Do the chemists know how to align the spins of electrons in molecules, parallel or antiparallel?
to get magnetic compounds ...

Understanding ...

why the spins of two neighbouring electrons (S = 1/2) become:

antiparallel? or parallel?

S=0

S=1
Interaction Models between Localised Electrons

\[ \hat{H} = -J \hat{S}_1 \hat{S}_2 \]

Scalar Coupling: describes, does not explain
Energy levels

Interaction antiferro

$J < 0$

Interaction ferro

$J > 0$
\[ J = 2k + 4\beta S \]

- If \( S = 0 \);
  - Orthogonality

- If \( S \neq 0 \); \(|\beta S| \gg k\)
  - Overlap

- If \( S \neq 0 \); \(|\beta S| \gg k\)
  - Overlap

- \( O_2 \)
  - Hund
  - Ferro

- \( H_2 \)
  - Aufbau
  - Antiferro
J. Miró
«Overlap»?
Catalogue raisonné, N°1317
J. Miró, Pomme de terre, detail
An old game ...

\[ \hat{H} = -J \hat{S}_1 \hat{S}_2 \]

Palace Museum, TaiPei, Neolithic period, Yang-Shao Culture
Exchange interactions can be very weak ...

Exchange interactions
order of magnitude: cm$^{-1}$ or Kelvins ...

« Chemical » bonds
Robust!

order of magnitude:
>> 150 kJ mol$^{-1}$ ...

Michelangelo, Sixtin Chapel, Rome
Negligible Interaction!

Problem:

How to create the interaction ... ?
Orbital Interaction

\[ \approx 5 \, \text{Å} \]

Orbital Interaction ...

Solution:
The ligand!
Examples with the ligand

• Cyanide
Non linear and linear bridges

Monet Claude, Charing Cross Bridge

Monet Claude, Waterloo Bridge
Cyanide Ligand

Friendly ligand: small, dissymmetric, forms stable complexes

Warning: dangerous, in acid medium gives HCN, lethal
Dinuclear $\mu$-cyano homometallic complexes
“Models” Compounds Cu(II)-CN-Cu(II)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$J/\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cu}_2(\text{tren})_2\text{CN}]^{3+}$</td>
<td>-160</td>
</tr>
<tr>
<td>$[\text{Cu}_2(\text{tmpa})_2\text{CN}]^{3+}$</td>
<td>-100</td>
</tr>
</tbody>
</table>

Overlap: antiferromagnetic coupling ...

Rodríguez-Fortea et al. *Inorg. Chem.* 2001, 40, 5868
Cr(III) Ni(II)

Dinuclear μ-cyano heterometallic complexes

NB : A dissymetric ligand helps to get stable heterometallic complexes ...
« Birds of the same feathers flock together » ...
Polynuclear complex, synthetic strategy

Hexacyanometalate “Heart”  Lewis Base

Mononuclear Complex  Lewis Acid

Polynuclear Complex
Electrons in
Hexacyanochromate complex

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

Cr(III)

$e_g$ $t_{2g}$ $z$ $t_{2g}$

$2$ oct
Polynuclear complex, ferromagnetic strategy

\[ \text{M-C≡N-M}' \]

\[ \pi \quad \text{C N M}' \quad \sigma \]

\[ \text{M C N} \quad S = 0, J_F = 2k \]

Orthogonality: Ferromagnetism!

Example:

\[ \text{Cr(III)}(t_{2g})^3 \quad J_F \quad \text{Ni(II)},(e_g)^2 \]

\[ \text{Cr(III)Ni(II)}_6 \quad S = 6 \times 1 + 3/2 = 15/2 \]
Polynuclear complex, ferrimagnetic strategy

\[
\begin{align*}
M - C\equiv N - M' \\
\end{align*}
\]

Overlap = antiferromagnetism

\[
S_{ab} \propto 0, \quad J_{AF} \propto S_{ab} \sqrt{(\delta^2 - \delta^2)}
\]

Example

\[
\begin{align*}
Cr(\text{III}) (t_{2g})^3 \\
J_{AF} \\
Mn(\text{II}) (t_{2g})^3
\end{align*}
\]

\[
Cr(\text{III})\text{Mn(II)}_6 \\
S = 6 \times 5/2 + 3/2 = 27/2
\]
Paul KLEE

Ferromagnetic ...

Eros

Nocturnal separation, 1922

Ferrimagnetic ...

Ferrimagnetic
High Spin Heptanuclear Complexes

CrCu6
$S = 9/2$

CrNi6
$S = 15/2$

CrMn6
$S = 27/2$

Hexagonal $R - 3$
$a = b = 15.27 \text{ Å}; \ c = 78.56 \text{ Å} $
$a = b = 90^\circ; \ g = 120^\circ; \ V = 4831 \text{ Å}^3$

Hexagonal $R - 3$
$a = b = 15.27 \text{ Å}; \ c = 41.54 \text{ Å} $
$a = b = 90^\circ; \ g = 120^\circ; \ V = 8392 \text{ Å}^3$

Hexagonal $R - 3$
$a = b = 23.32 \text{ Å}; \ c = 40.51 \text{ Å} $
$a = b = 90^\circ; \ g = 120^\circ; \ V = 19020 \text{ Å}^3$

Marvaud et al., Chemistry, 2003, 9, 1677 and 1692
Chemists have transformed good old Prussian blue,
a blue pigment that Michael Faraday precipitated
in his time at Royal Institution,
into a room temperature magnet
also useful in display devices.
This painting does not depict neither W.T. Brande nor Michael Faraday making Prussian blue, Thomas Philips RA, ca 1816 (from Alfred Bader, Hon FRSC)
1704 ... 2004 : 300th anniversary !

Diesbach, draper in Berlin ...

... prepares a blue pigment « Prussian blue »

... said to be the first coordination compound
Anna Atkins, Cyanotype in Hart-Davis Adam Chain Reactions, pioneers of british science and technology National Portrait Gallery London, 2000
Classical coordination chemistry...

\[ \text{Fe}^{2+}_{\text{aq}} + 6\text{CN}^-_{\text{aq}} \rightarrow [\text{Fe(CN)}_6]^{4-}_{\text{aq}} \]

Complexes as Ligands, or « bricks »

\[ 3[\text{Fe(CN)}_6]^{4-}_{\text{aq}} + 4\text{Fe}^{3+}_{\text{aq}} \rightarrow \{\text{Fe}_4[\text{Fe(CN)}_6]_3\}^0 \cdot 15\text{H}_2\text{O} \]

+ Lewis Acid-Base Interaction
since: 1936, modified 1972 ...

an evergreen in inorganic chemistry ...

Stoichiometry

\[ \left[A^{\text{II}}\right]_4[B^{\text{II}}(\text{CN})_6]_3 \]

or \( A_4B_3 \)

\[ \left[A^{\text{II}}\right]_4 \left[B^{\text{II}}\right]_3 \square_1 \]

\( \square = \text{vacancy} \)

a simple face-centered cubic structure ...

J.F. Keggin, F.D. Miles, Nature 1936, 137, 577

A. Ludi, H.U. Güdel, Struct. Bonding (Berlin) 1973, 14, 1
Coming back to Prussian Blue

\[ T_c \propto z |J| \]

- \( z \): number of magnetic neighbours
- \( |J| \): coupling constant between nearest neighbours

Néel, Annales de Physique, 1948
Coming back to Prussian Blue

\[ T_C \propto z |J| \]

- \( z \) : number of magnetic neighbours
- \(|J|\) : coupling constant between nearest neighbours

\[ T_C = 5.6 \text{ K} \]

Néel, Annales de Physique, 1948
Towards Prussian blue analogues...

\[ T_c \propto z |J| \]

\[ J_{\text{Ferro}} > 0 \]

Orthogonality

\[ T_c > 5.6 \text{ K} \]
Towards Prussian blue analogues ...

\[
T_c \propto z |J|
\]

\[J_{\text{Antiferro}} < 0\]

Overlap ...

\[T_c \gg 5.6 \text{ K}\]
$V_4[Cr(CN)_6]_{8/3} \cdot nH_2O$

Room Temperature $T_c$
On a rational basis!

- $d^3$ orbitals
- $(t_{2g})^3$ configuration
- 9 AF interactions
- 3 F interactions
- 6 F interactions
- Ni$^{II}$
- $d^8$ configuration
- $d^5$ configuration
- Mn$^{II}$
- $d^4$ configuration
- Cr$^{II}$
- $d^3$ configuration
- V$^{II}$
- $d^5$ configuration
- Ti
- Fe
- Co
- Ni
- Cu
- Zn

Ferlay et al., *Nature*, 1995
Mallah et al., *Science*, 1993
$V_4[Cr(CN)_6]_{8/3}.nH_2O$

Room Temperature $T_c$

On a rational basis!
$2[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-} + 3\text{V}_{\text{aq}}^{2+} \rightarrow [\text{V}_3[\text{Cr}^{\text{III}}(\text{CN}_6)]_2]^0$

A blue, transparent, low density magnet at room temperature
Oscillating Magnet: Experiment

1. Permanent Magnet
2. Screen
3. Lens
4. Light, Sun...

Magnetic Molecular

Holder

Image

(1) (2) (3)
A thermodynamical machine transforming Light in Mechanical Energy
QuickTime™ et un décompresseur DV - PAL sont requis pour visualiser cette image.
Other device

Magnetic Switch...

Or thermal probe ...

Permanent Magnet

Hot

Couple

Sample (□ MM)
Up to 2004 ... magnetic analogues used as ... devices and demonstrators
Chemists have managed to transform isolated single molecules into magnets.
molecule-based magnets? Why?

Specific properties

- Low density
- Transparent
- Nanosized, identical molecules
- Often biocompatible and biodegradable
- Very flexible chemistry
- Mild chemistry: Room T, Room P, Solution Chemistry

To improve

- Fragile
- Aging
- Diluted

To overcome
Nanosystems

- Top down
  - 3D Metals Oxydes
  - Fragments Threads Dots
- Bottom up
  - Giant Molecular Clusters
  - 0D, Molecules

Nanosystems
- New Physics
- Quantum / Classical
- Quantum tunneling
- Nice Chemistry
- Single molecule magnets

Applications (far ...)
- Recording
- Quantum computing
... Single molecule magnets

Giant Molecular Clusters

High Spin + Anisotropy
\[ \Delta E = D S_z^2 \]

New Materials

See Gatteschi Hendrickson Christou Winpenny ...
What is named Single Molecule Magnet?

High Spin

Anisotropic
High Spin Paramagnetic Molecule
Single Molecule Magnet

Towards information storage at the molecular level?
Single Molecule Magnet

Towards information storage at the molecular level?
Single molecule magnets

\[ DS_z^2 = 400K \]
\[ |D| = 1K \]
\[ S = 20 \]

\( D < 0 \)
Spin = 2
\[ \text{Ni(II)}(\text{Rad}^\circ)_2 \]
Spin = 1
\[ \text{Ni(II)}(\text{tetren}) \]

2nd generation

1rst generation

Complex

K. Vostrikova, P. Rey et al., JACS 2000, 122, 718
Some examples ... 

$S = 27/2$

$S = 39/2$ (AF)

$S = 14/2$

Decurtins, Angewandte, 2000
Hashimoto, JACS, 2000

Marvaud, Chemistry, 2003, 9, 1677 y 1692

Rey, JACS 2000, 122, 718
Marvaud et al., Chemistry, 2003, 9, 1677 and 1692
Ariane Scuiller, Caroline Decroix, Martine Cantuel, Fabien Tuyèras...
Anisotropy

High spin

CrNi
CrNi2
CrNi3
CrCo3
CrNi6
CrNi5

CoCo2
CoCu2
CoCo6
CoNi2
CoNi3
CoCu3
CoCo3
CoNi5

$\frac{5}{2}$
$\frac{7}{2}$
$\frac{9}{2}$
$\frac{27}{2}$

V. Marvaud
\[ \text{[Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{COOH}\cdot4\text{H}_2\text{O} \]

or \( \text{Mn}_{12} \)

\[ S = 8 \times 2 - 4 \times \frac{3}{2} = S = 10 \]

From D. Gatteschi and R. Sessoli
Mn12 is a hard magnet

Bistability: in zero field the magnetisation can be positive or negative depending on the story of the sample.

From D. Gatteschi and R. Sessoli
Ground State Energy Levels

\[ H = 0 \]

From D. Gatteschi and R. Sessoli
At low temperature, a magnetic field populates only the $M = -S$ state.
Going back to equilibrium: Thermal activation: trivial

Axial symmetry

\[ E(M) = DM^2 \]

\[ H=0 \]

\[ \Delta E = DS^2 \]

\[ \tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \]

From D. Gatteschi and R. Sessoli
Towards equilibrium:

Tunneling effect: new!

\[ H=0 \]

\[ M=S \quad \text{and} \quad M=-S \]

From D. Gatteschi and R. Sessoli
Mn12 is a Hard Magnet

+ Steps in the magnetisation curve

From D. Gatteschi and R. Sessoli
Resonant Tunneling Effect for $H = nD/g\mu_B$

From D. Gatteschi and R. Sessoli
Conditions to observe tunnelling effect

- Degenerated wave functions must superpose
- A transversal field must couple the two wave functions
- Coupling splits the two levels: “tunnel splitting”
- Tunnelling Effect Probability increases with tunnel splitting

From D. Gatteschi and R. Sessoli
Tunneling Effect

From D. Gatteschi and R. Sessoli
No resonant Tunneling Effect with a magnetic field parallel to $z$

\[ H \neq nD/g\mu_B \]

From D. Gatteschi and R. Sessoli
No tunneling effect

From D. Gatteschi and R. Sessoli
Feasibility of « Molecular nanowires » (or SCM) ?

Anisotropic precursor

\[ \text{[Fe(III)(bipy)(CN)\textsubscript{4}]^{-}} \]

R. Lescouëzec, M. Julve, Valencia, Spain D. Gatteschi, W. Wernsdorfer
Angewandte Chem. 2003, 142, 1483-6
Trinuclear species

Double zig-zag chains

Bis double zig-zag chains

\[[\text{Fe}^{III}(L)(\text{CN})_4]_2\text{M}^{II}(\text{H}_2\text{O})_4\] \cdot 4\text{H}_2\text{O}

\[[\text{Fe}^{III}(L)(\text{CN})_4]_2\text{M}^{II}(\text{H}_2\text{O})_4\] \cdot 4\text{H}_2\text{O}

\[[\text{Fe}^{III}(L)(\text{CN})_4]_2\text{M}^{II}(\text{H}_2\text{O})_4\] \cdot 4\text{H}_2\text{O}

\[[\text{Fe}^{III}(\text{bpy})(\text{CN})_4]_2\text{M}^{II}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN} \cdot 1/2\text{H}_2\text{O}\ [\text{M} = \text{Mn}, \text{Co}, \text{Cu}]

[L = 2,2’-bipy and 1, 10-phen],

M = Mn, Co, Cu, Zn]
Slow relaxation of the magnetisation ...

Magnetization as a function of time

Thermally activated relaxation of the magnetization

\[ E_a = 142 \text{ K}, \quad \tau_0 = 6.10^{-11} \text{ s} \]

\[ M \text{ vs. } t \text{ plots along the } b \text{ axis.} \]

W. Wernsdorfer, Grenoble
The dream...

- Magnetic Tip

- Surface

High Spin "down" to the left

High Spin "down" to the right

≈ 10 nm
Surface

Magnetic Tip

\[ H \approx 10 \text{ nm} \]

High Spin "down"

≈ 10 nm

High Spin "down"

Surface
The dream ...

Magnetic Tip

High Spin "down"

HSM «up»

Surface

≈ 10 nm

... information storage at the molecular level!
Nanosciences ...

High Spin "down"

≈ 10 nm

HSM «up»

Surface

... a challenge for chemists and friends ...