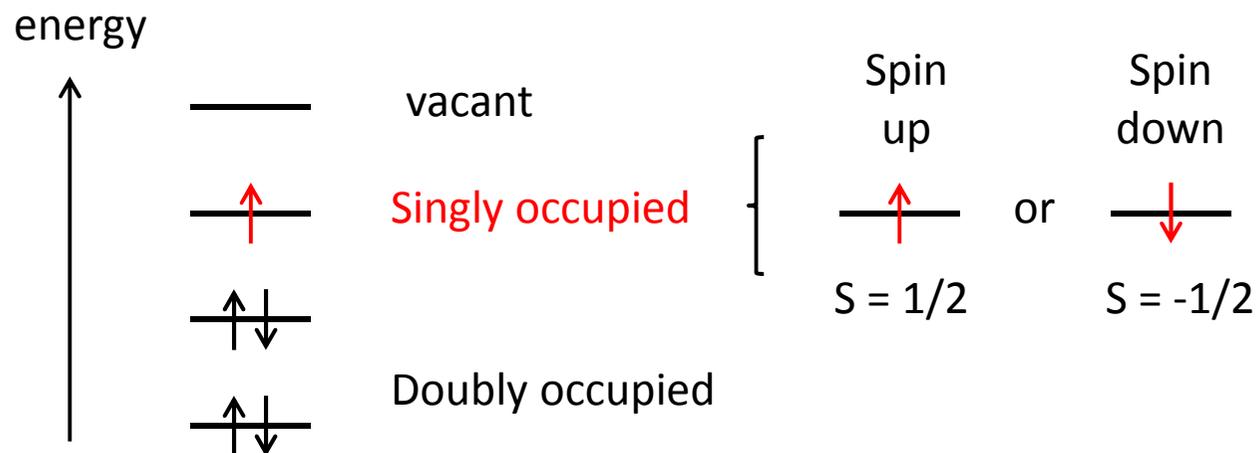
Property

↪ Exchange interaction, magnetic anisotropy, additional property

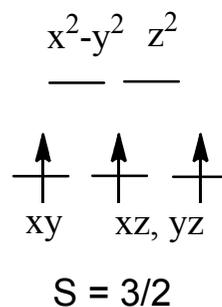
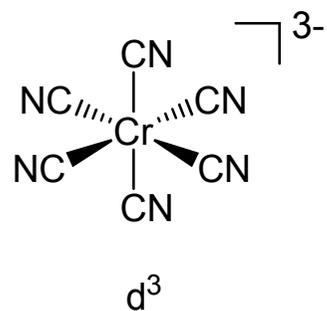
⇒ Some rules and tools to guide the chemist

Electrons in orbitals ...

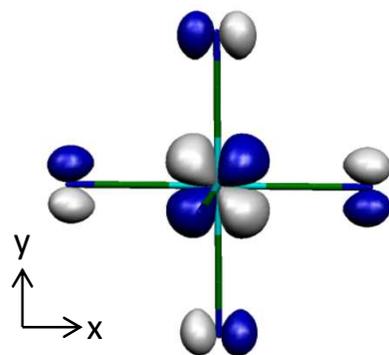
Singly Occupied Molecular Orbital (SOMO) or “magnetic” orbitals



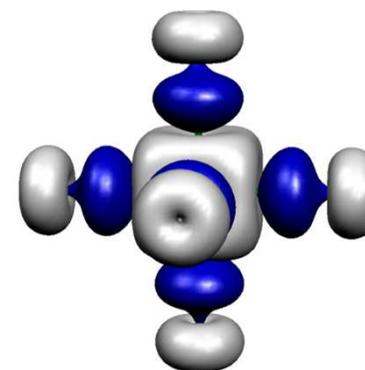
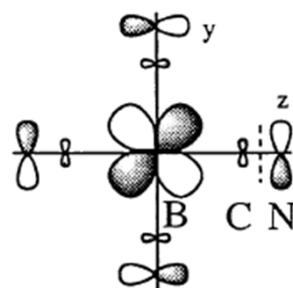
Magnetic orbitals in metal complexes:



Cr^{III} in O_h symmetry
 $(\mu_{eff} = 3.90 \mu_B; C = 1.875 \text{ cm}^3\text{mol}^{-1})$



(SOMO : Singly Occupied Molecular Orbital)



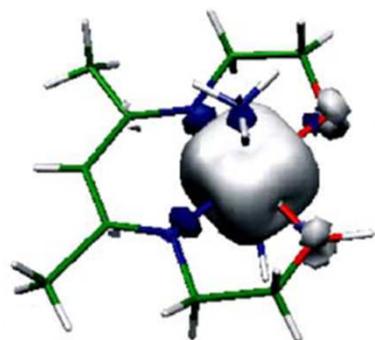
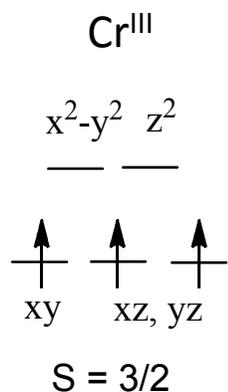
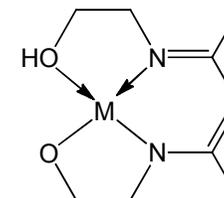
Spin density distribution

Cr: $+3.042 \mu_B$
 C: $-0.088 \mu_B$
 N: $+0.0686 \mu_B$

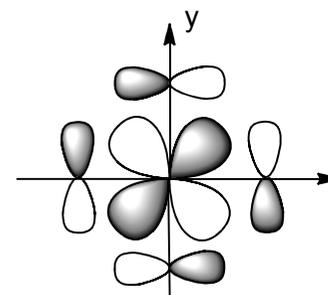


The magnetic orbitals contribute to the delocalization of the magnetic orbital from metal to the ligands

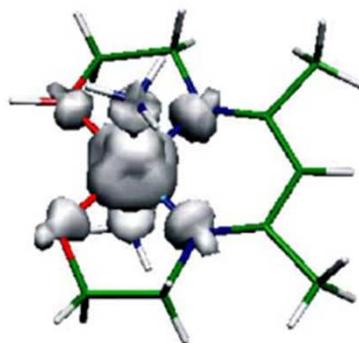
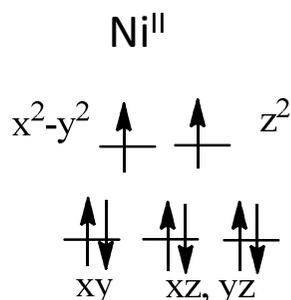
The magnetic orbitals depend on the electronic configuration of the metal ion and on the ligands



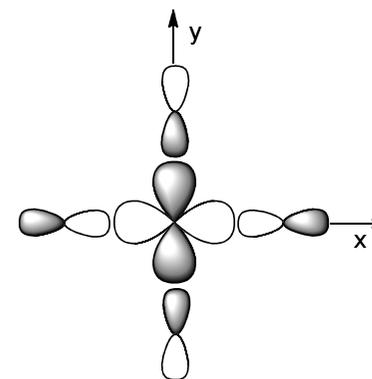
Spin density borne by π orbitals of the O and N atoms



Desplanches *et coll.* Chem. Comm. **2002**, 2614



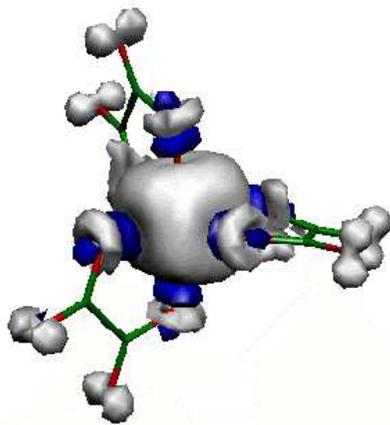
The spin density is found in the σ orbitals of the ligand atoms



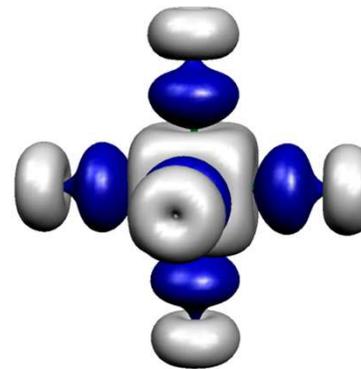
Magnetic orbital :	on metal ion		on ligand's atoms
	t_{2g}	↔	π
	e_g	↔	σ

Magnetic orbitals of a molecular unit:

- **molecular orbitals** formed with the orbitals bearing the unpaired electrons
- they contribute to the **delocalization** of the magnetic information **from metal to the ligands**
- they are visualized by the spin density distribution
- they **mediate** the exchange interactions



$[\text{Cr}(\text{oxalate})_3]^{3-}$
+0.0120 μ_B on the peripheral
O atoms



$[\text{Cr}(\text{CN})_6]^{3-}$
Cr: +3.042 μ_B
C: -0.088 μ_B
N: +0.0686 μ_B

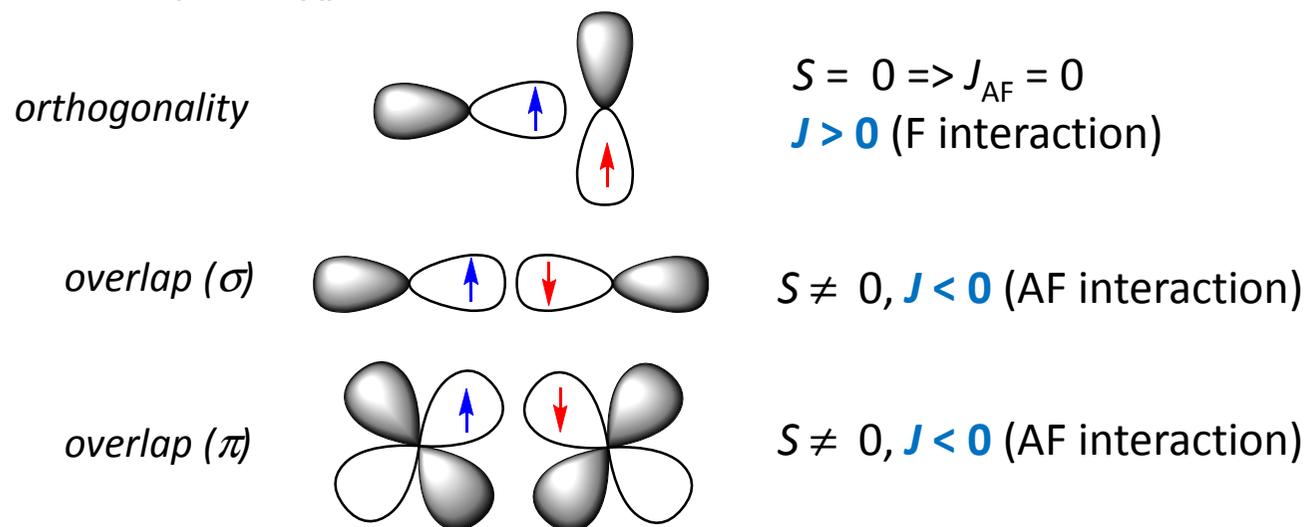
Orbital overlap and sign of the exchange interaction

The exchange interaction: Kahn's model ¹

$$J = 2k + 4\beta S$$

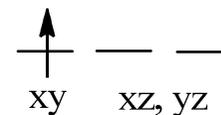
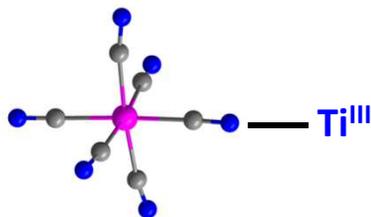
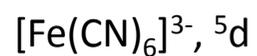
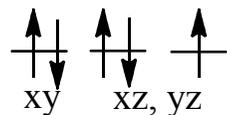
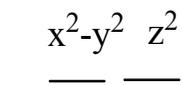
> 0 < 0
 \downarrow \downarrow
 J_F J_{AF}

k = bielectronic exchange integral (> 0)
 β = monoelectronic transfer integral (< 0)
 S = monoelectronic overlap integral (> 0)



¹ Kahn et coll. *Chem. Phys. Lett.* **1981**, 82, 534

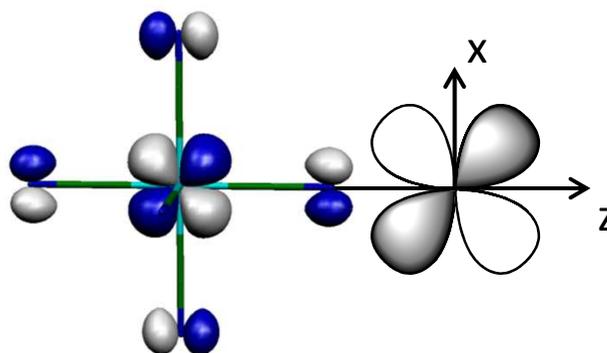
Case of two centers with single unpaired electron



1 AF exchange pathway

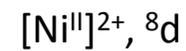
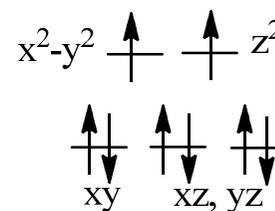
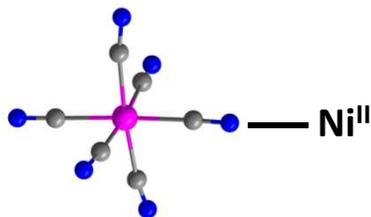
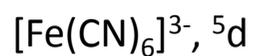
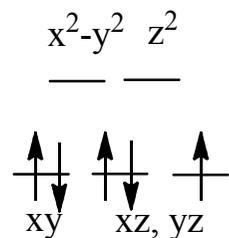


$$J_{\text{FeTi}} = J_{\text{AF}} (< 0)$$

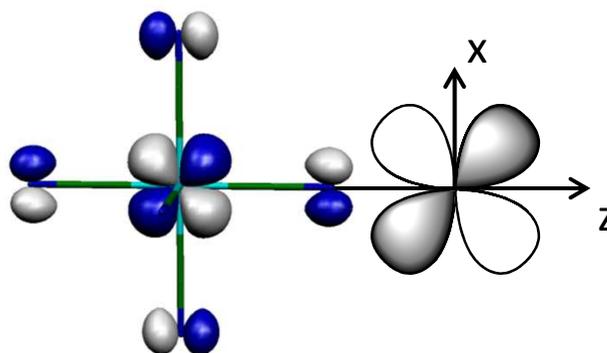


- One unpaired electron on each site
- Overlap of the magnetic orbitals

Case of two centers with several unpaired electrons (example 1)



0 AF exchange pathway

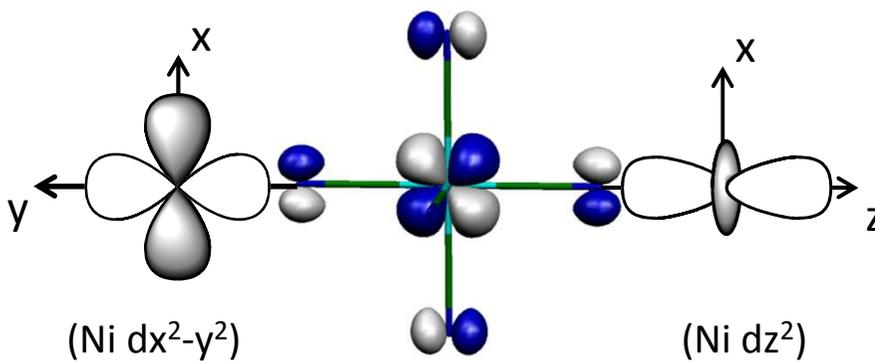


No unpaired electrons in these orbitals

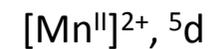
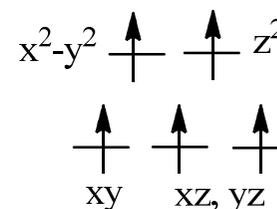
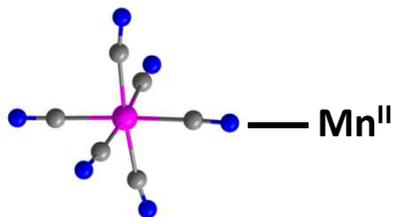
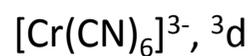
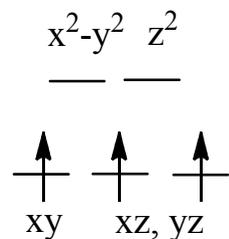
2 F exchange pathways



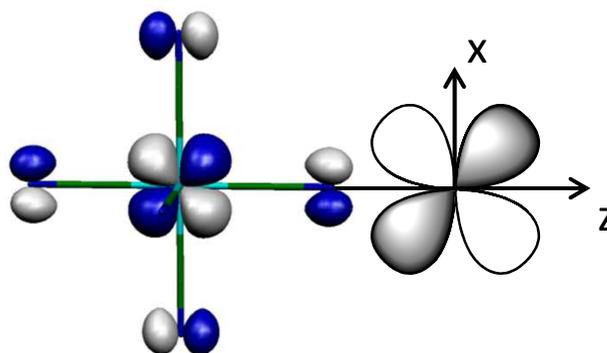
$$J_{\text{FeNi}} = 2J_{\text{F}} (> 0)$$



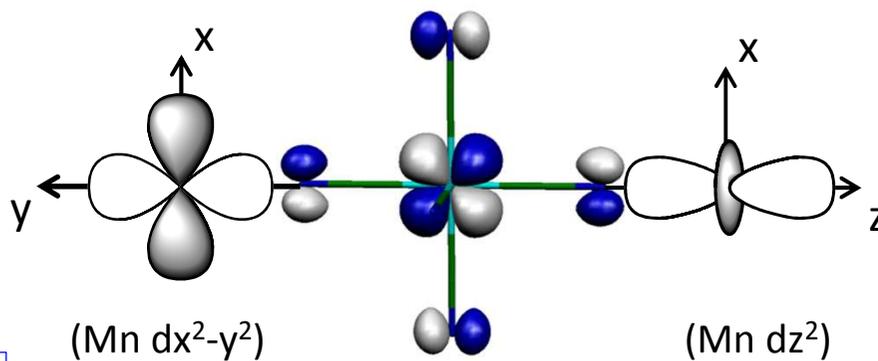
Case of two centers with several unpaired electrons (example 2)



9 AF exchange pathways

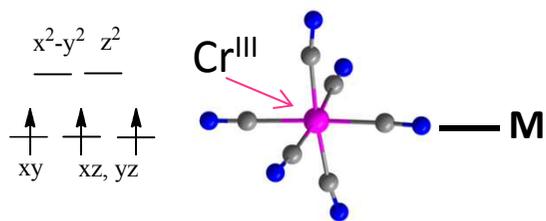


6 F exchange pathways

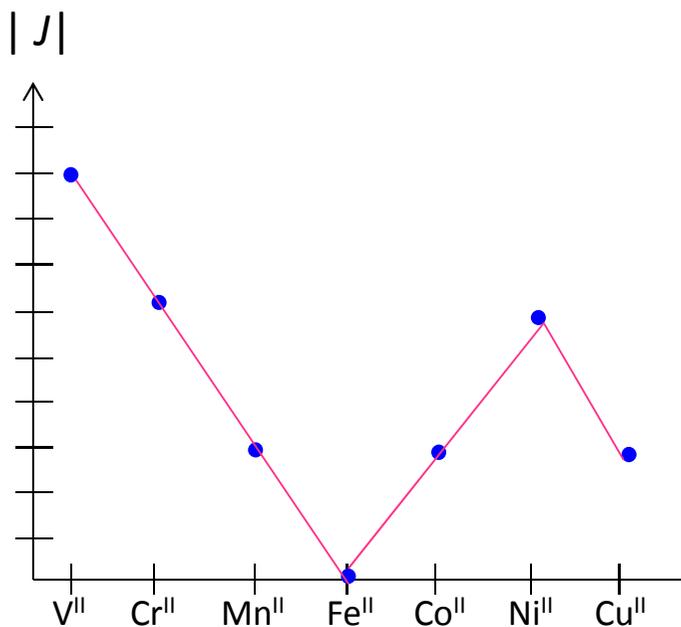


$$J = 6J_F + 9J_{AF}$$

→ $J_{\text{CrMn}} < 0$ (antiferromagnetic)

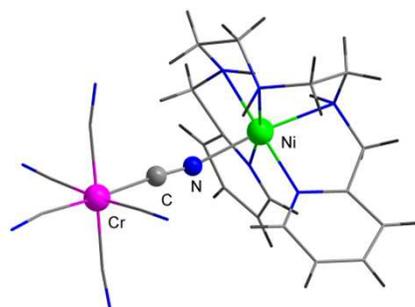


Variation of the strength of J_{CrM} along the series for $|J_F| = |J_{AF}|$, actually the AF contribution is stronger than the F one.

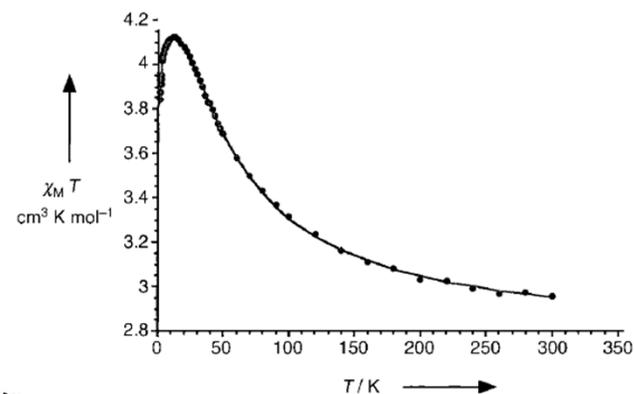
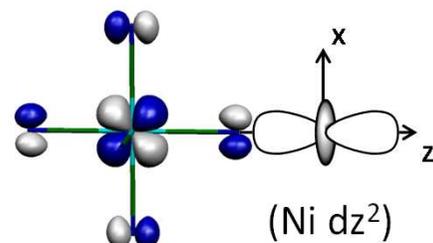
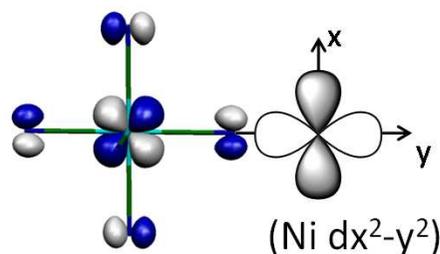


M	Electronic configuration (High spin state)	Exchange pathways	Anticipated J_{CrM}
V ^{II} , d ³	x^2-y^2 — — z^2 \uparrow \uparrow \uparrow xy xz, yz	$9J_{AF}$	AF (9)
Cr ^{II} , d ⁴	x^2-y^2 \uparrow — z^2 \uparrow \uparrow \uparrow xy xz, yz	$3J_F + 9J_{AF}$	AF (6)
Mn ^{II} , d ⁵	x^2-y^2 \uparrow \uparrow z^2 \uparrow \uparrow \uparrow xy xz, yz	$6J_F + 9J_{AF}$	AF (3)
Fe ^{II} , d ⁶	x^2-y^2 \uparrow \uparrow z^2 $\uparrow\downarrow$ \uparrow \uparrow xy xz, yz	$6J_F + 6J_{AF}$	none
Co ^{II} , d ⁷	x^2-y^2 \uparrow \uparrow z^2 $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow xy xz, yz	$6J_F + 3J_{AF}$	F (3)
Ni ^{II} , d ⁸	x^2-y^2 \uparrow \uparrow z^2 $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ xy xz, yz	$6J_F$	F (6)
Cu ^{II} , d ⁹	x^2-y^2 $\uparrow\downarrow$ \uparrow z^2 $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ xy xz, yz	$3J_F$	F (3)

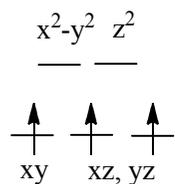
Orbital overlap and sign of the exchange interaction: essential role of the bridging ligand and its connection to the metal ions



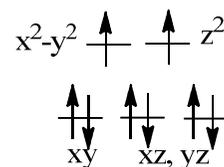
$J_{\text{CrNi}} = 18 \text{ cm}^{-1}$ (ferromagnetic)



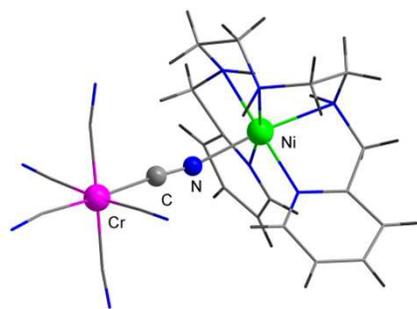
Cr^{III}



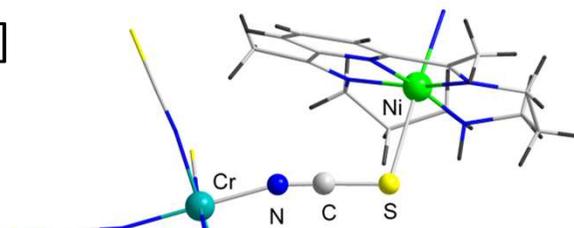
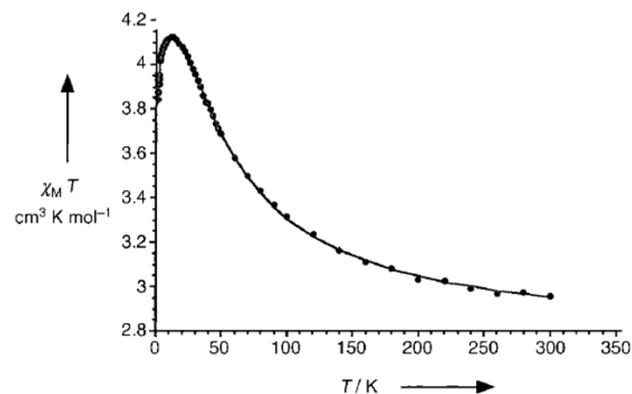
[Ni]



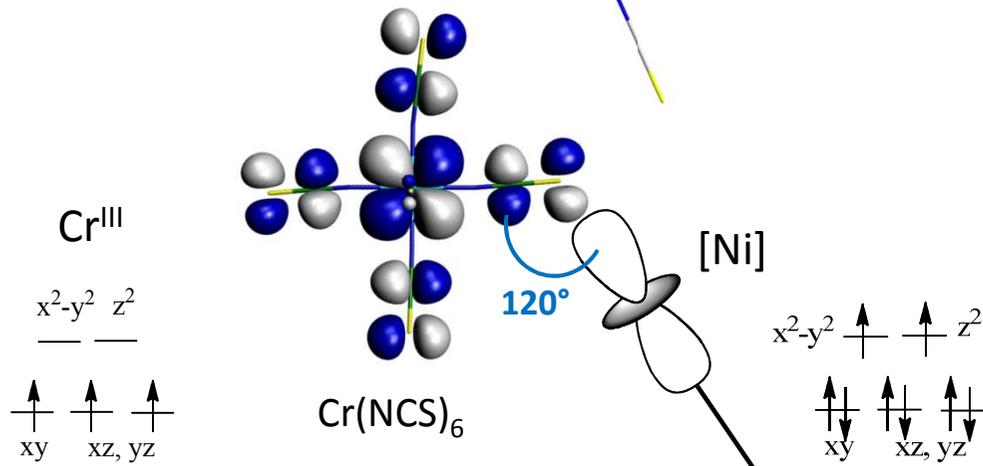
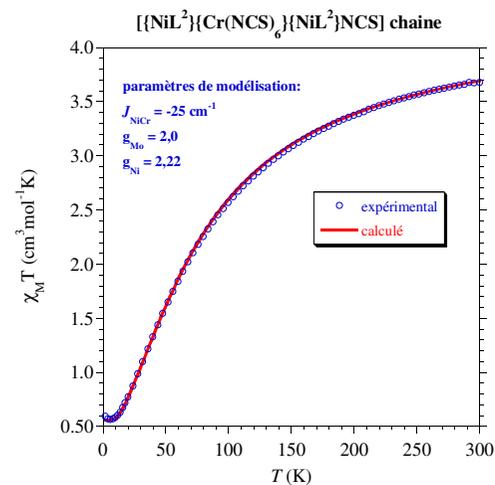
Orbital overlap and sign of the exchange interaction: essential role of the bridging ligand and its connection to the metal ions



$J_{\text{CrNi}} = 18 \text{ cm}^{-1}$ (ferromagnetic)

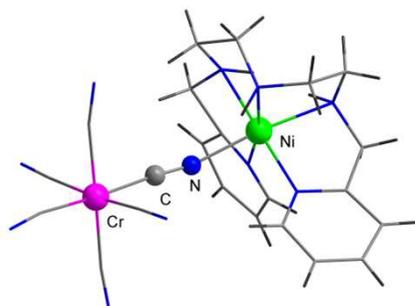


$J_{\text{CrNi}} = -25 \text{ cm}^{-1}$ (antiferromagnetic)

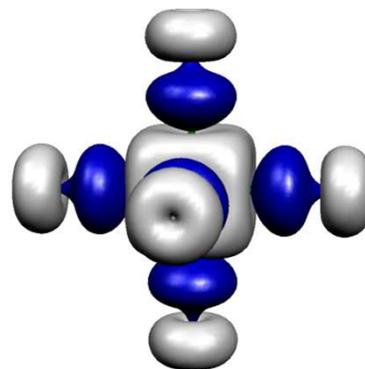


Orbital overlap and strength of the exchange interaction: importance of the metal center (3d vs 4d vs 5d)

Exchange interactions \longleftrightarrow spin density on the bridging ligand

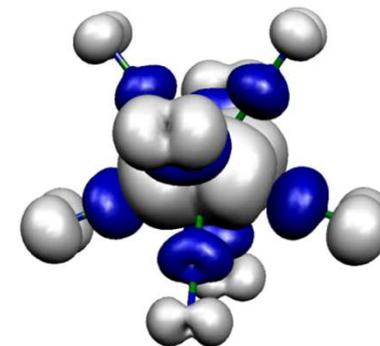


Cr^{III}: $J = 18 \text{ cm}^{-1}$ [1]
 Mo^V: $J = 27 \text{ cm}^{-1}$ [2]
 W^V: $J = 37 \text{ cm}^{-1}$ [2]



$[\text{Cr}(\text{CN})_6]^{3-}$

Cr: $+3.042 \mu_B$
 C: $-0.088 \mu_B$
 N: $+0.0686 \mu_B$



$\{\text{W}(\text{CN})_8\}^{3-}$

M $+0.825 \mu_B$
 C_A $-0.0244 \mu_B$
 C_B $-0.0416 \mu_B$
 N_A $+0.0322 \mu_B$
 N_B $+0.0779 \mu_B$

[1] V. Marvaud et al. *Chem. Eur. J.* **2003**, *9*, 1692

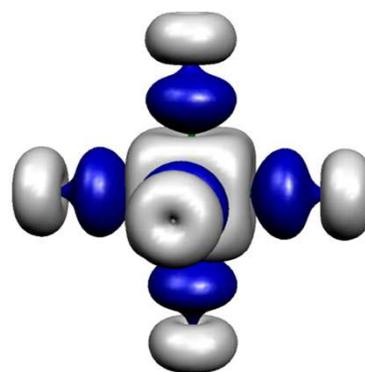
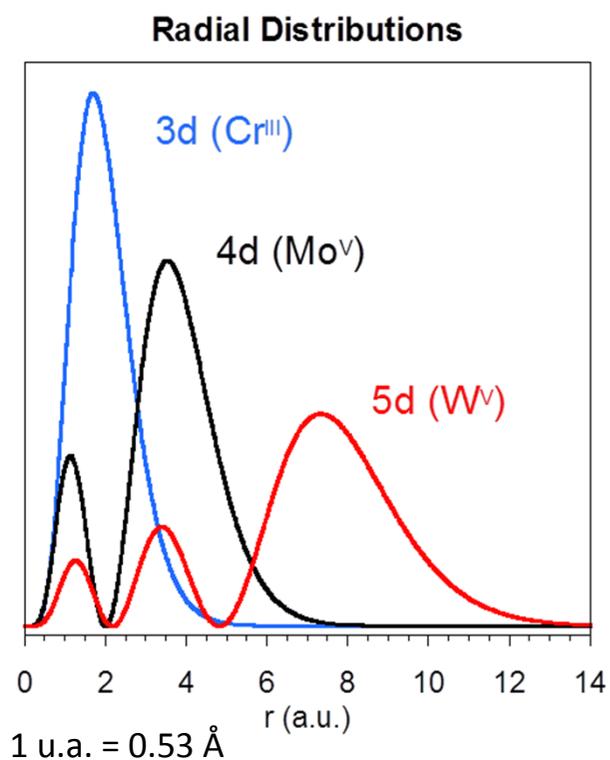
[2] Visinescu et al. *JACS* **2006**, *128*, 10202

Orbital overlap and strength of the exchange interaction: importance of the metal center (3d vs 4d vs 5d)

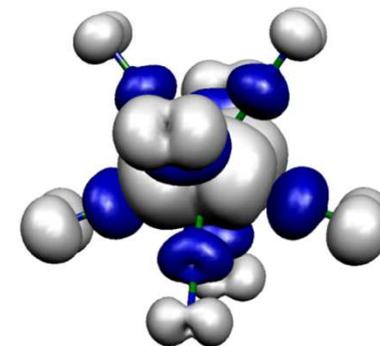
Spatially more extended orbitals
(3d < 4d < 5d)



Better overlap with ligands' orbitals, hence
more spin density on the bridging ligand



Cr: +3.042 μ_B
C: -0.088 μ_B
N: +0.0686 μ_B



M +0.825 μ_B
C_A -0.0244 μ_B
C_B -0.0416 μ_B
N_A +0.0322 μ_B
N_B +0.0779 μ_B

$J_{3d} < J_{4d} < J_{5d}$

Tools for a rational design of magnetic properties

- 👉 **the magnetic orbitals of the building units**
- 👉 **The orbital overlap and sign of the exchange interaction**

The **sign of the exchange coupling** and its **strength** are defined by the spin carriers (metal ions or organic radicals) and the bridging ligands chosen to construct the material (*cf* exchange pathways).

The **chemical structure** (discrete, 1-D, 2-D or 3-D), hence the type of material, is directed by the **molecular building units** used to synthesize the material.

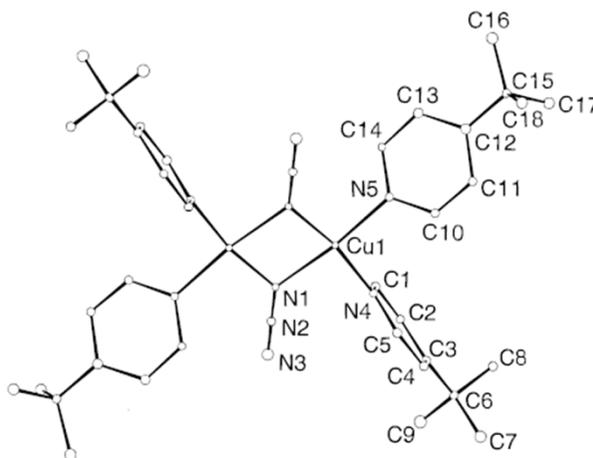
Chemical Tools (metal-based materials)

Homometallic compounds

M^{n+} + diamagnetic bridging ligand

Usually AF interactions take place between identical centers; as a result the ground state of the compound is non-magnetic !

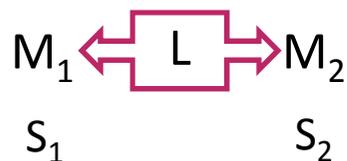
This approach makes sense only when the interaction is ferromagnetic. This applies with the azido ligand (N_3^-) in μ -1,1- coordination mode. Note that other coordination mode take place for this ligand and control is difficult.



Kahn *et coll.* Inorg. Chem. **1983**, 2877. JACS **1986**, 2574.

Chemical Tools (metal-based materials)

Heterometallic approach:



$$(S_1 \neq S_2 \neq 0)$$

Whether the interaction $J_{M_1M_2}$ is ferro- or antiferromagnetic, the spin (S) of the ground state is not zero.

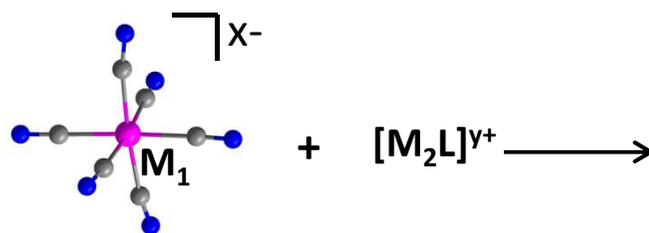
$$J_{M_1M_2} > 0 \text{ (ferromagnetic interaction)}$$

$$S = S_{M_1} + S_{M_2}$$

$$J_{M_1M_2} < 0 \text{ (antiferromagnetic interaction)}$$

$$S = S_{M_1} - S_{M_2}$$

☆ A resourceful and widely used approach in molecular magnetism ☆



Metallo-ligand
or building unit

L = ligand (optional)

I. Molecular Magnetism: Rational design of a magnet

Example of «Prussian blue»¹ derivatives

Relation between the magnetic susceptibility and T_C for a ferrimagnet proposed by Néel.²

$$kT_C = \frac{z|J|\sqrt{C_A C_B}}{Ng^2\beta^2}$$

⇒ To increase T_C the chemist can vary:

- the stoichiometry A:B to maximize z
- the strength of J
- the spin centers (that is C_A and C_B)

T_C : magnetic ordering temperature

k : Boltzmann constant

z : number of neighbours for a magnetic centers

$|J|$: strength of the exchange interaction

C_A and C_B : Curie constants for centers A and B

N : Avogadro number

g : Lande factor

β : Bohr magneton

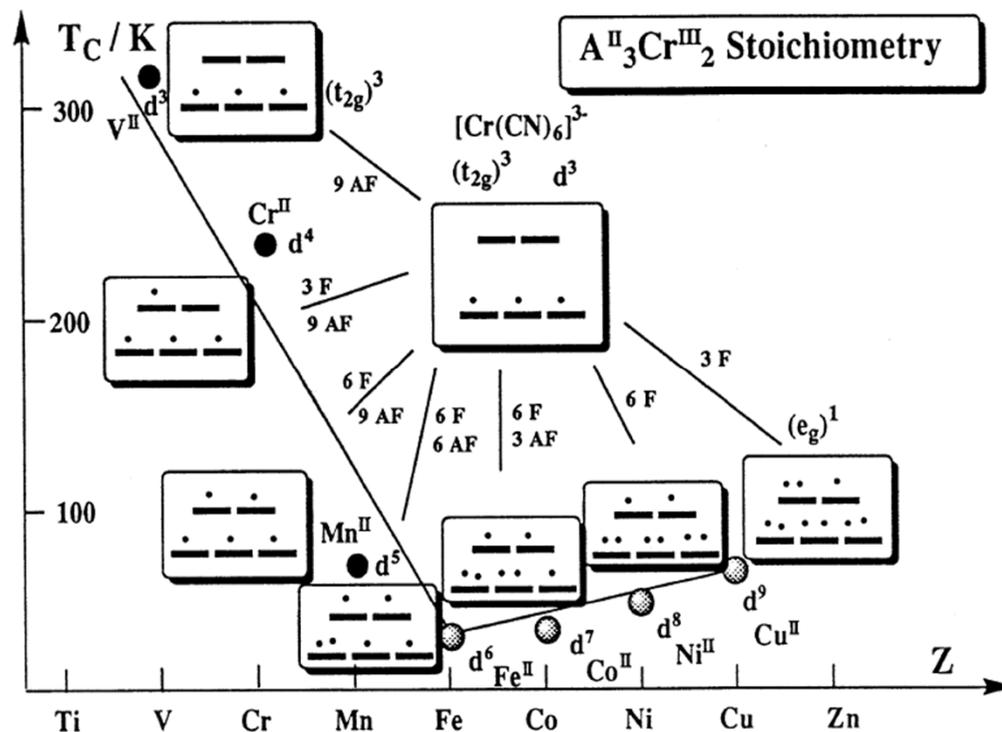
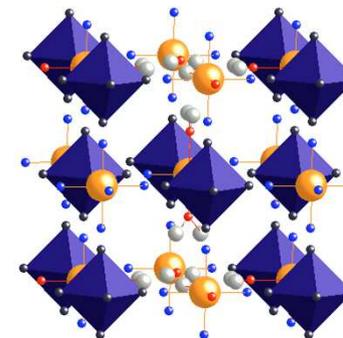
1. Verdaguer et coll. *Coord. Chem. Rev.* **1999**, 190-192, 1023.
2. Néel L. *Ann. Phys. Paris*, **1948**, 3, 285.

Rational design of a magnet: Example of «Prussian blue»¹ derivatives

Using the Néel's prediction, Verdaguer and co-workers have developed a family of magnets of formula $[(M^{II})_3\{Cr(CN)_6\}_2]$. For these compounds, $z = 4$ and C_B remain fixed, only J and C_A vary.

The compound $[(V^{II})_3\{Cr(CN)_6\}_2]$ for which the largest J was anticipated, is a magnet at room temperature ($T_C > 310$ K).

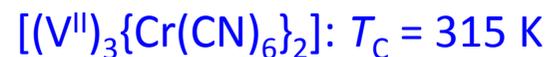
The variation for T_C as a function of M^{II} confirms also the validity of the hypothesis that $J = J_F + J_{AF}$



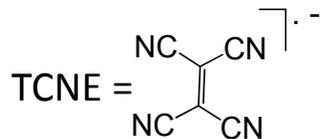
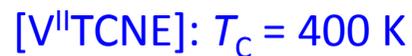
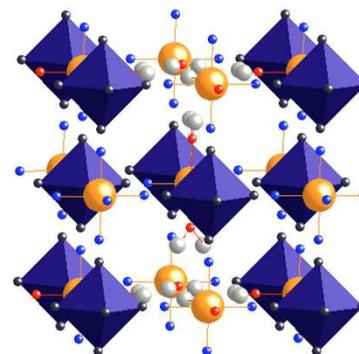
1. Verdaguer et coll. *Coord. Chem. Rev.* **1999**, 190-192, 1023. M. Verdaguer and G. S. Girolami, in *Magnetism: Molecules to materials*, eds. J. S. Miller and M. Drillon, Wiley-VCH, Weinheim, 2005, vol. 5, pp. 283-346.

Molecule-based magnets with $T_C > 300$ K:

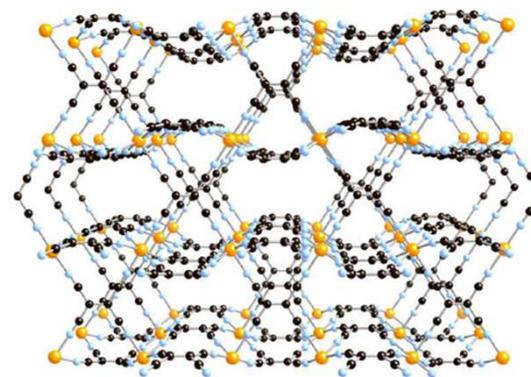
Only two are known!



S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Nature*, 1995, **378**, 701.



J.S. Miller et coll. *Science* **1991**, 252, 1415



Proposed structure

!! Both are highly unstable in air !

II. Poly-functional Magnets

Besides simple juxtapositions of properties, the real interest for polyfunctional materials is the synergy that may exist between two (or more) of its properties. For instance the magnetic ordering can modify an optical property (ex. second harmonic generation) of the material, or give rise to new phenomena (ex. magneto-chiral dichroism). The magnetic features may also be modified, for instance by structural changes or charge transfer triggered by an external stimuli.

The versatility of molecular chemistry and the flexibility of molecular materials, their synthesis, allow construction of such complex systems.

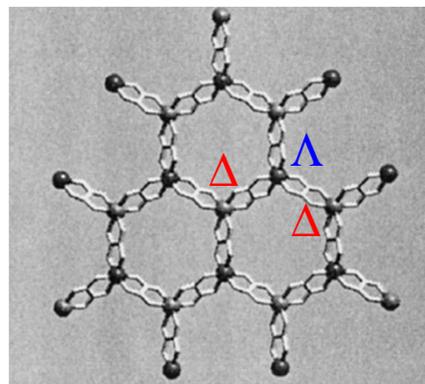
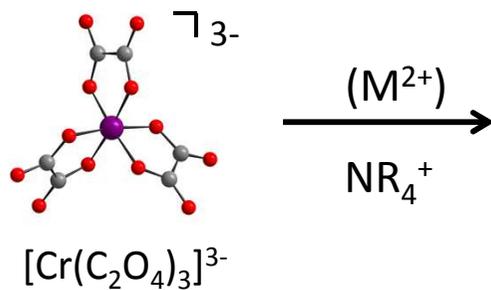
Chiral magnets: → Structure motivations
→ synergy between magnetic and optical features

Photo-triggered magnets: → Magnet ON/OFF by light

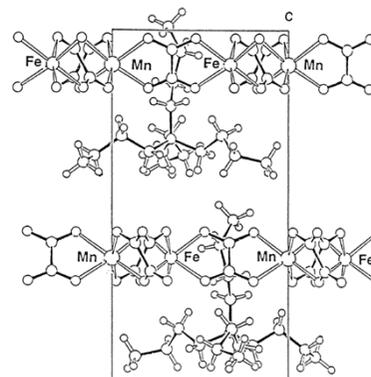
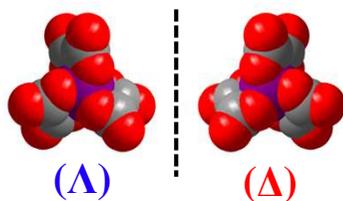
Porous magnets: → Modulation of magnet's feature by sorption state

Chiral magnets: structure motivation

Chiral 3-D network *versus* achiral 2-D polymer

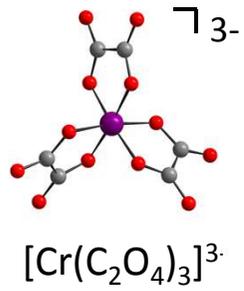


2-D $[M\{Cr(C_2O_4)_3\}]^-$

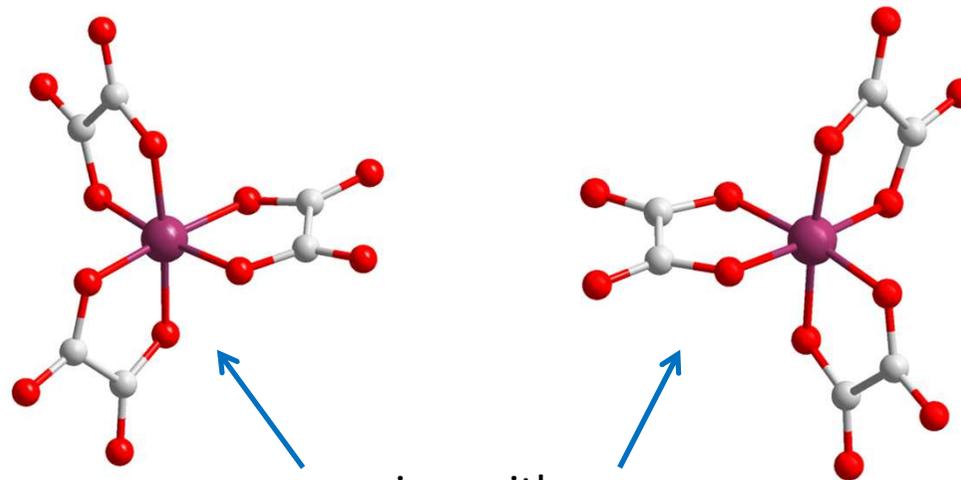


Chiral magnets: structure motivation

Chiral 3-D network *versus* achiral 2-D polymer



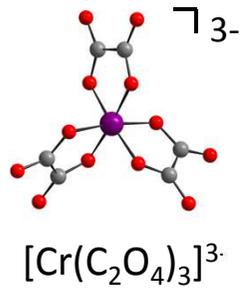
The two complexes found in the structure



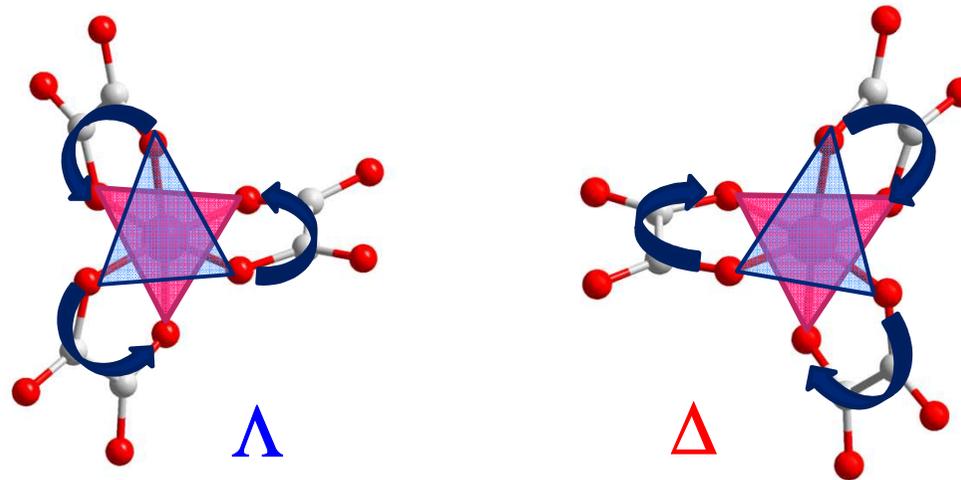
view with
3 O-atom in an upper plan
And 3 in a lower plan

Chiral magnets: structure motivation

Chiral 3-D network *versus* achiral 2-D polymer



The two complexes found in the structure



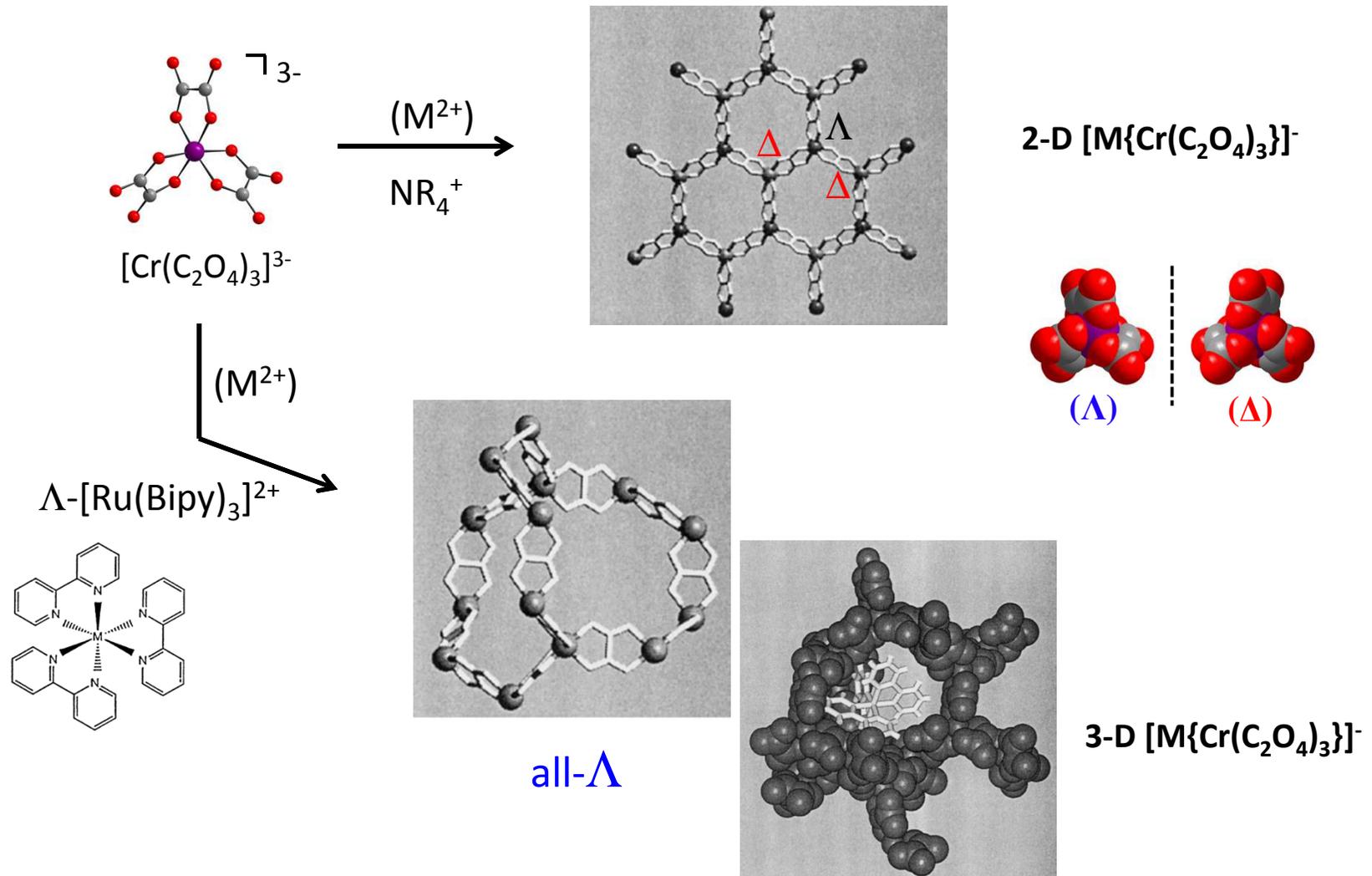
Left-turn ..

Right-turn ..

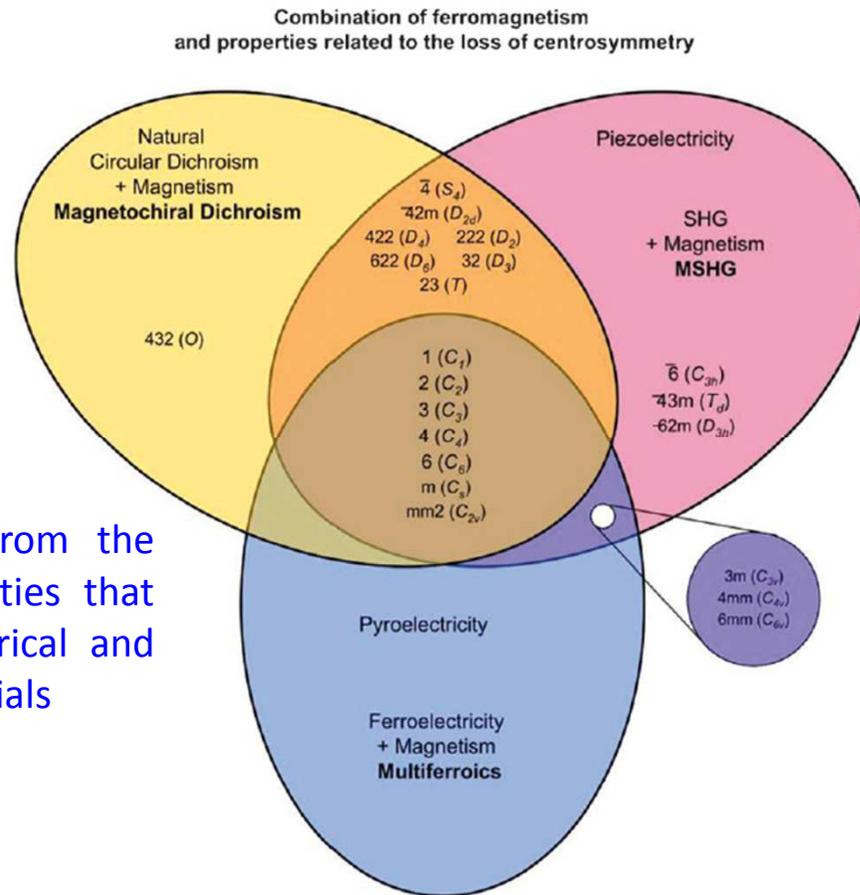
...to go from higher to lower atom linked to the metal center for each chelating ligand

Chiral magnets: structure motivation

Chiral 3-D network *versus* achiral 2-D polymer



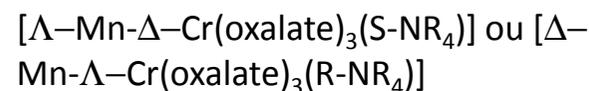
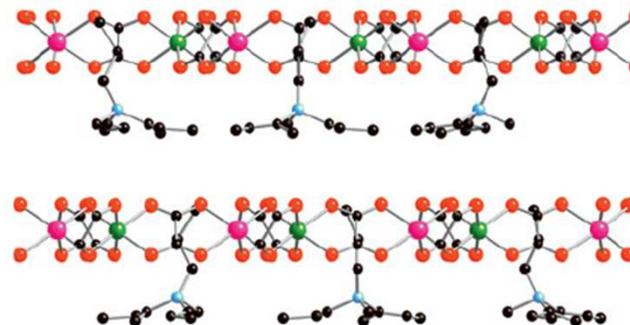
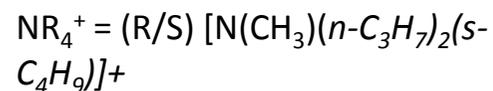
Chiral magnets: properties motivation



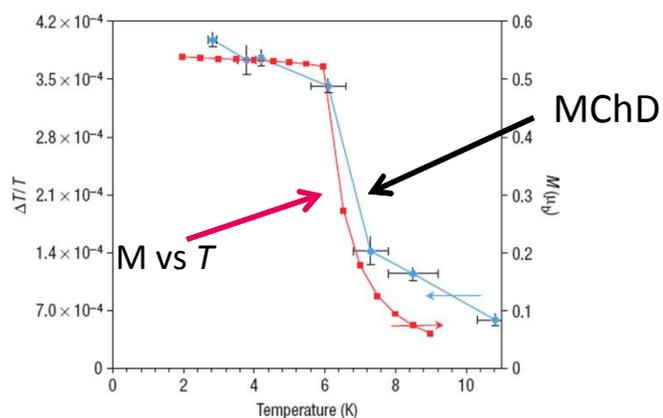
Physico-chemical effects arising from the interaction between some properties that might exist in non centrosymmetrical and long-range magnetic ordered materials

Chiral magnets: synergy between magnetic and optical features

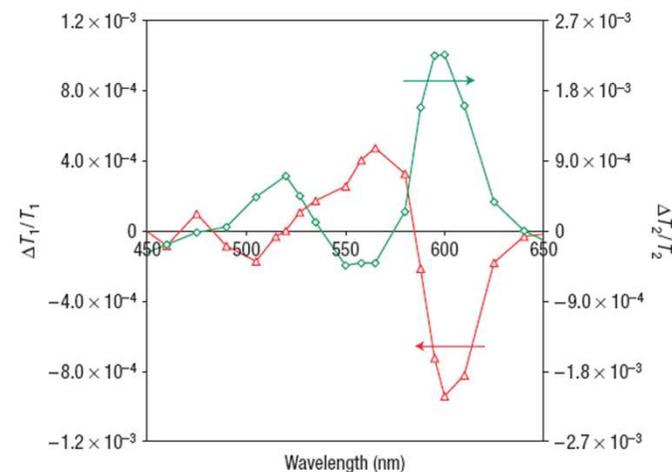
Magneto-chiral dichroism



$$\varepsilon(\mathbf{k}, \mathbf{M}) = \varepsilon_0 + \alpha_{\text{NCD}} \mathbf{k} + \beta_{\text{MCD}} \mathbf{M} + \gamma_{\text{MChD}} \mathbf{k} \cdot \mathbf{M}.$$



Enhancement of magneto-chiral dichroism at the Curie temperature

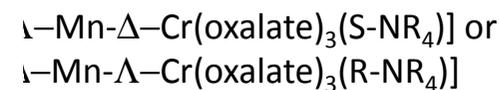
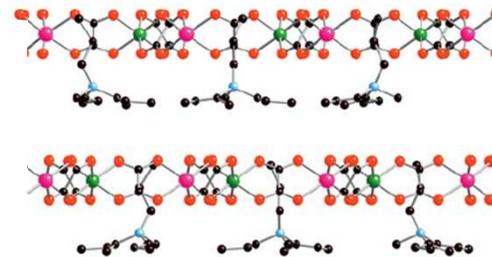
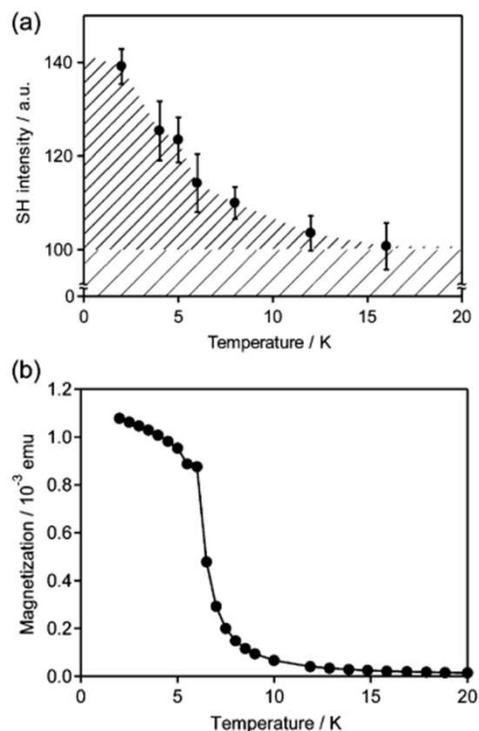
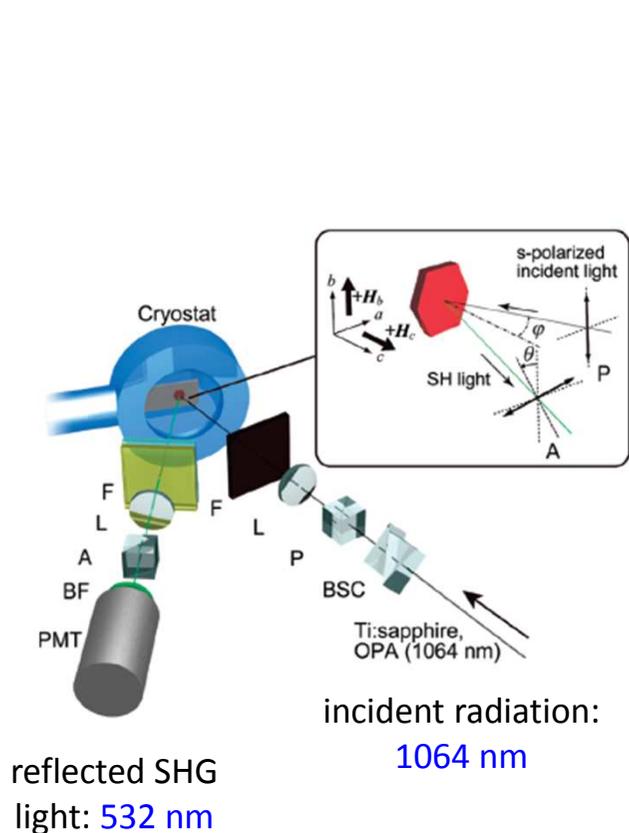


Inversion of the magneto-chiral dichroism with the enantiomer. Magneto-chiral dichroism measured at 4.0 K

Train & coll. *Nature Mater.* **2008**, 7, 729.

Chiral magnets: synergy between magnetic and optical features

Magnetization-Induced Second Harmonic Generation

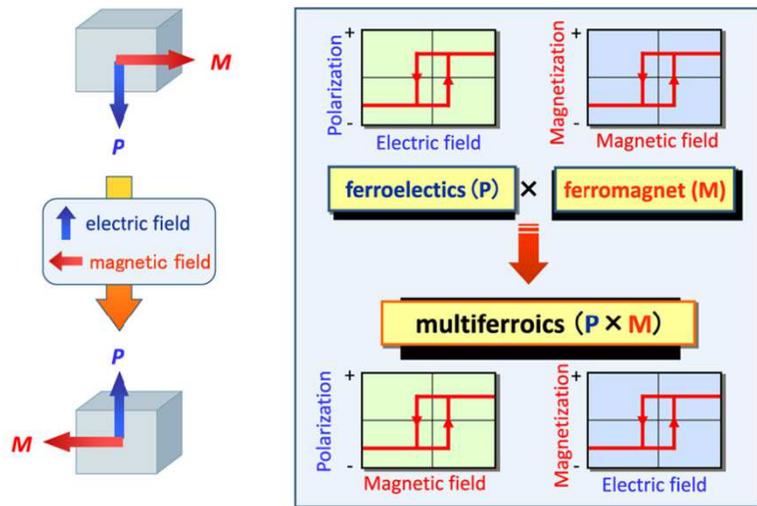


(a) Thermal variation of the SHG signal for a single crystal of N*[MnCr] in a 30 mT magnetic field applied along the *c*-axis.
 (b) Fieldcooled curve in a 1.0 mT field applied along the *c* axis.

Chiral magnets: towards multiferroics

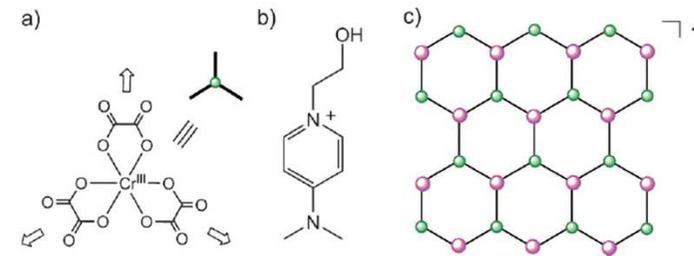
Coexistence of magnetic and electric orders

what are multiferroics? Multiferroics are materials that exhibit simultaneously several ferroic order parameters. In a solid combining electric and magnetic orders, electric field (E) induces electric polarization (P) and magnetic field (H) induces magnetization (M). A coupling between P and M will enable the magneto-electric (ME) effect, that is the mutual control of the magnetism and electricity

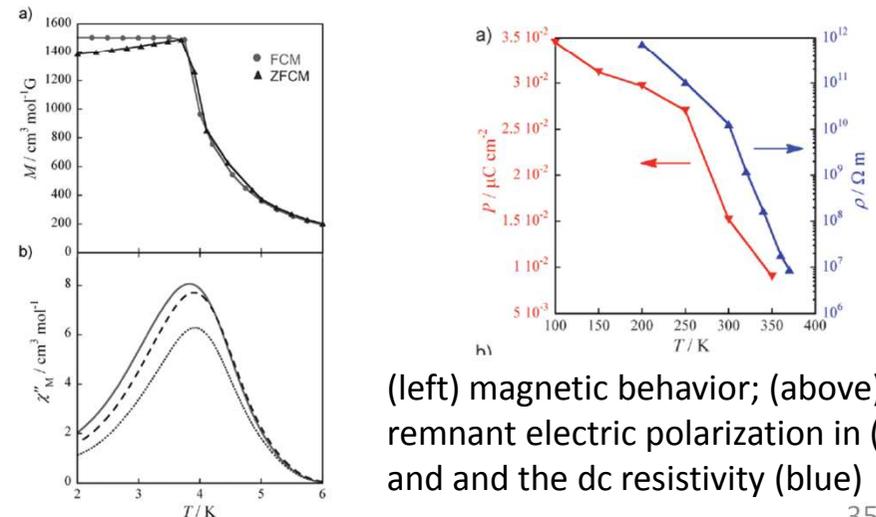


Multiferroics and M (magnetization)– P (polarization) cross-control by electric and magnetic field.

Reports on Progress in Physics **2014**, 77, 076501



Scheme 1. Metal ligand design strategy of **1** using a) the tris(bidentate) mononuclear chromium(III) complex anion as molecular tecton with b) a pyridinium-based polar cation, c) leading to the formation of 2D bimetallic oxalate-bridged layers.



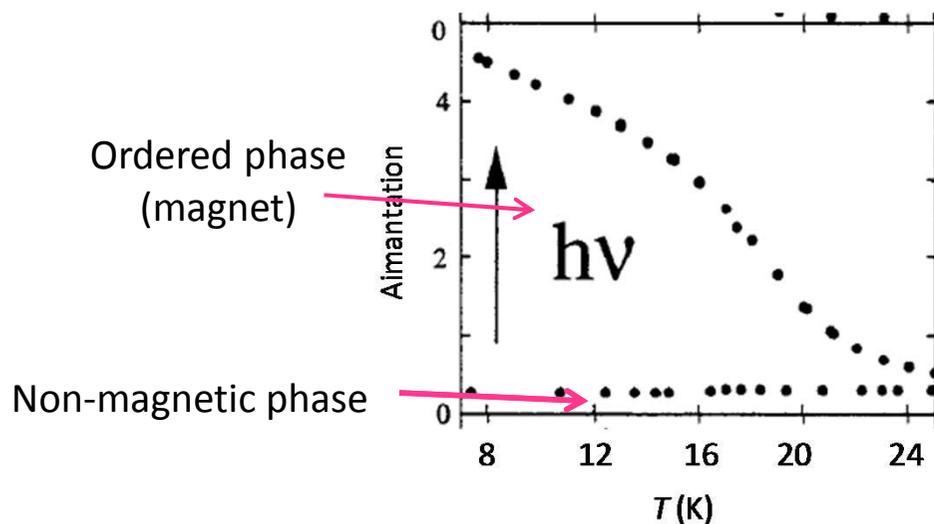
(left) magnetic behavior; (above) the remnant electric polarization in (red) and the dc resistivity (blue)

Angew. Chem. Int. Ed. **2012**, 51, 8356

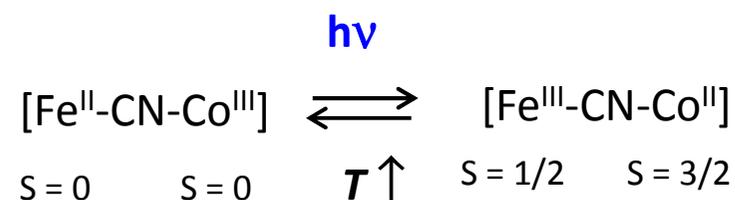
Light-induced magnets (photo-magnets)

Light-triggered ON-OFF switching by charge transfer

Magnetic behavior for $[\text{Rb}_{1.8}\text{Co}^{\text{III}}_{3.3}\text{Co}^{\text{II}}_{0.7}[\text{Fe}^{\text{II}}(\text{CN})_6]_{3.3} \cdot 13\text{H}_2\text{O}]$ before and after light irradiation

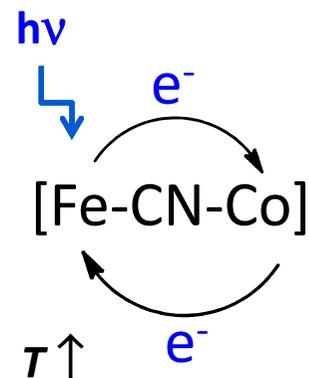


Based on a charge-transfer phenomenon



A reversible charge transfer takes place.

At low temperature, the paramagnetic pair can be produced by light radiation.^{1,2}



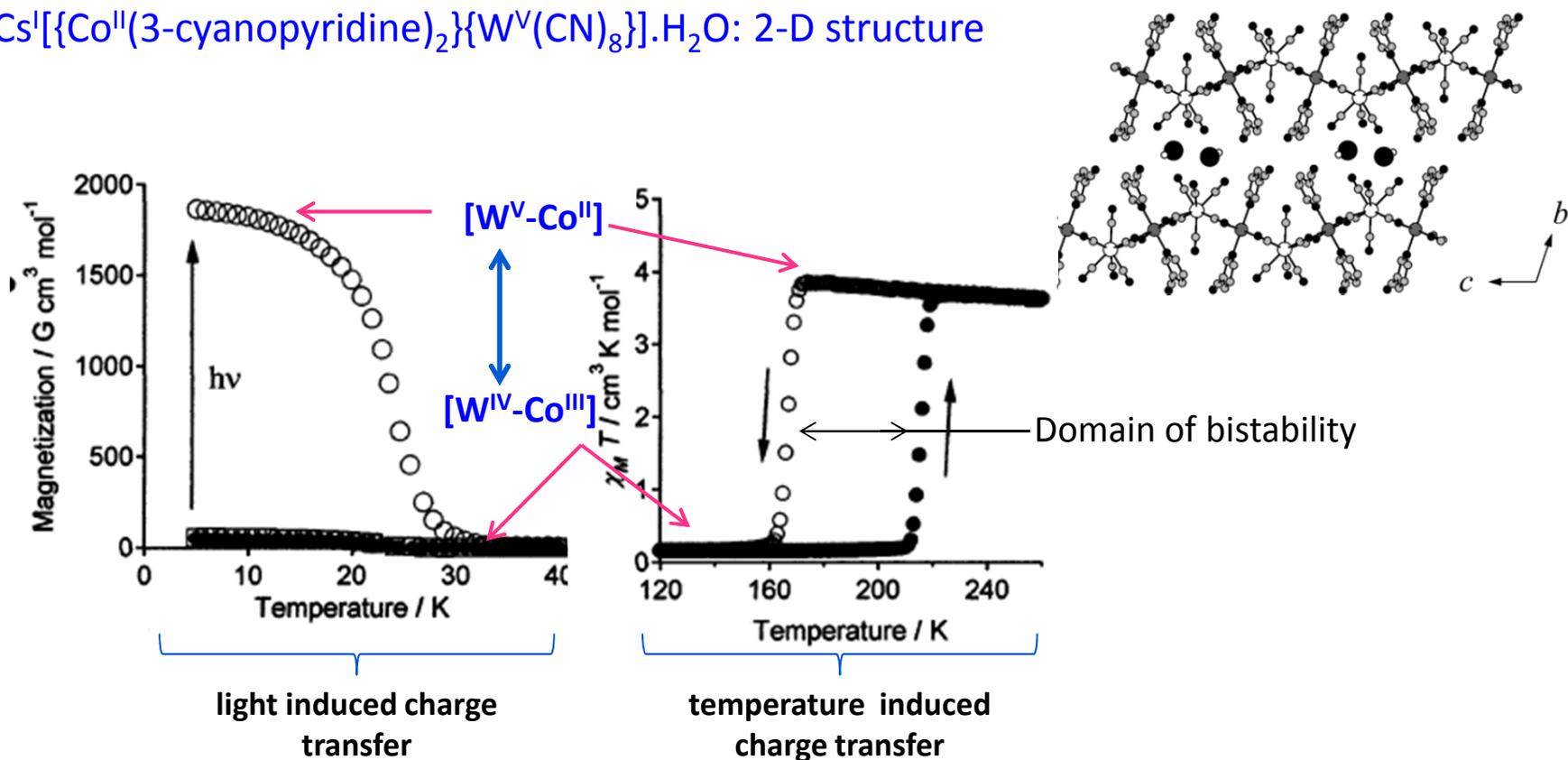
1. Hashimoto et coll. *Science* **1996**, 272, 704
2. Bleuzen et coll. *JACS* **2000**, 122, 6648

Light-induced magnets (photo-magnets)

Light-triggered ON-OFF switching by charge transfer

Related light-induced magnetizations have been found for $[\text{Fe}^{\text{III}}\text{-CN-Mn}^{\text{II}}]$ -pair systems and $[\text{W}^{\text{V}}\text{-CN-Co}^{\text{II}}\text{L}]$.

$\text{Cs}^{\text{I}}\{[\text{Co}^{\text{II}}(\text{3-cyanopyridine})_2]\{[\text{W}^{\text{V}}(\text{CN})_8]\}\cdot\text{H}_2\text{O}$: 2-D structure



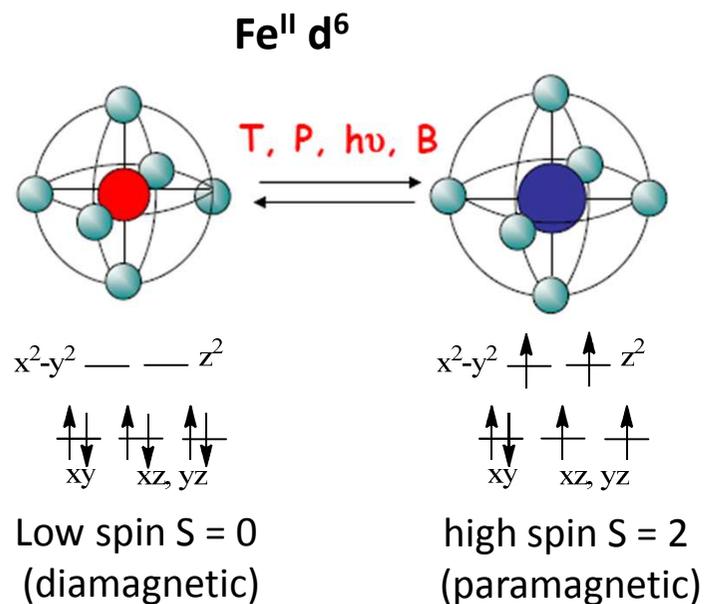
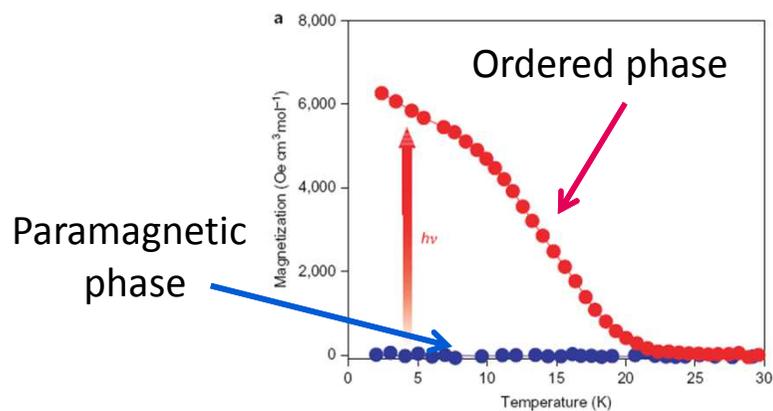
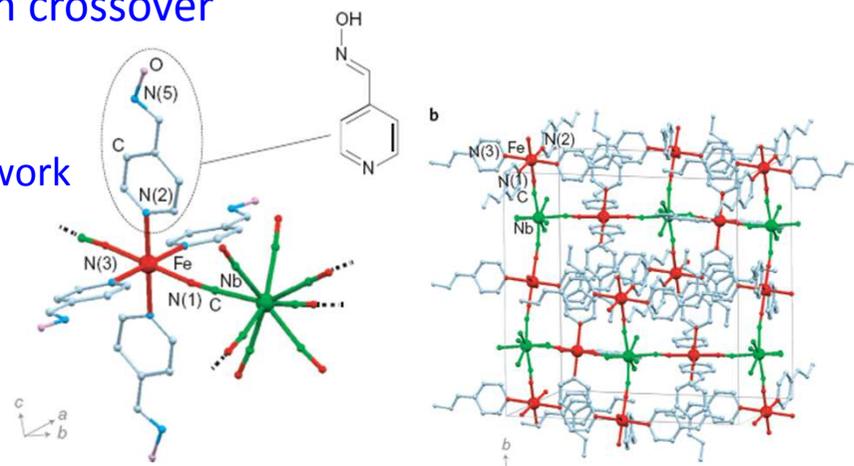
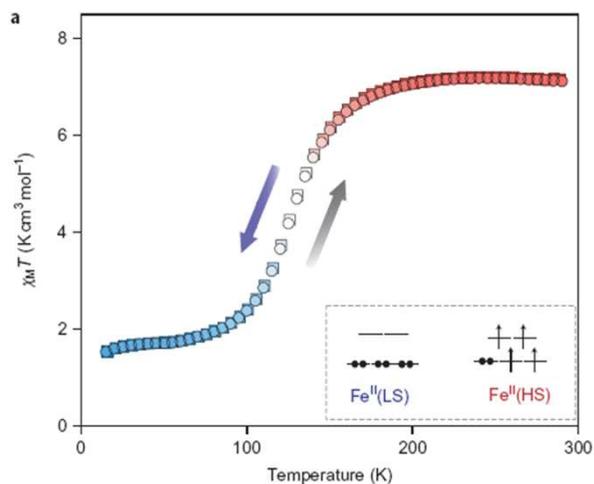
1. S. Ohkoshi et coll. *Coord. Chem. Rev.* **2005**, 249, 1830
2. Ohkoshi et coll. *JACS* **2003**, 125, 9240

Light-induced magnets (photo-magnets)

Light-triggered ON-OFF switching by spin crossover

Based on spin crossover of Fe^{II}

$[(FeL_4)_2\{Nb(CN)_8\}]$: a 3-D [Nb-CN-Fe] network

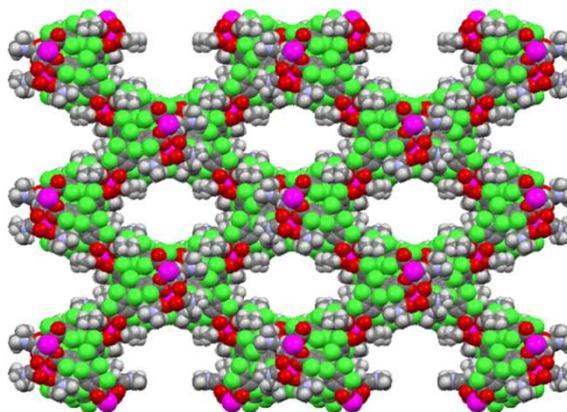


Porous magnets: modulation of the magnet's feature through sorption state

⇒ Open-framework structures

- Accessible void in the structure
- Reversible sorption properties
- Magnetic ordering (it's a magnet!)

Interest: possibility to modulate the magnetic features (T_C , coercive field) simply by guest molecule exchange



Porous magnets: modulation of the magnet's feature through sorption state

Difficulty for the chemist:

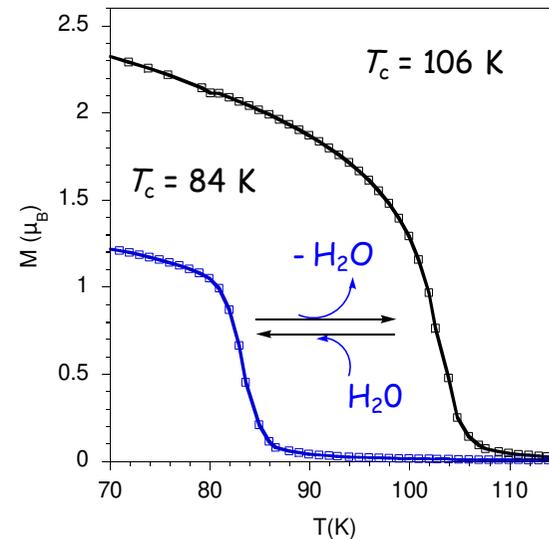
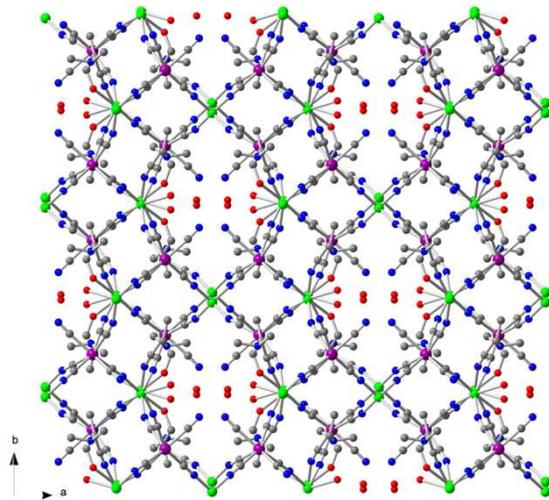
- ❑ High T_c => strong exchange interactions
- ❑ Large channels => large spacing ligands

Antagonistic properties ?!

compromise has to be found between highly porous solids and efficient magnet

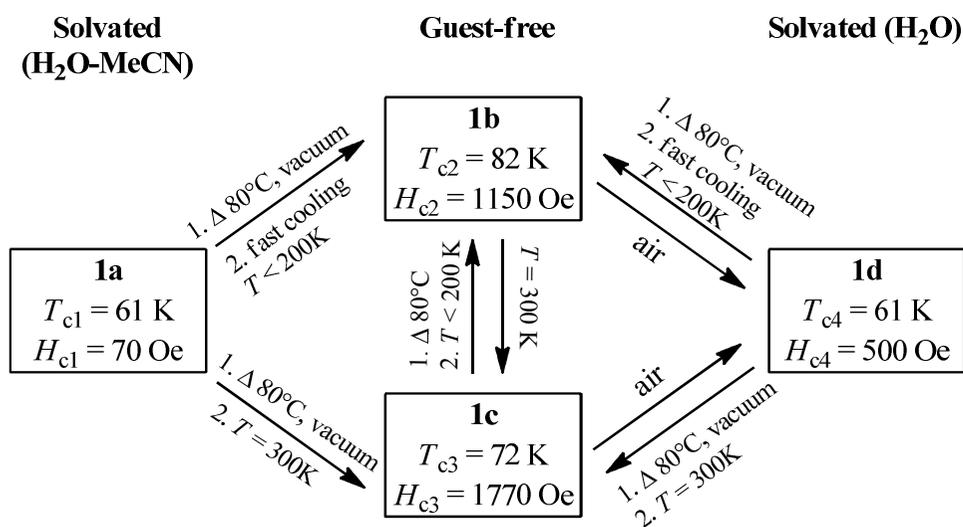
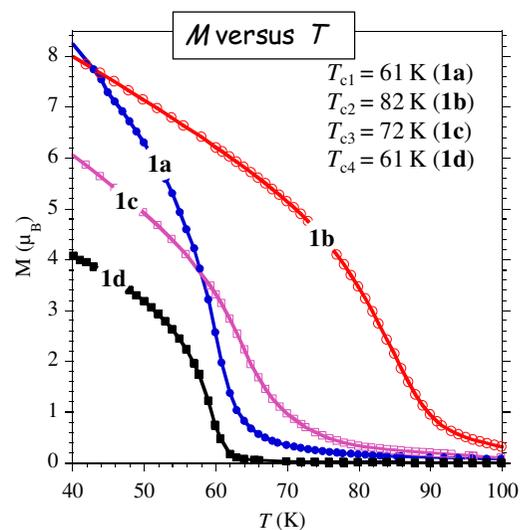
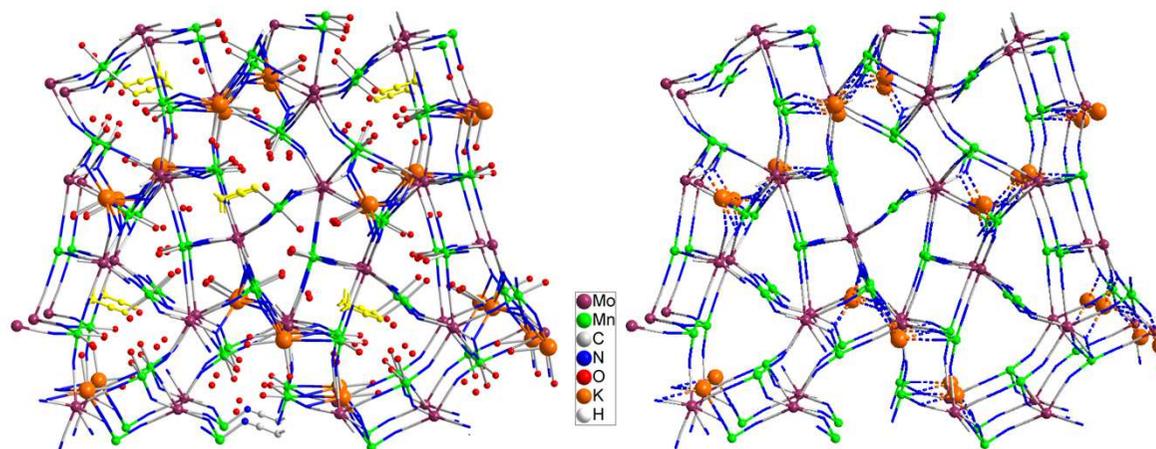
Interesting results with low symmetry building unit $[\text{Mo}(\text{CN})_7]^{3-}$

$[\text{Mn}_3\text{L}_2\{\text{Mo}(\text{CN})_7\}]$: accessible void, 9 %

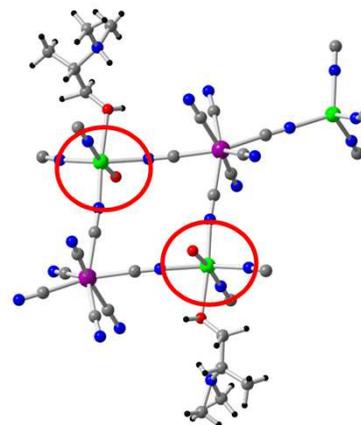


Porous magnets: modulation of the magnet's feature through sorption state

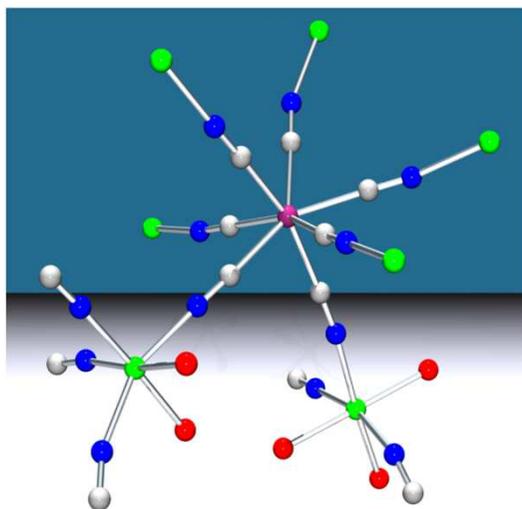
$[\text{K}_2\text{Mn}_5\{\text{Mo}(\text{CN})_7\}_3] \cdot 14\text{H}_2\text{O} \cdot \text{MeCN}$: 28 % porosity



Origin of the reversible T_c switching :
⇒ the coordination sphere Mn centers

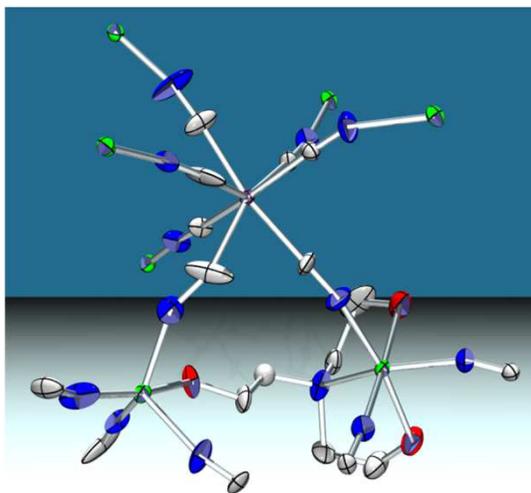


→ $T_c = 51$ K



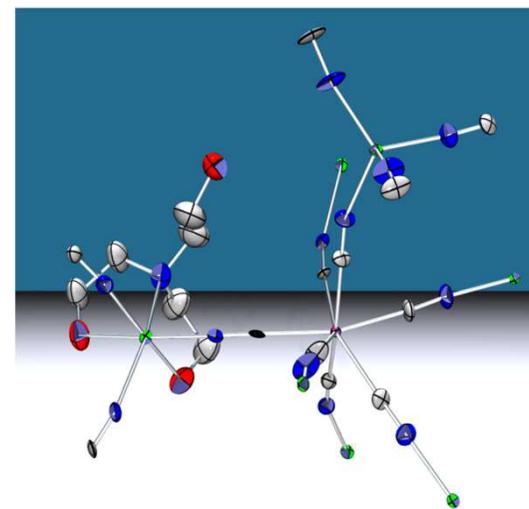
Mn←NC bond lengths:
2.158 - 2.242 Å

→ $T_c = 75$ K



Mn(sp)← NC bond lengths:
2.064-2.123 Å

→ $T_c = 106$ K



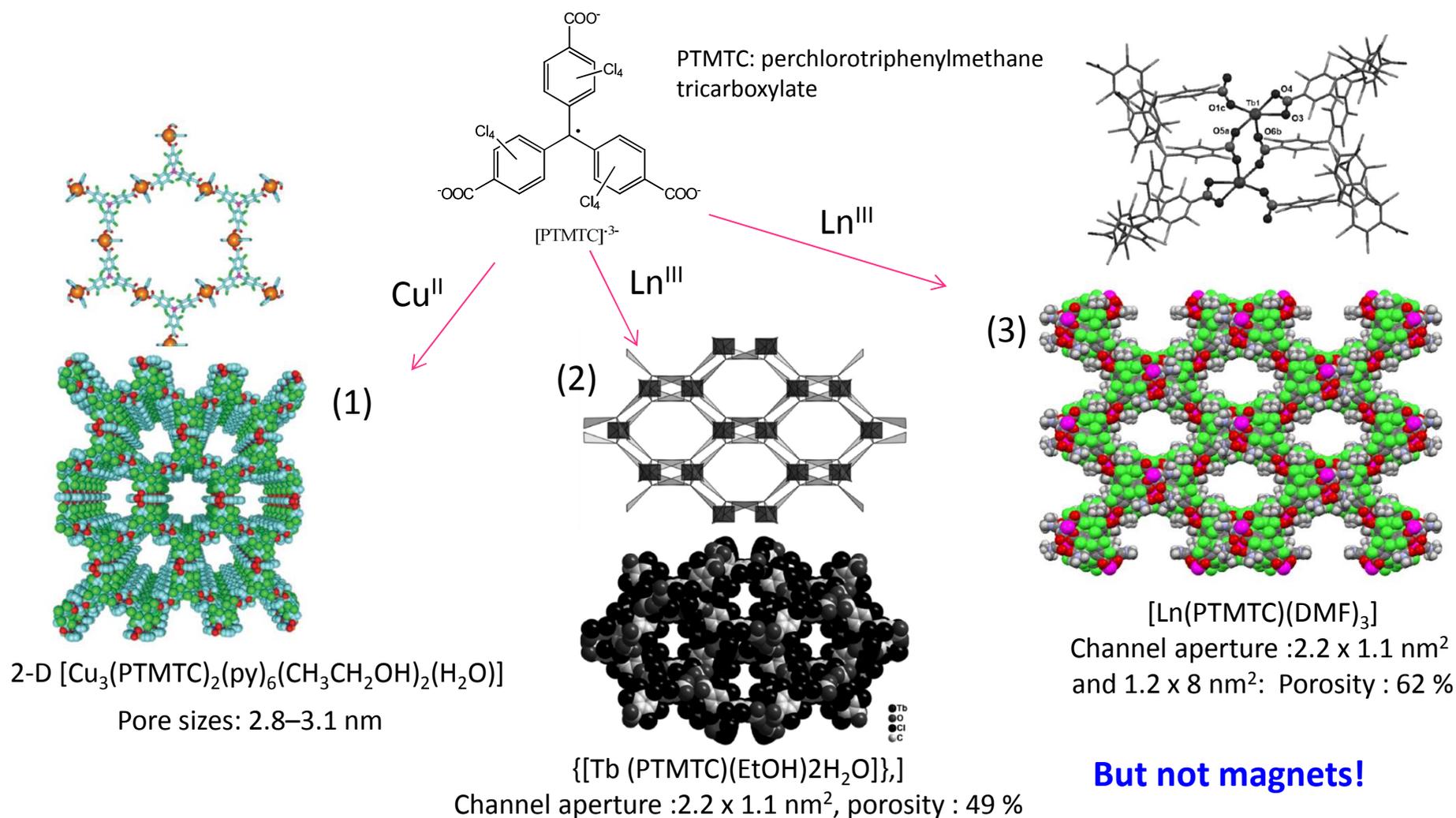
Mn(T_d)← NC bond lengths:
2.02-2.083 Å

Trend: T_c (octahedral) < T_c (square-pyramidal) < T_c (tetrahedral)

→ As Mn←NC-Mo becomes shorter the exchange interaction is improved and T_c increases.

Porous magnets: modulation of the magnet's feature through sorption state

Open-frameworks involving paramagnetic bridging ligands:



(1) J. Veciana *et al.* *Nat. Chem.* **2003**, 2, 190. (2) J. Veciana *et al.* *Chem. Eur. J.* 2011, 3644 (3) J. Veciana *et al.* *Chem. Eur. J.* 2012, 152

II. Poly-functional Magnets

The versatility of molecular chemistry and the flexibility of molecular structures, their synthesis, allow construction of materials that combine and interrelate several properties. Among these:

Chiral magnets

Photo-triggered magnets

Porous magnets

Conducting magnets

Multiferroic magnets

have been reported.

For additional information on such molecule-based magnets see:

M. Kurmoo, *Chem. Soc. Rev.* **2009**, *38*, 1353.

D. Maspoch, D. Ruiz-Molina, J. Veciana, *Chem. Soc. Rev.* **2007**, *36*, 770

N. Roques, V. Mugnaini, J. Veciana, *Top. Curr. Chem.* **2010**, *293*, 207

P. Dechambenoit, J. R. Long, *Chem. Soc. Rev.* **2011**, *40*, 3249

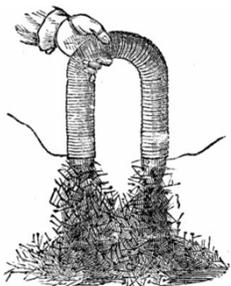
W. Zhang, R.-G. Xiong, *Chem. Rev.* **2012**, *112*, 1163

M. Ohba, K. Yoneda and S. Kitagawa, *Cryst Eng Comm*, **2010**, *12*, 159-165

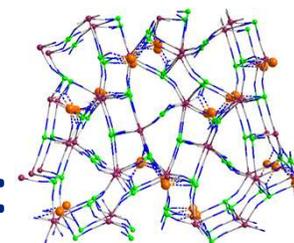
Train, C.; Gruselle, M.; Verdaguer, M., *Chem. Soc. Rev.* **2011**, *40*, 3297

G. Rogez et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 1921

K. S. Pedersen, et al, *Nature Chemistry* **2018**, *10*, 1056

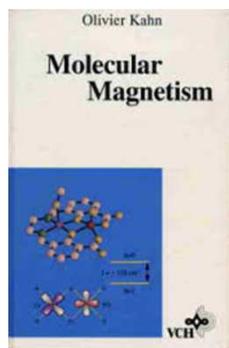


MOLECULE-BASED MAGNETIC MATERIALS: concept and design



Some books

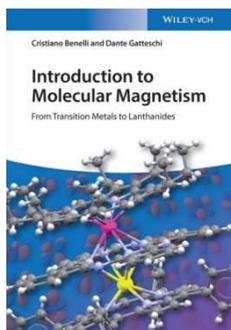
Molecular Magnetism, O. Kahn, VCH-Wiley, **1993**



Magnetism: Molecule to materials, Eds. Drillon et Miller, VCH-Wiley, **2001**, Vol. I-V

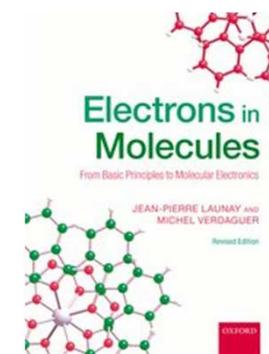
Molecular Nanomagnets; Gatteschi, D.; Sessoli, R.; Villain, J.; Oxford University Press, **2006**

Single-Molecule Magnets and Related Phenomena, Ed. R. Winpenny, Springer **2006** vol. 122



Introduction to Molecular Magnetism: From Transition Metals to Lanthanides. Benelli, C.; Gatteschi, D., Wiley: **2015**.

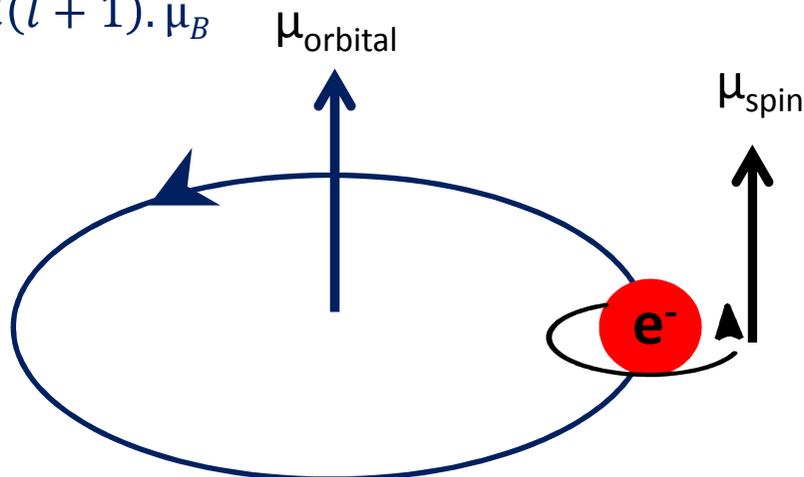
Electrons in Molecules: From Basic Principles to Molecular Electronics; J.-P. Launay and M. Verdaguer Oxford University Press **2017**



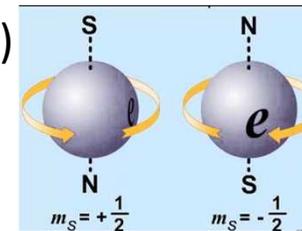
Memo: Origin of the magnetism, the electron

“Orbital” magnetic moment

$$\mu_{orbital} = \sqrt{l(l+1)} \cdot \mu_B$$



“intrinsic” magnetic moment
of the electron ($s = 1/2$)



$$\mu_{spin} = g_S \times \mu_B \times s \times 1/\hbar$$

g : Landé factor ≈ 2

μ_B : Bohr magneton

\hbar : reduced Plank constant

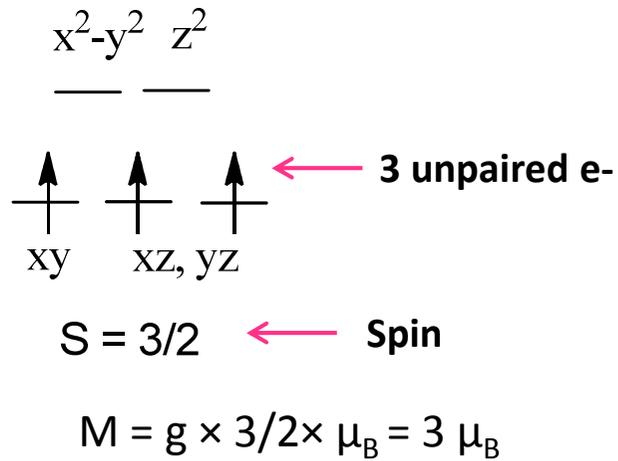
$$\text{Magnetic moment: } \mu_{total} = \mu_{orbital} + \mu_{spin}$$

For organic radicals and transition metal complexes $\mu_{orbital}$ is usually quenched and the magnetic moment result only from the contribution of the electrons' spin and becomes

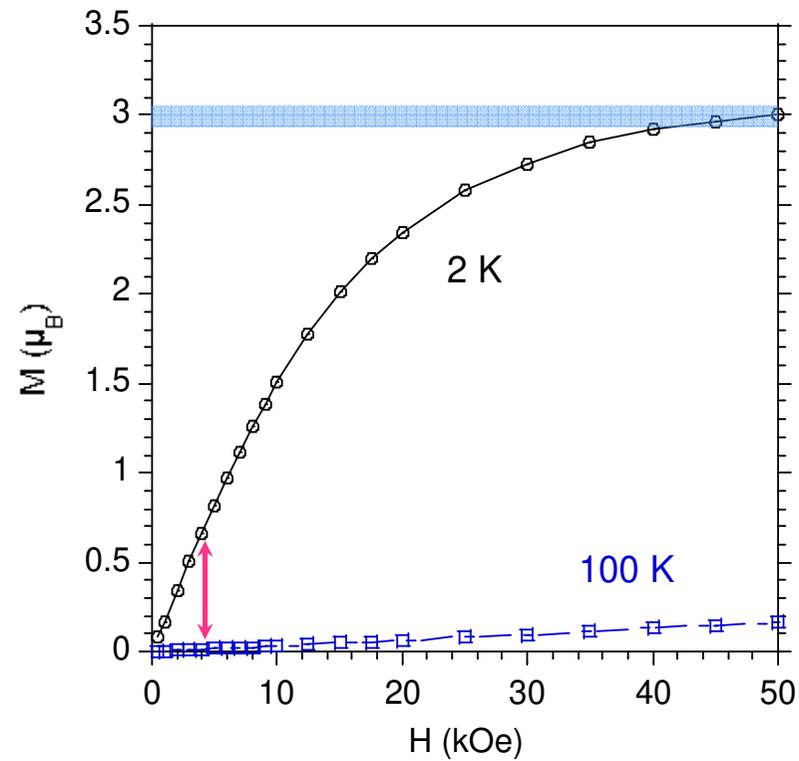
$$M = g \times S \times \mu_B$$

Memo: magnetic susceptibility, Curie constant and exchange interactions

ex. d^3 ion in Oh symmetry



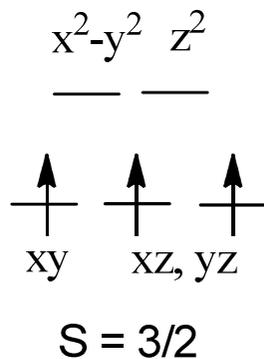
Field dependence of the magnetization
(at fixed temperature)



Memo: magnetic susceptibility, Curie constant and exchange interactions

magnetic susceptibility, χ_M

ex. d^3 ion in Oh symmetry



$$\chi_M = M/H$$

! applies only in the domain of linear variation of M with applied field. Typically for fields $H < 5000$ Oe.

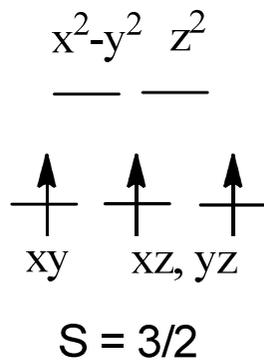
$$\chi_M = \frac{N g^2 \beta^2}{3kT} S(S + 1) = \frac{1}{8} \frac{g^2}{T} S(S + 1)$$

If $\chi_M T$ is considered:

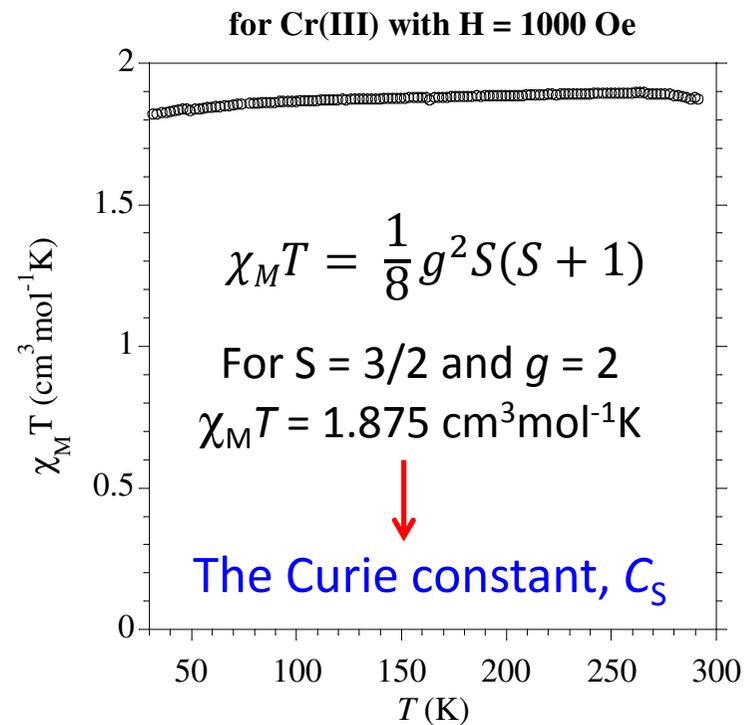
$$\chi_M T = \frac{1}{8} g^2 S(S + 1) \Rightarrow \text{a fixed value defined by } S$$

Memo: magnetic susceptibility, Curie constant and exchange interactions

ex. d³ ion in Oh symmetry



Temperature dependence of the magnetic susceptibility plotted as $\chi_M T$



Memo: magnetic susceptibility, Curie constant and exchange interactions

The Curie Constants:

$$C_S = \frac{N_A \mu_B^2}{3k} g^2 S(S + 1) = \chi_M T$$

for any spin, a characteristic value independent of T

S	0	½	1	3/2	2	5/2	...
C_S cm ³ mol ⁻¹ K	0	0.375	1.0	1.875	3	4.375	
ions	Dia.	Cu(II), radicals	Ni(II)	Cr(III)	Mn(III), HS-Fe(II)	Fe(III), Mn(II)	

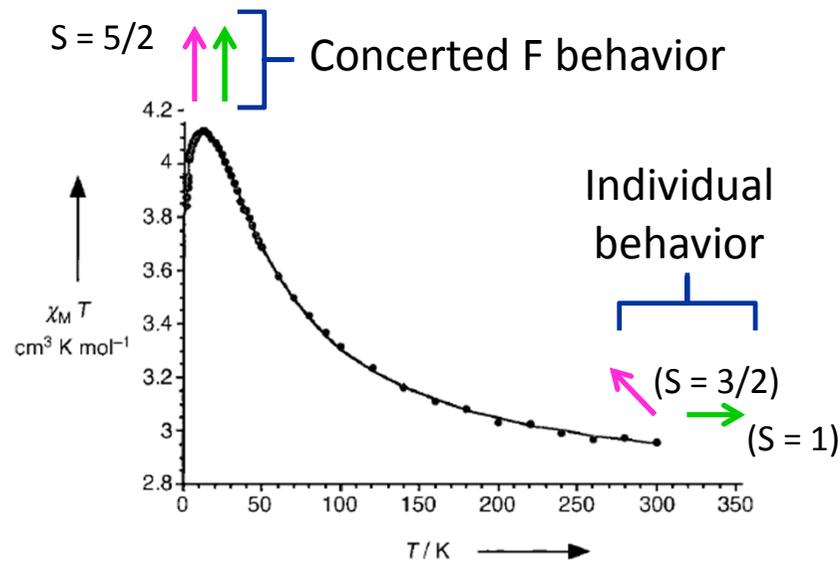
A $\chi_M T = f(T)$ behavior for which the $\chi_M T$ value remains constant is characteristic of paramagnetism (= isolated magnetic centers with no exchange interaction between them).

Deviation from a constant value reveals exchange interactions.

Memo: magnetic susceptibility, Curie constant and exchange interactions

$\chi_M T$ varies with $T \Rightarrow$ exchange interactions are taking place between the magnetic centers

Ferromagnetic (F) interaction



Antiferromagnetic (AF) interaction

