



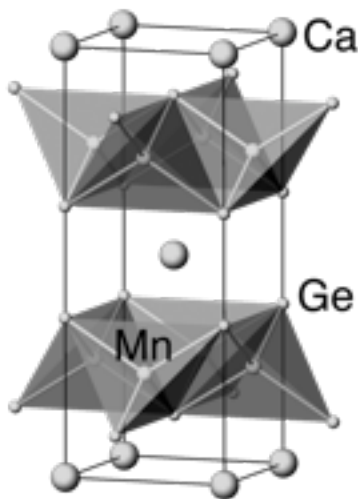
# Research topics in 2000

Coordination chemistry  $\leftrightarrow$  molecular magnetism

Intermetallic compounds  
( $\text{CaMn}_2\text{Ge}_2$ )

$T_N = 675 \text{ K}$

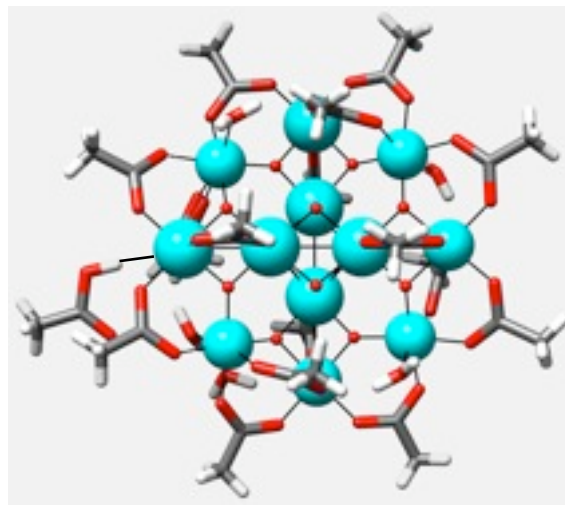
R. Welter, *J. MMM.*, **1998**, 187, 278



Single Molecule Magnet  
[ $\text{Mn}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}$ ]

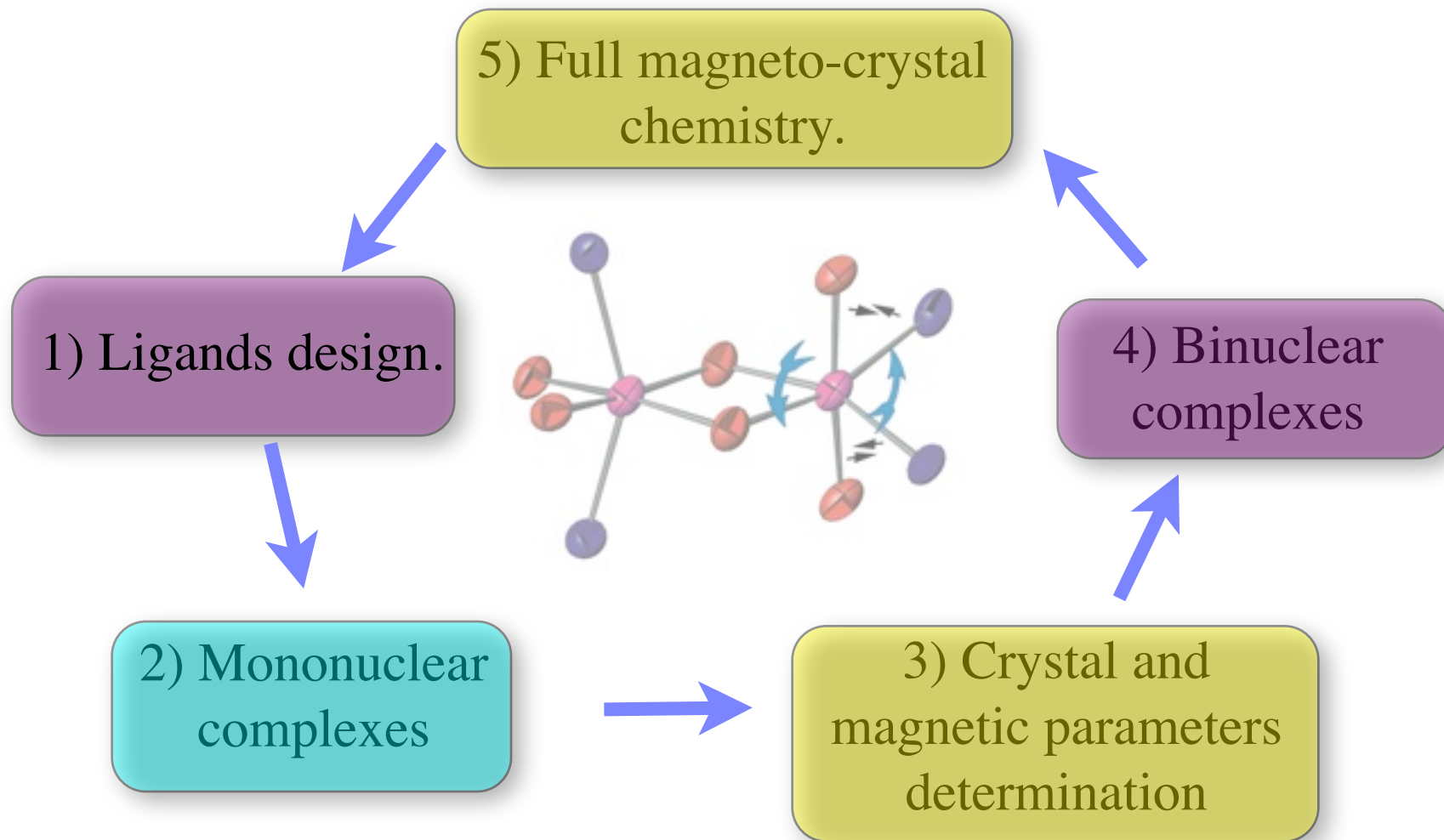
$T_B = 5 \text{ K}$

T. Lis, *Acta Cryst.*, **1980**, B36, 2042  
D. Gatteschi et al, *Nature*, **1993**, 365

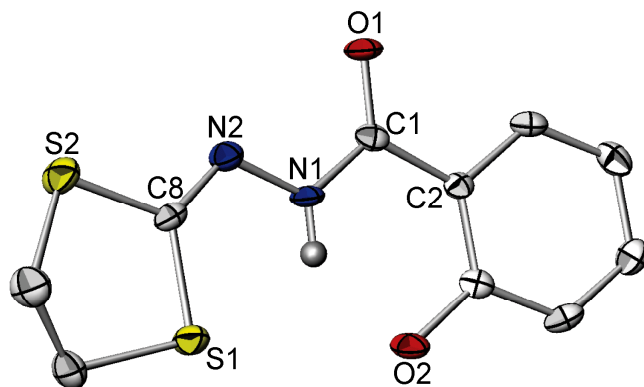


New magnetic materials - New magnetic systems ?

# *Methodology*

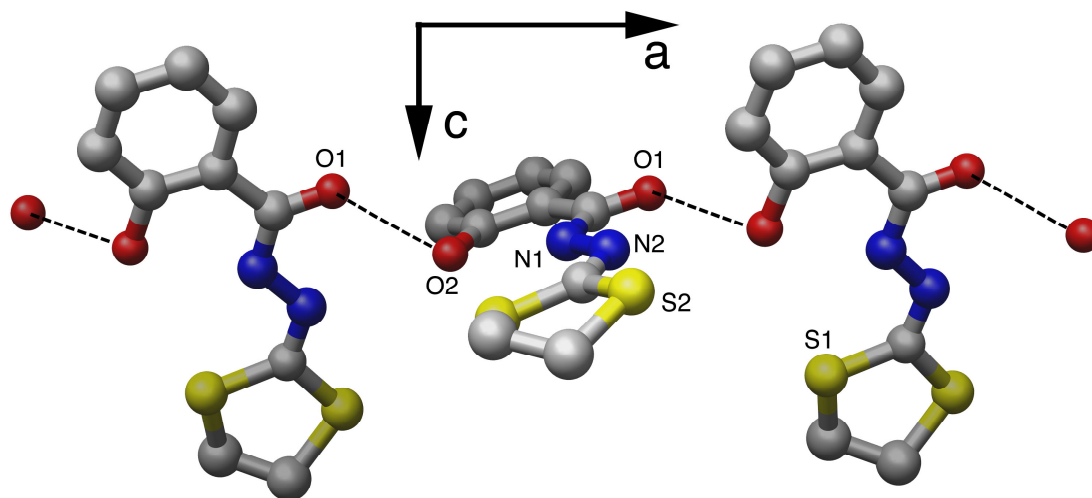


# *2-hydroxy-1,3-dithiolan-2-ylidenehydrazide benzoïque acid ( $H_2L_2$ )*



*Asymmetric unit of  $H_2L_2$*

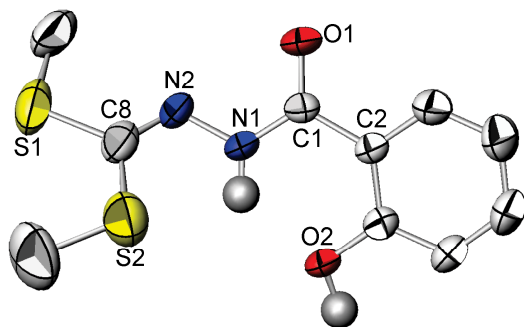
Orthorhombic space group :  $Pnca2_1$   
Formula :  $C_{10}H_{10}N_2O_2S_2$



*Supramolecular packing of  $H_2L_2$  along the a axis*

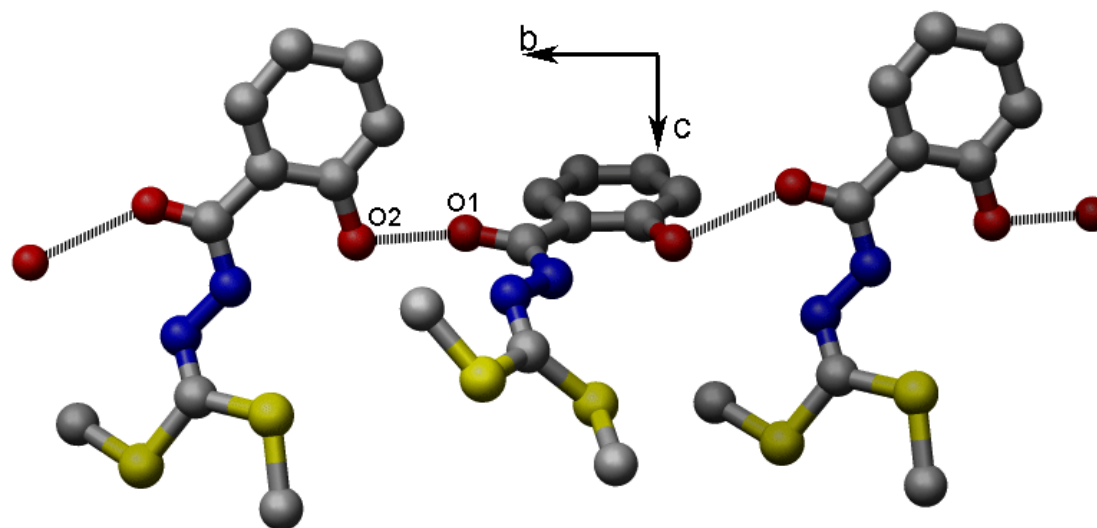


# *2-hydroxy[bis(methylthio)methylene]hydrazide benzoique acide (H<sub>2</sub>L<sub>3</sub>)*



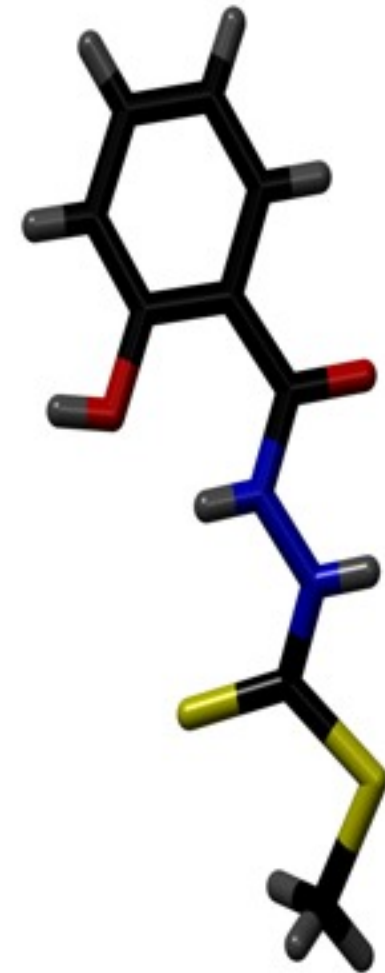
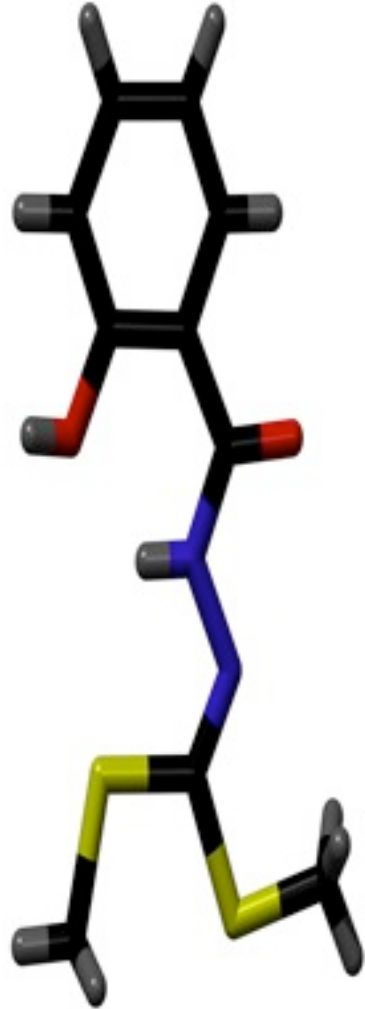
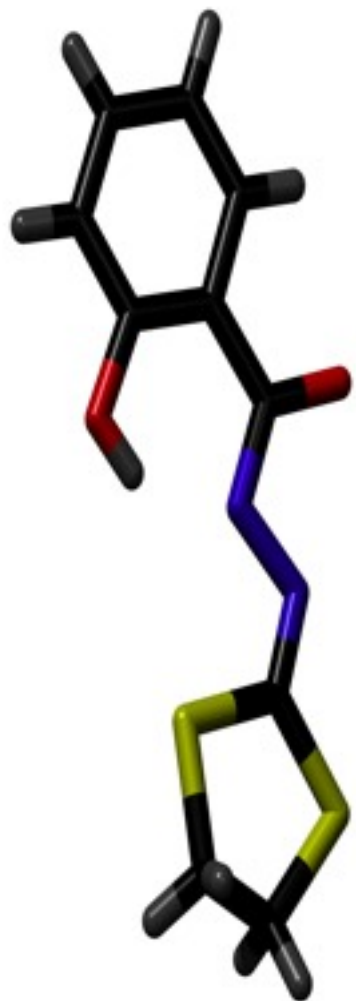
*Asymmetric unit of H<sub>2</sub>L<sub>3</sub>*

Orthorhombic space group : P b c a  
Formula : C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>

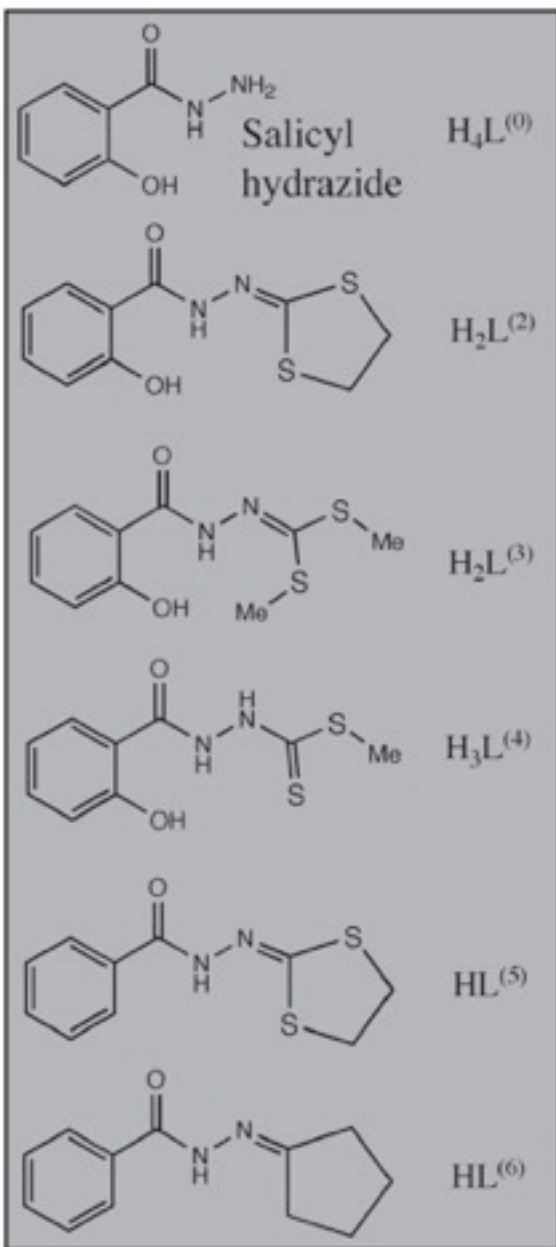


*supramolecular packing of H<sub>2</sub>L<sub>3</sub> along the b axis*

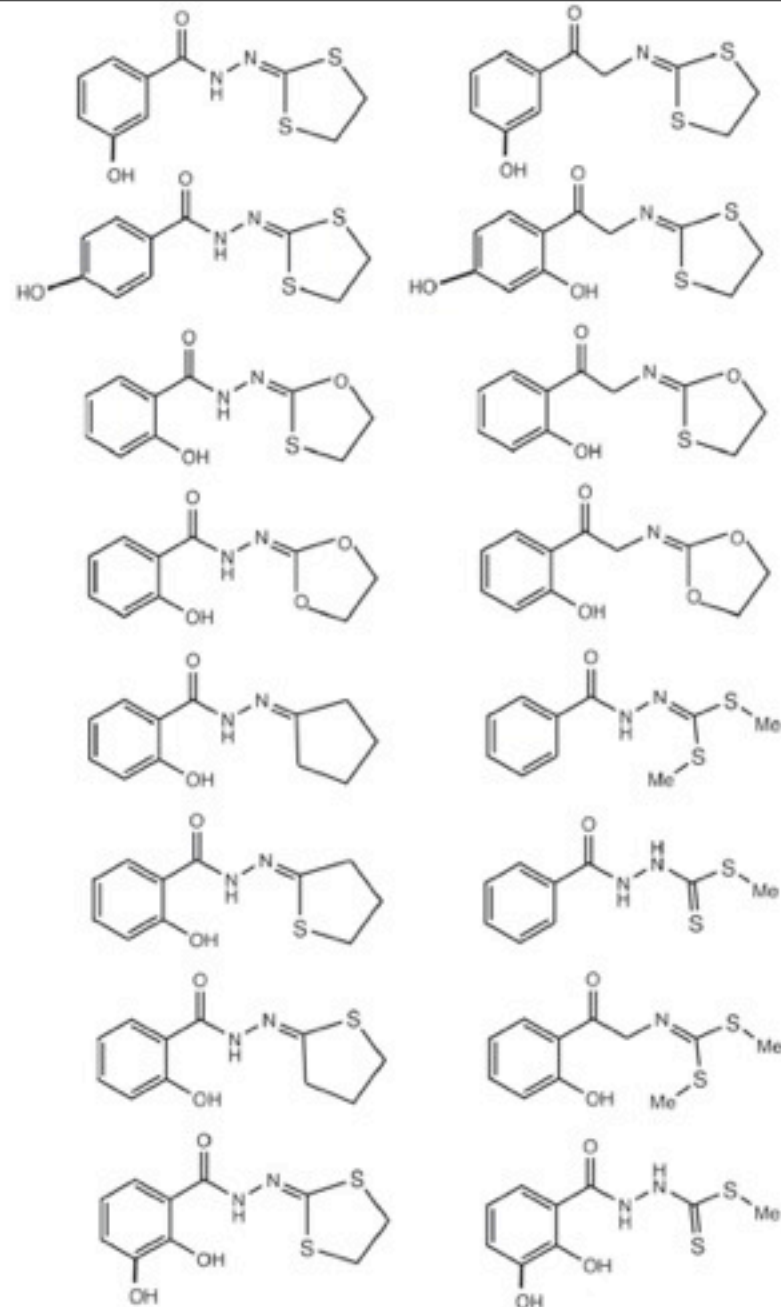
They run  
together !



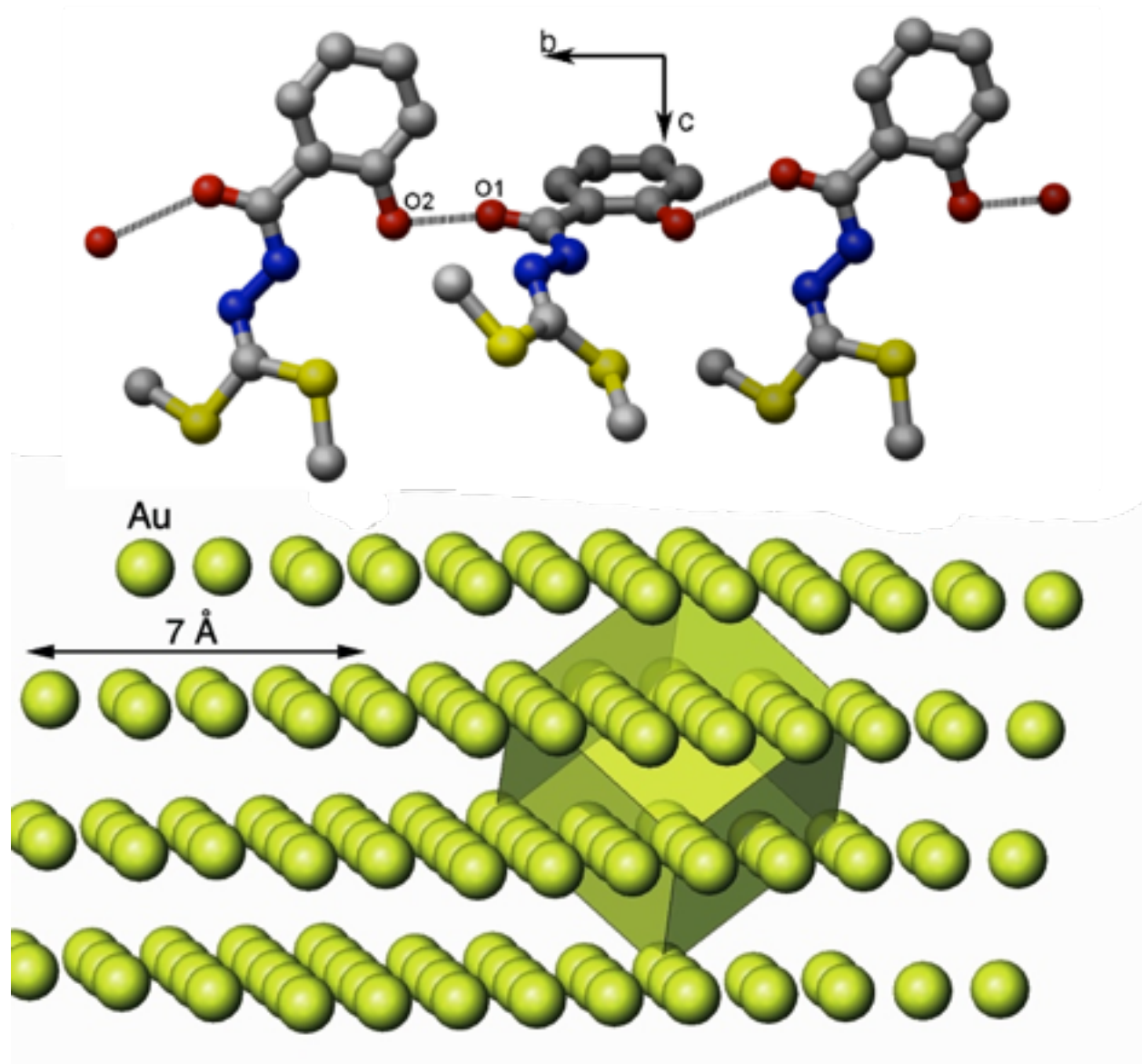
They run again ! ---> **ligands ready for the competition?**



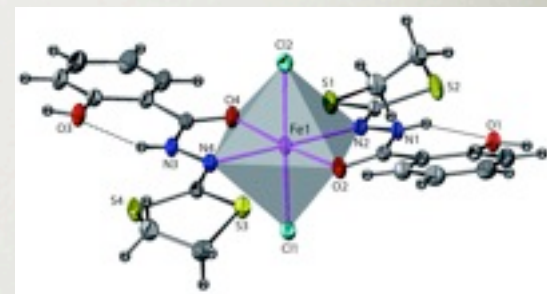
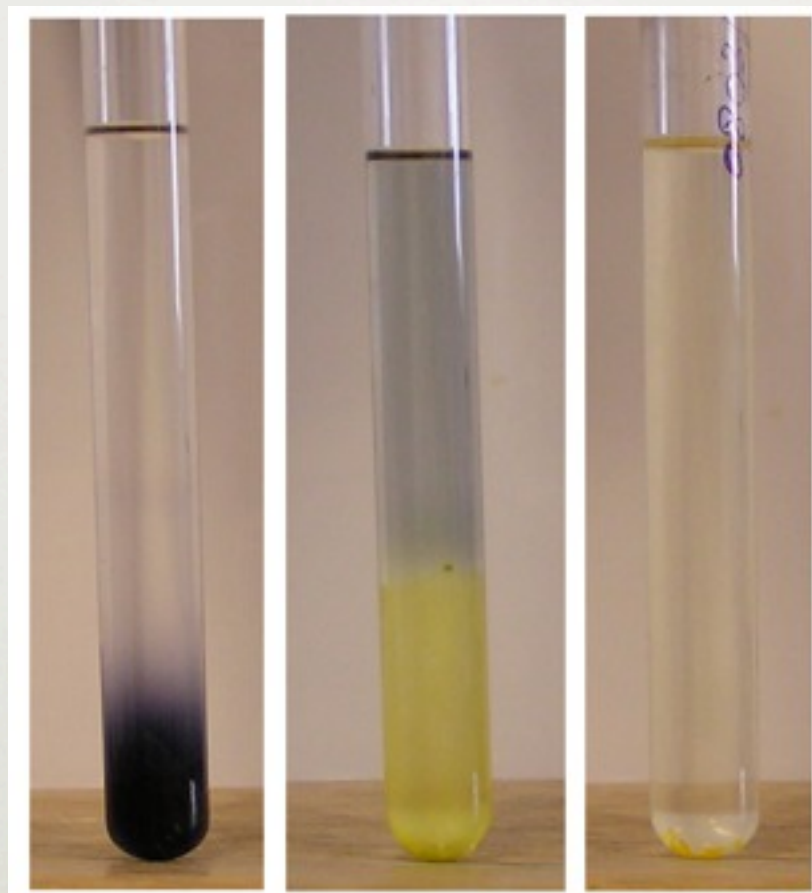
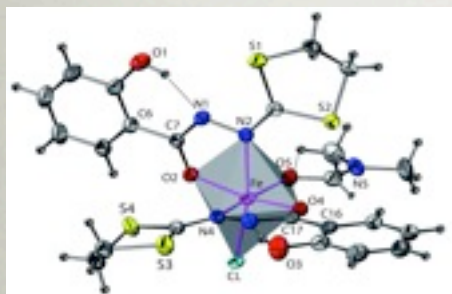
Ligands already synthesized



Example of ligands planned to be prepared with this project



# Iron complexes

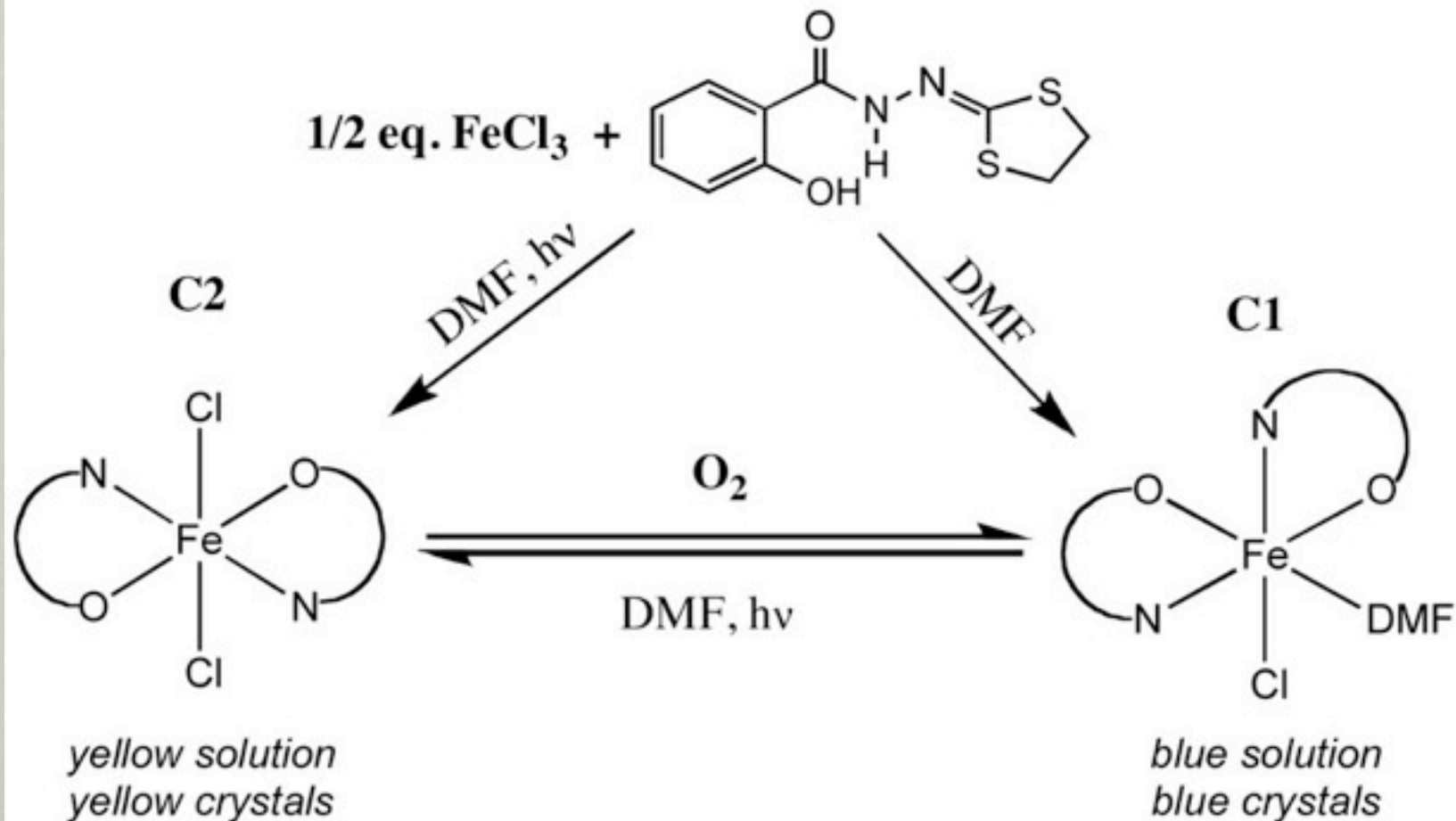


**Synthesis and Magnetic Properties of New Mono- and Binuclear Iron Complexes with Salicyloylhydrazono Dithiolane Ligand,**

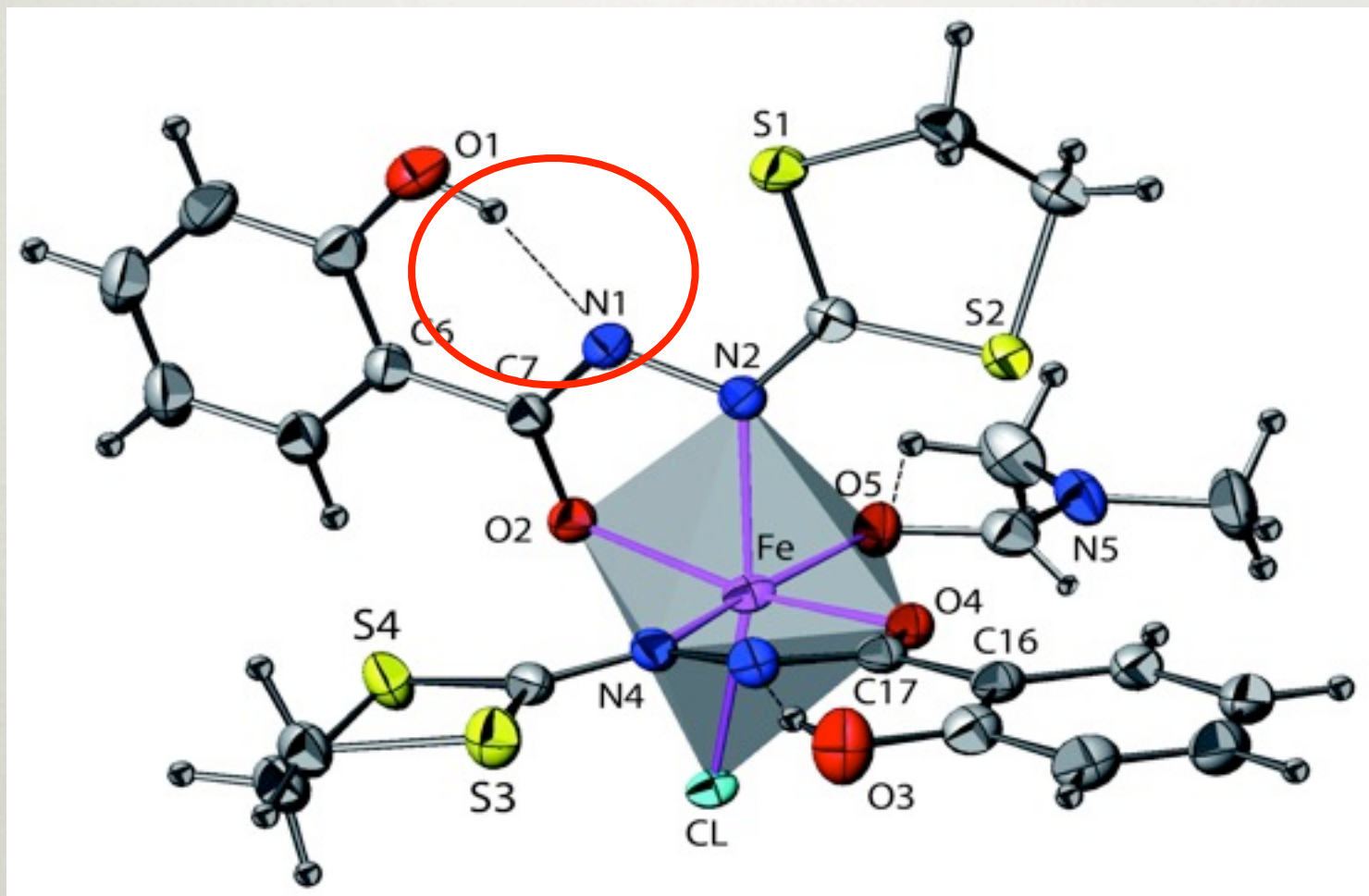
Bouslimani, N.; Clément, N.; Rogez, G.; Turek, P.; Bernard, M.; Dagorne, S.; Martel, D.; Cong, H. N.; Welter, R. *Inorg. Chem.*; (Article); 2008; 47(17); 7623-7630.



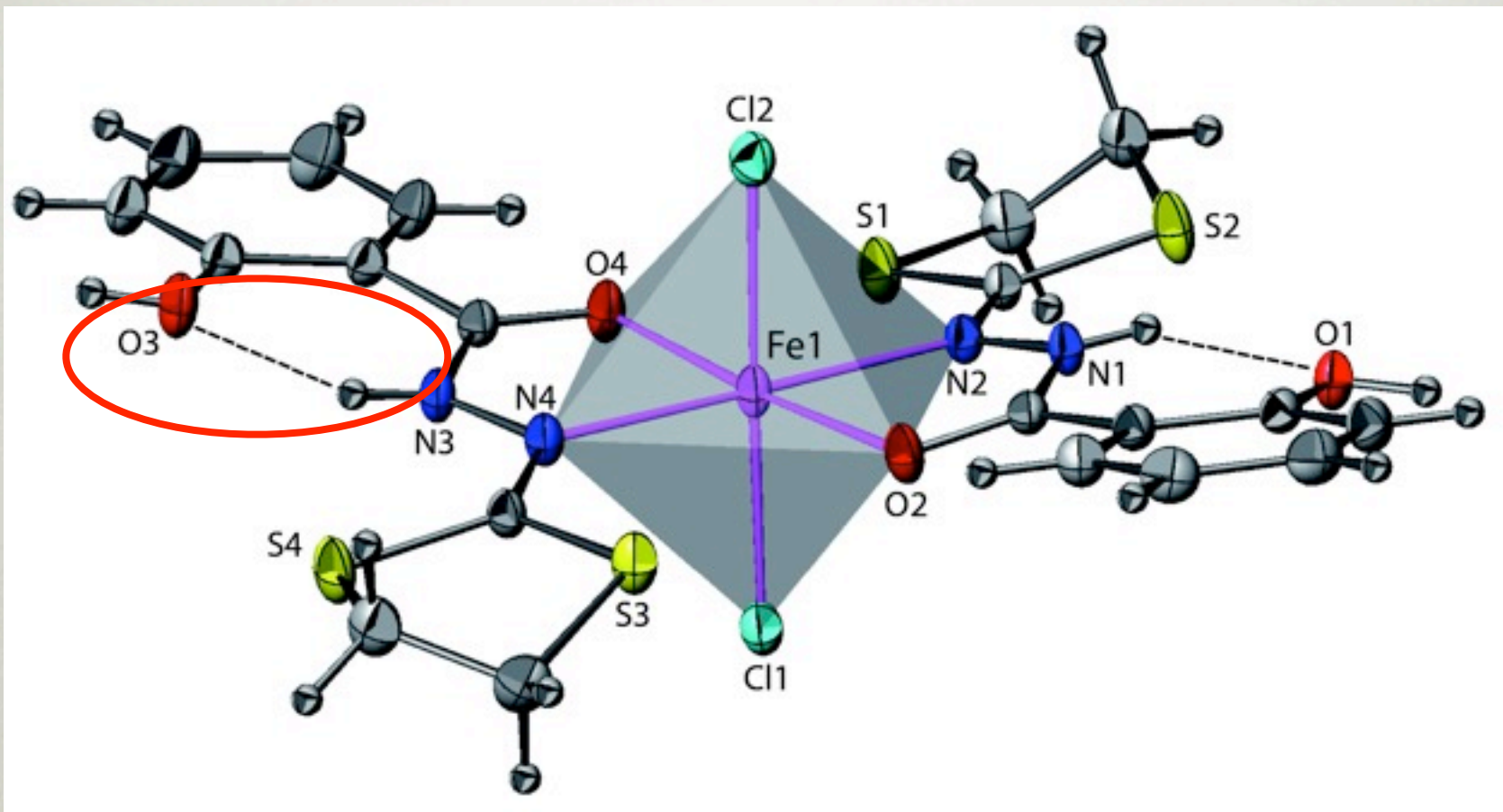
# A photo reduction process



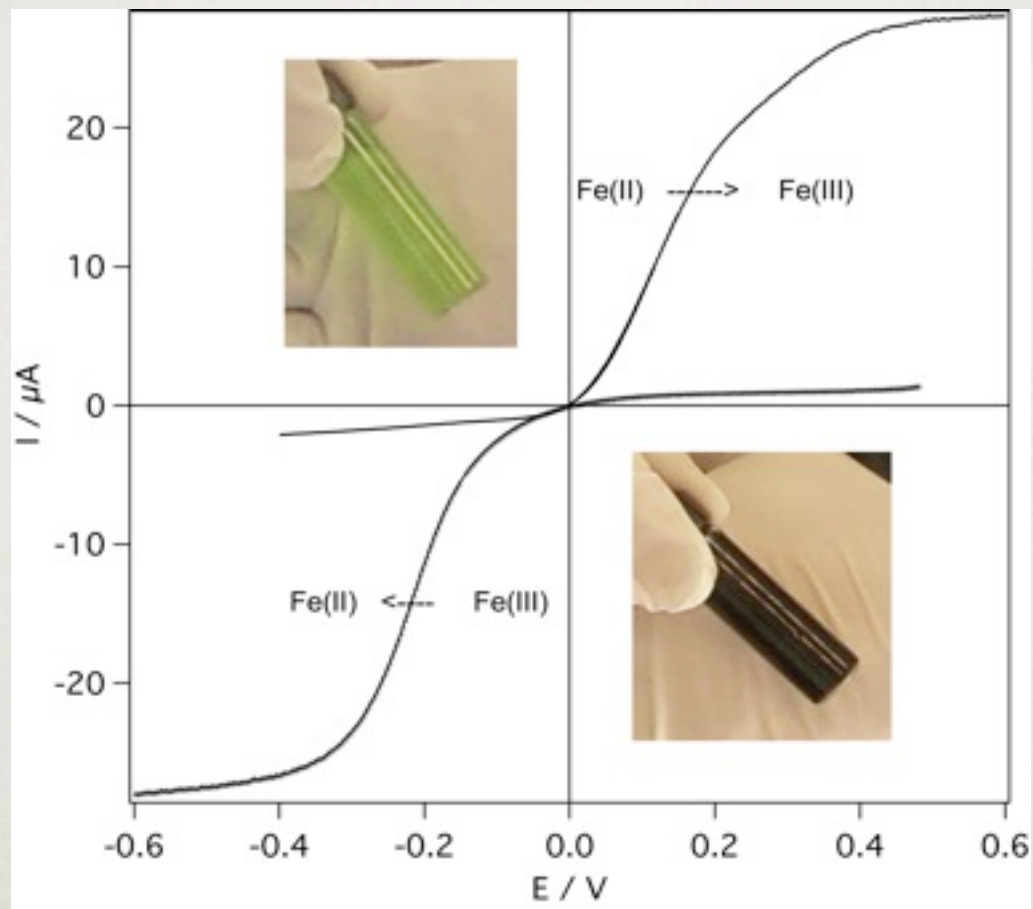
# Fe<sup>III</sup> complex --- Ligand -1 (basic form)



# Fe<sup>II</sup> complex --- Ligand O (acid form)



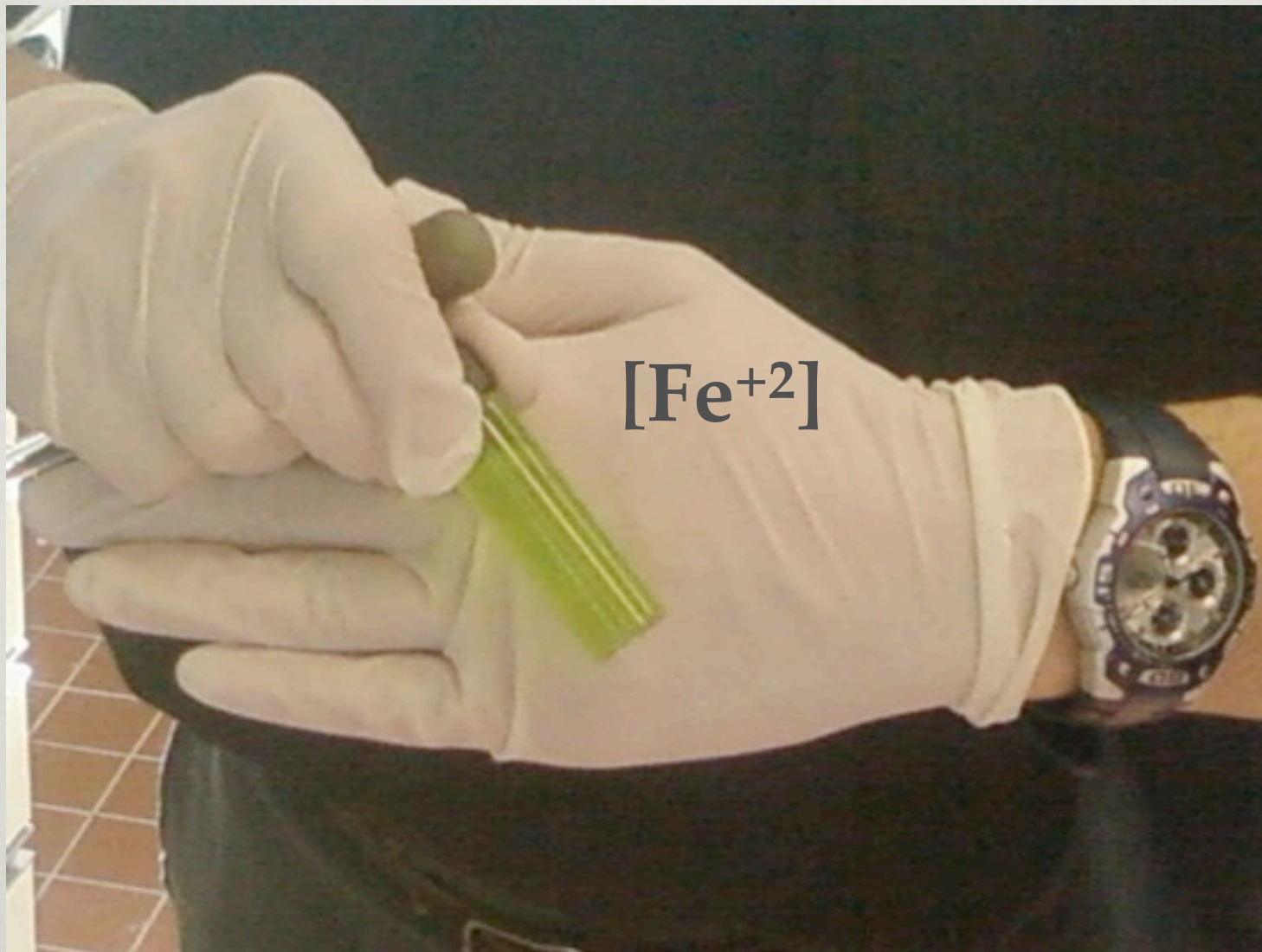




**Synthesis and Magnetic Properties of New Mono- and Binuclear Iron Complexes with Salicyloylhydrazono Dithiolane Ligand**

Bousslimani, N.; Clément, N.; Rogez, G.; Turek, P.; Bernard, M.; Dagorne, S.; Martel, D.; Cong, H. N.; [Welter, R.](#)

**Inorg. Chem.; (Article); 2008; 47(17); 7623-7630.**



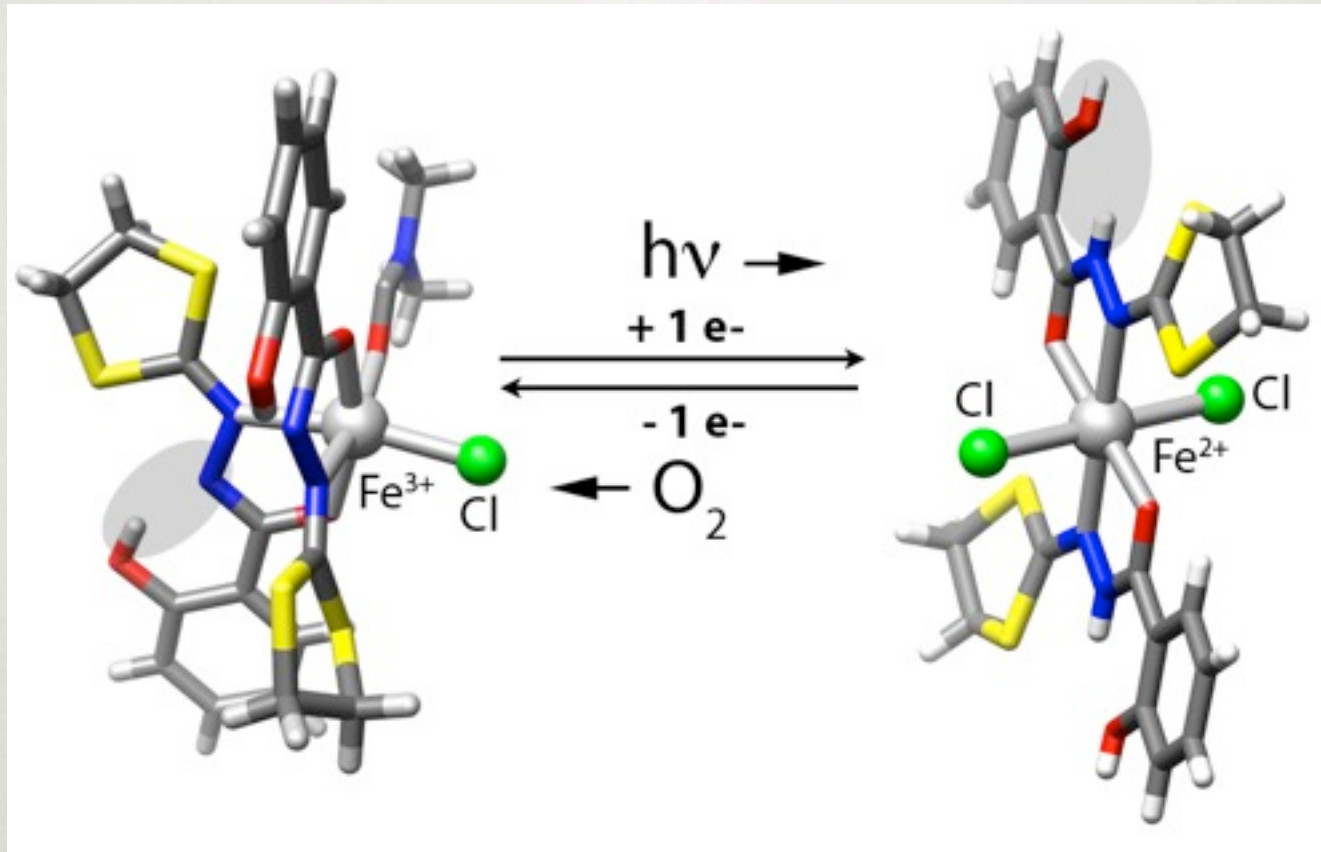
$[Fe^{+2}]$





$[Fe^{+3}]$

# Light Induced Reduction of Iron (III) to Iron (II)

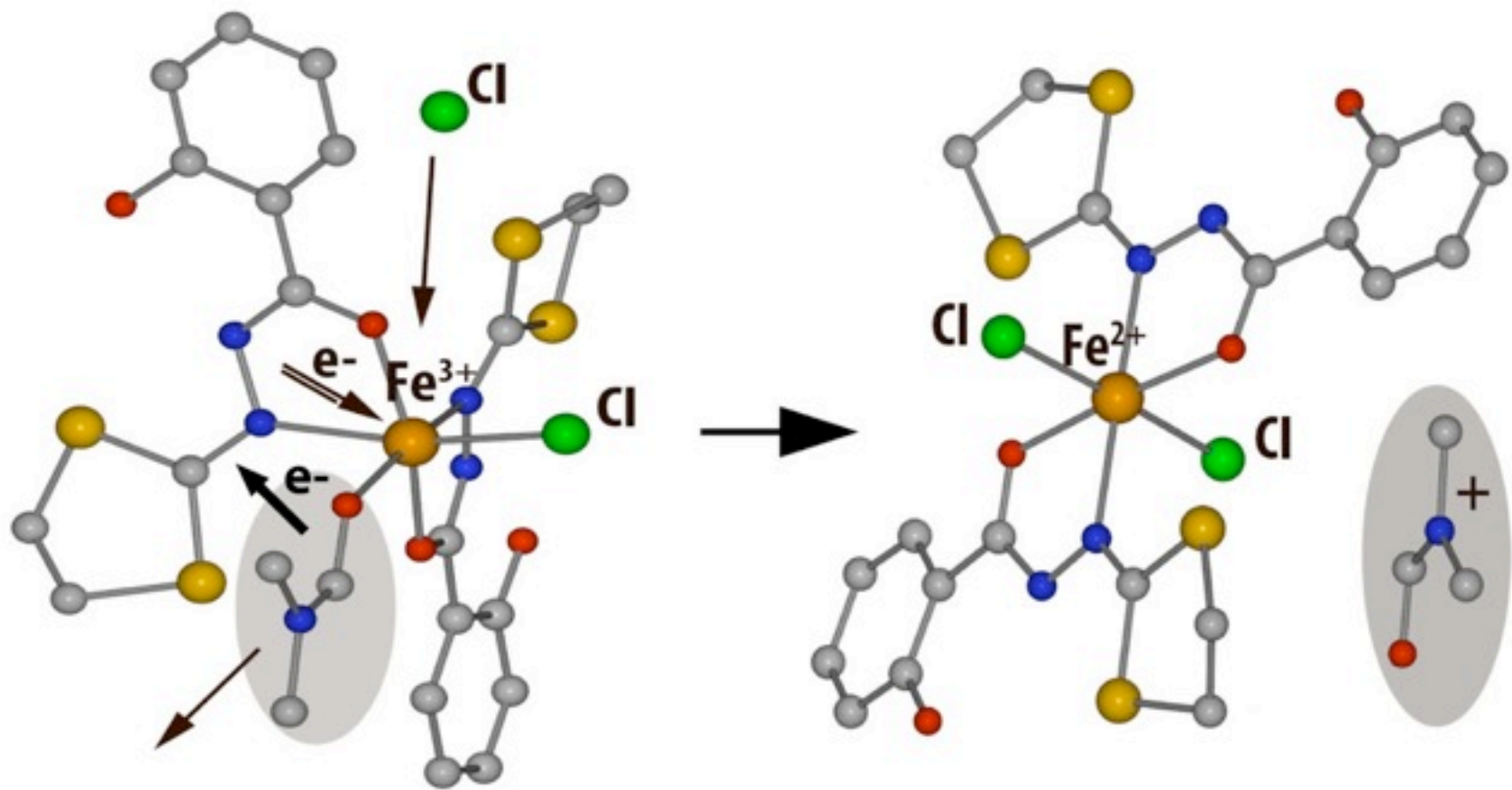


Only one example founded in 1955 - EDTA / not well characterized

**Large application in electricity production  
and storage at low cost :**

Patent (2009)

# Proposed mechanism

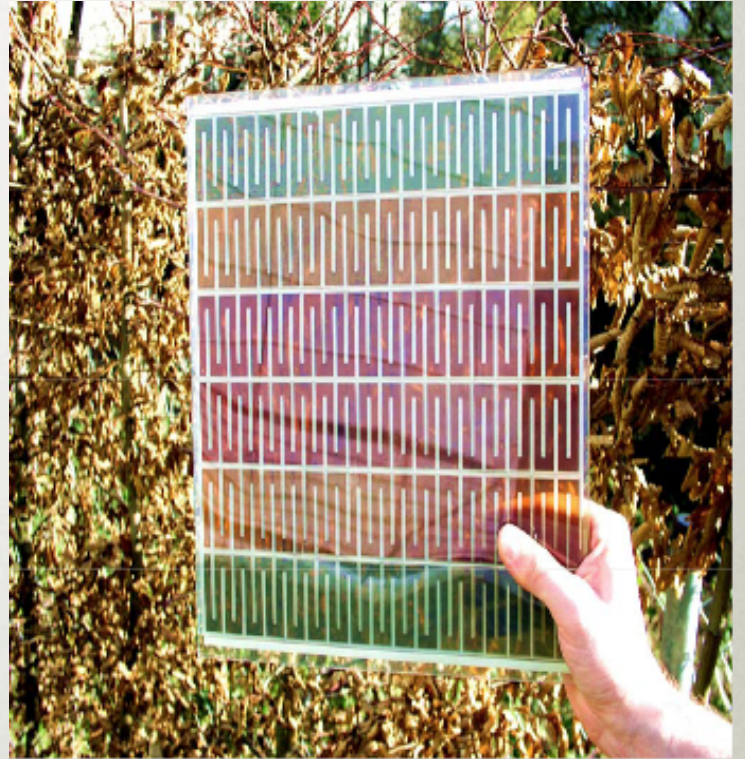






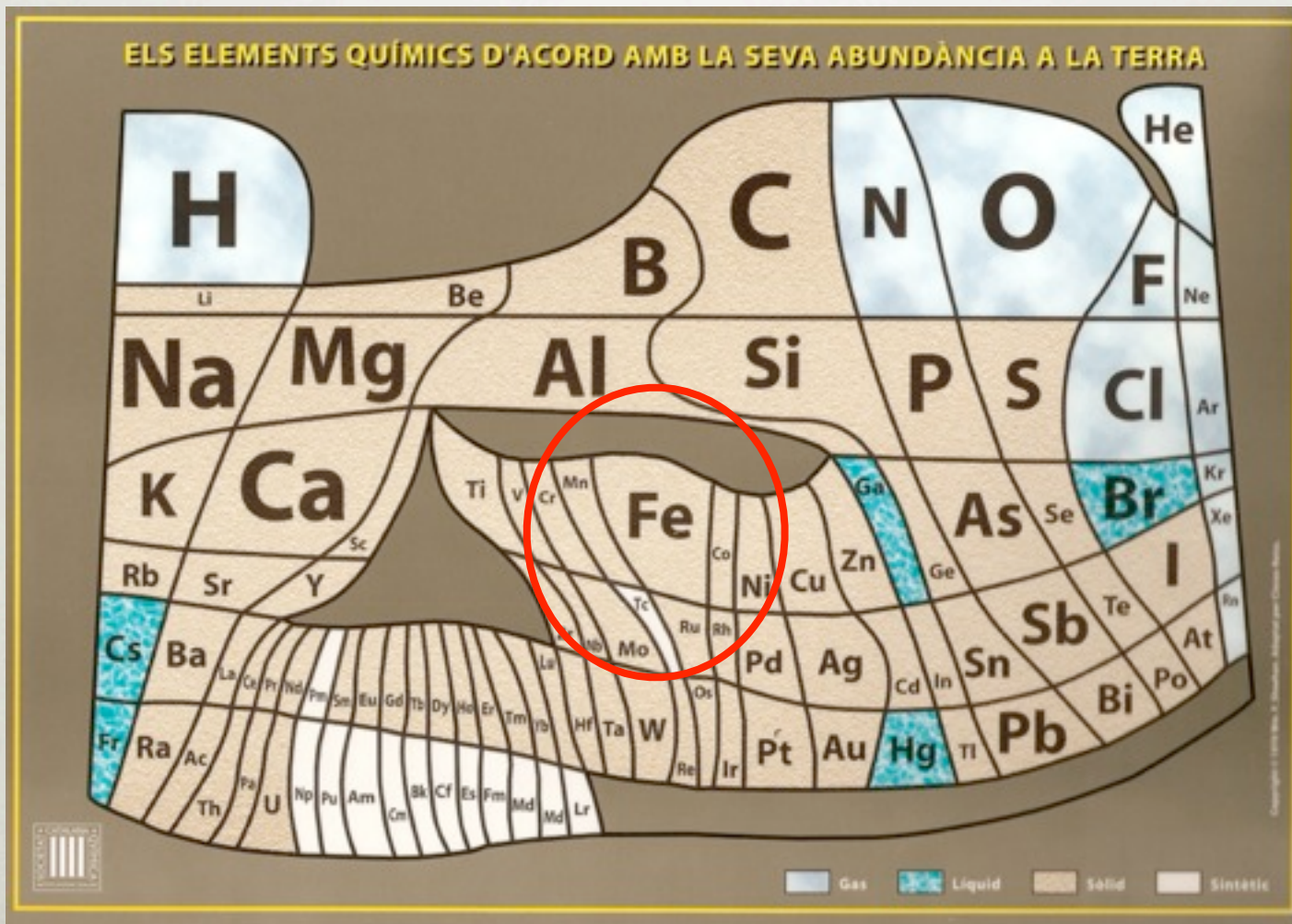








# Easy access to iron on earth





**Photo device given 310 mV et 15  $\mu$ A.**

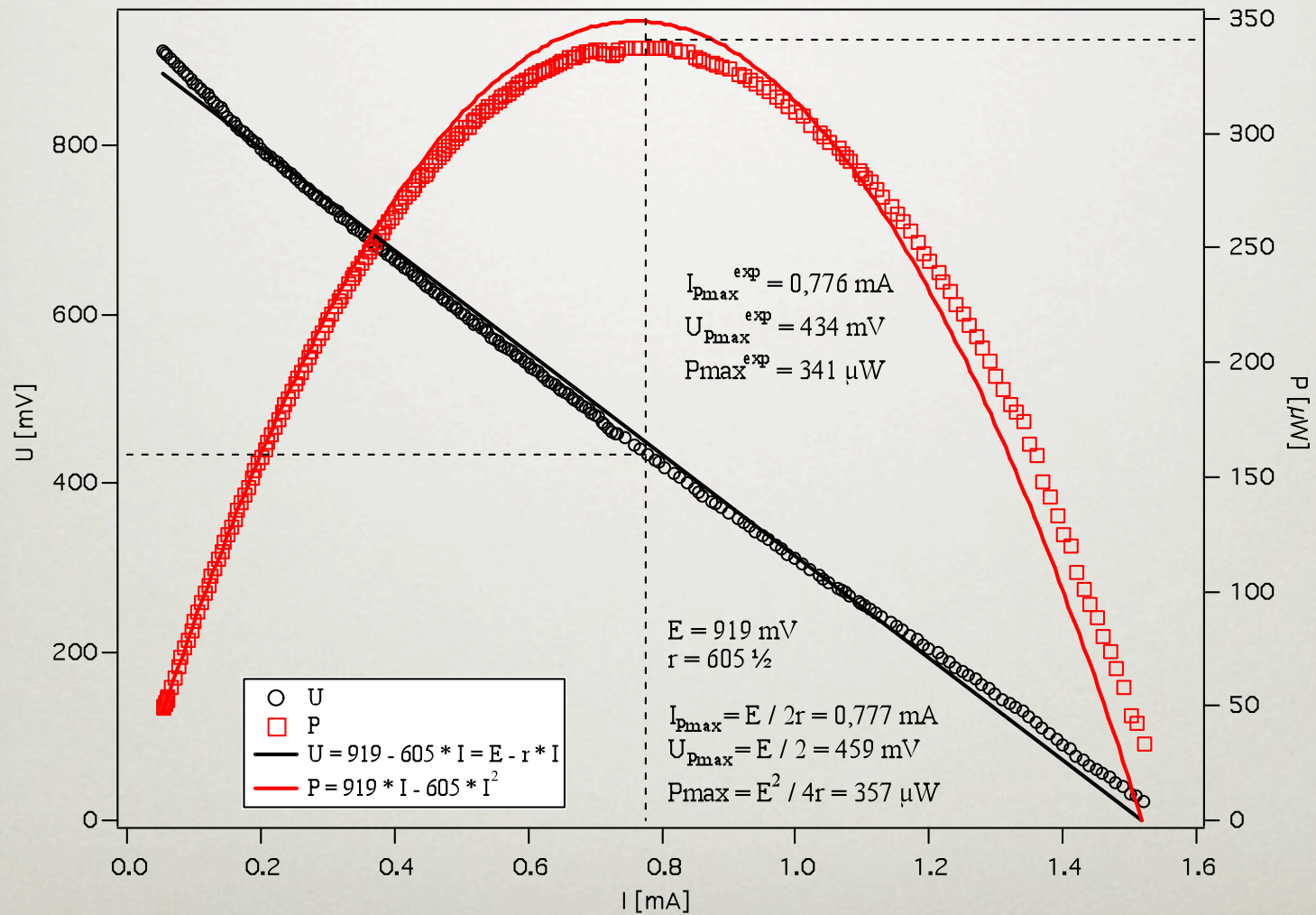
Easy technology

Low cost

'green'



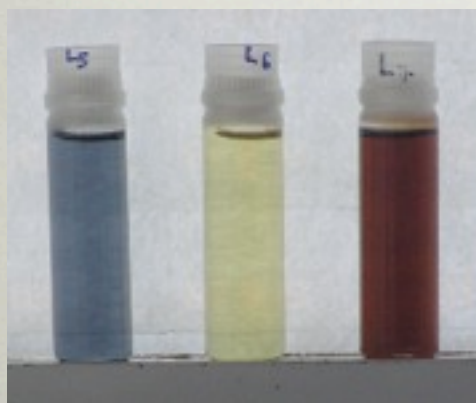
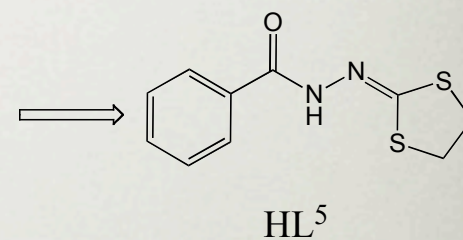
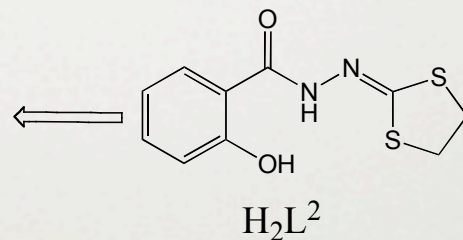
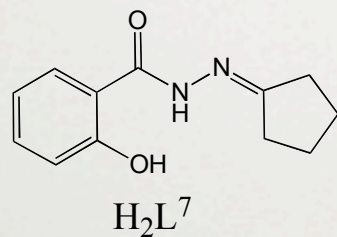
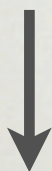
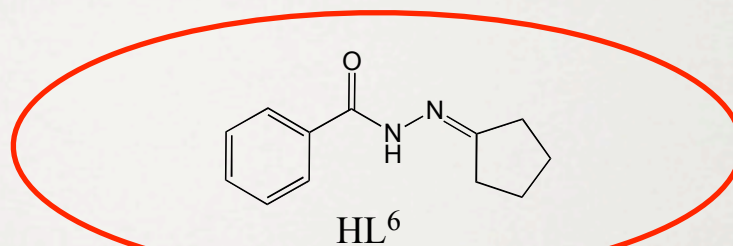
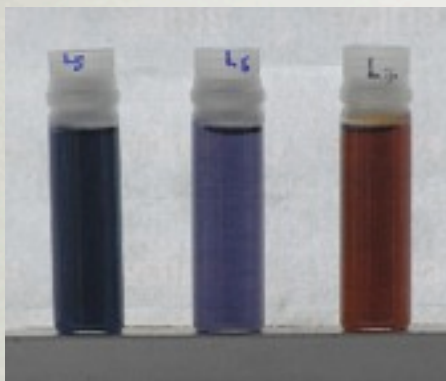
# Power vs I : a classical cell



# Other applications

- Energy storage
- Chemical reduction process :  $\text{Cu}^{2+} \rightarrow \text{Cu}^{+1}$  for instance
- Nanoelectronics : molecular switch induced by light
- \* Depollution ( $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{III}}$ )
- \* etc...

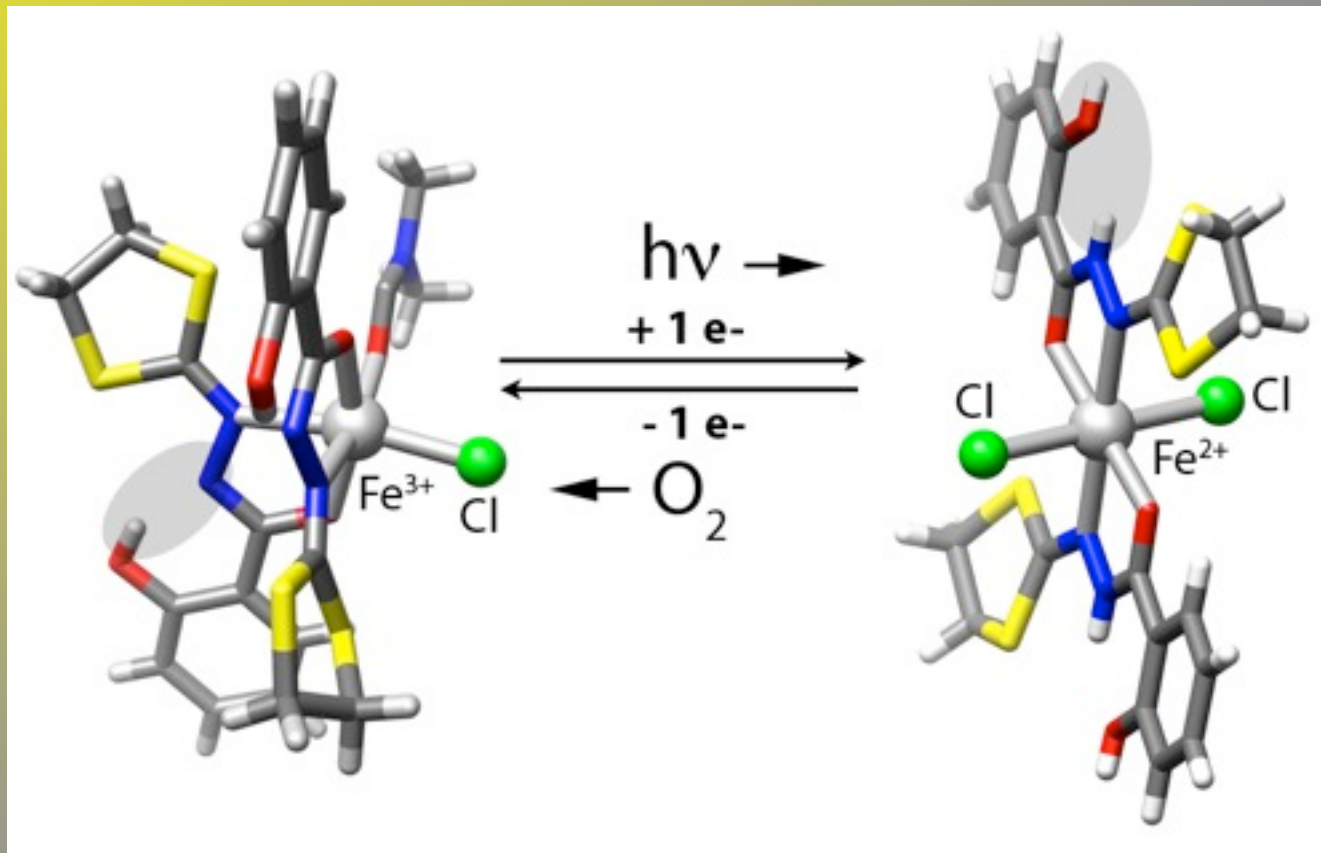
# Other candidates



*Spontaneous Reduction of High-Spin Fe<sup>III</sup> Complexes Supported by Benzoic Hydrazide Derivative Ligands.*

N. Bouslimani, N. Clément, C. Toussaint, S. Hameury, P. Turek, S. Choua, S. Dagorne, D. Martel<sup>c</sup> and R. Welter

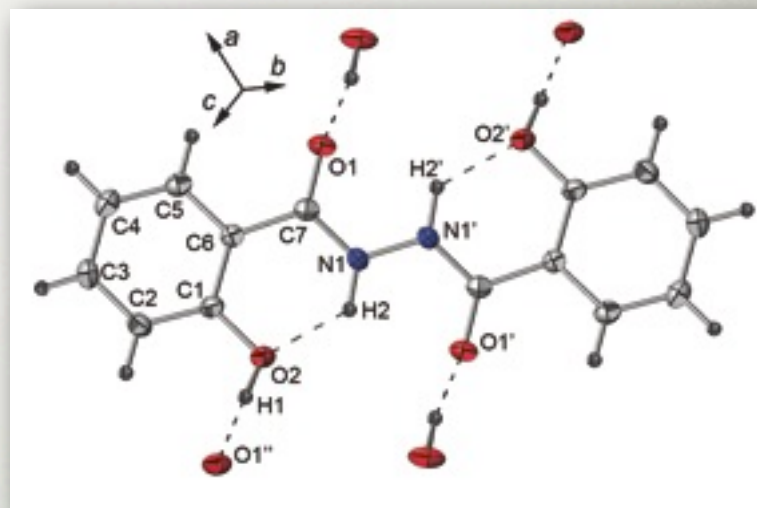
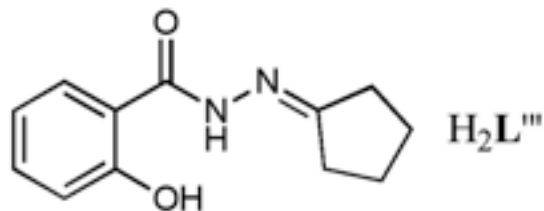
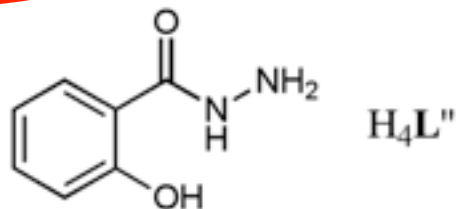
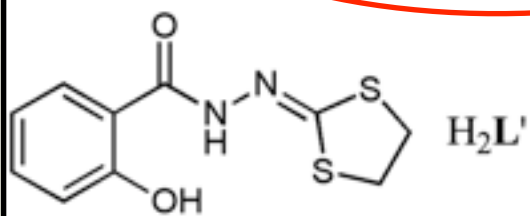
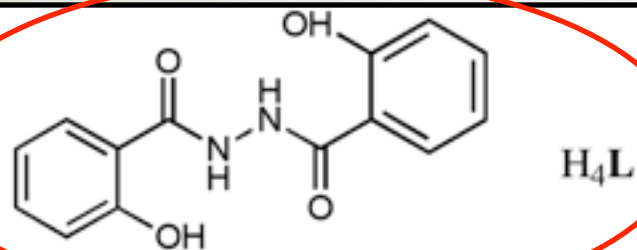
*European Journal of Inorganic Chemistry, (2009), 3734-3741*

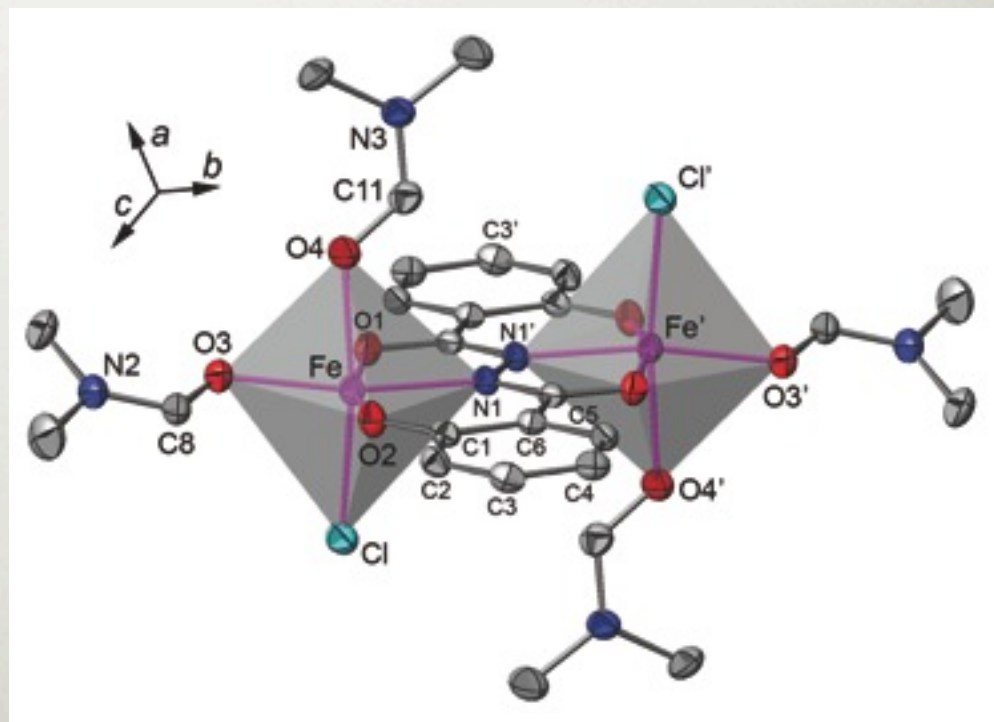
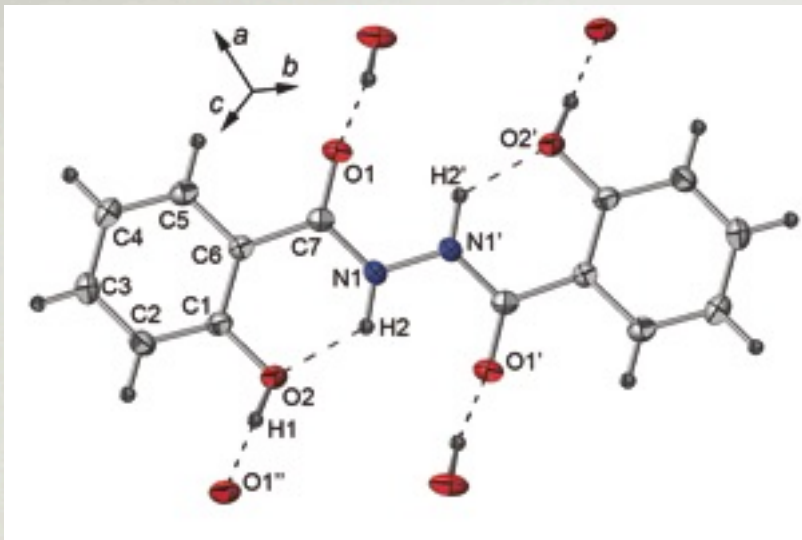


2010 --> I. S. 2, private compagny

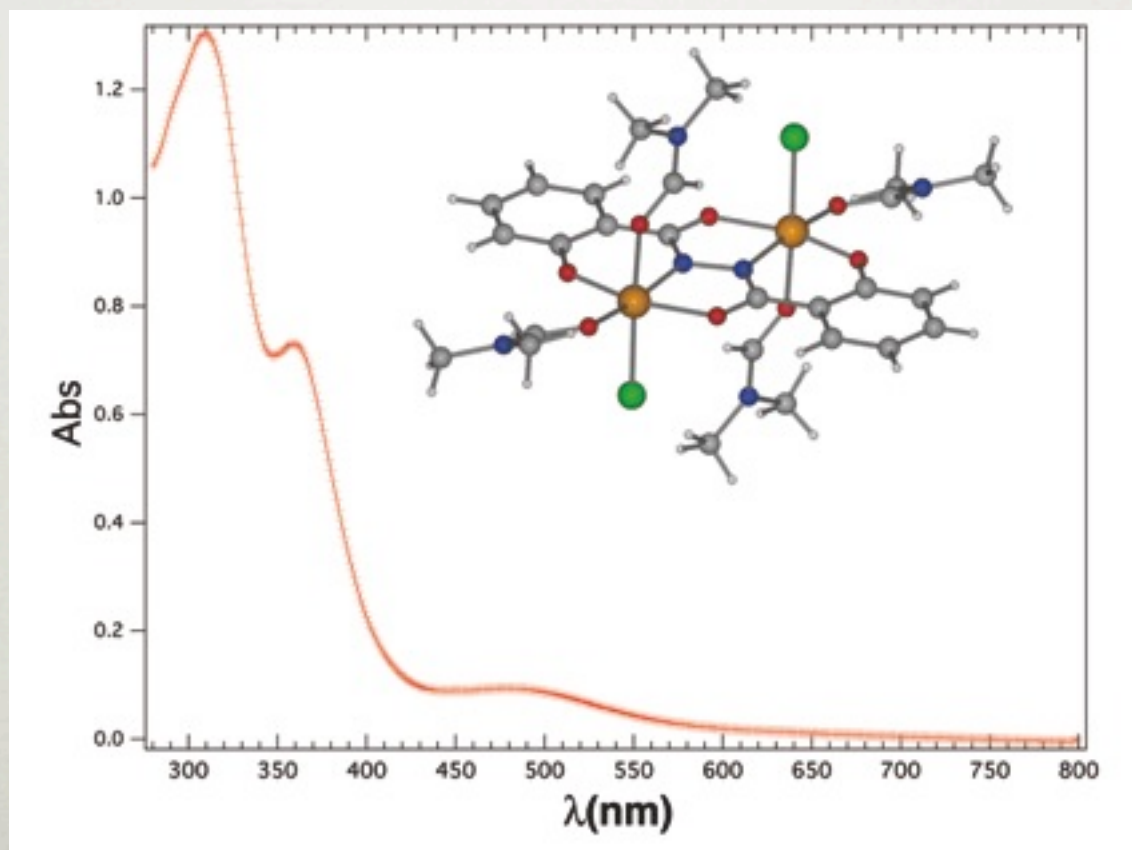


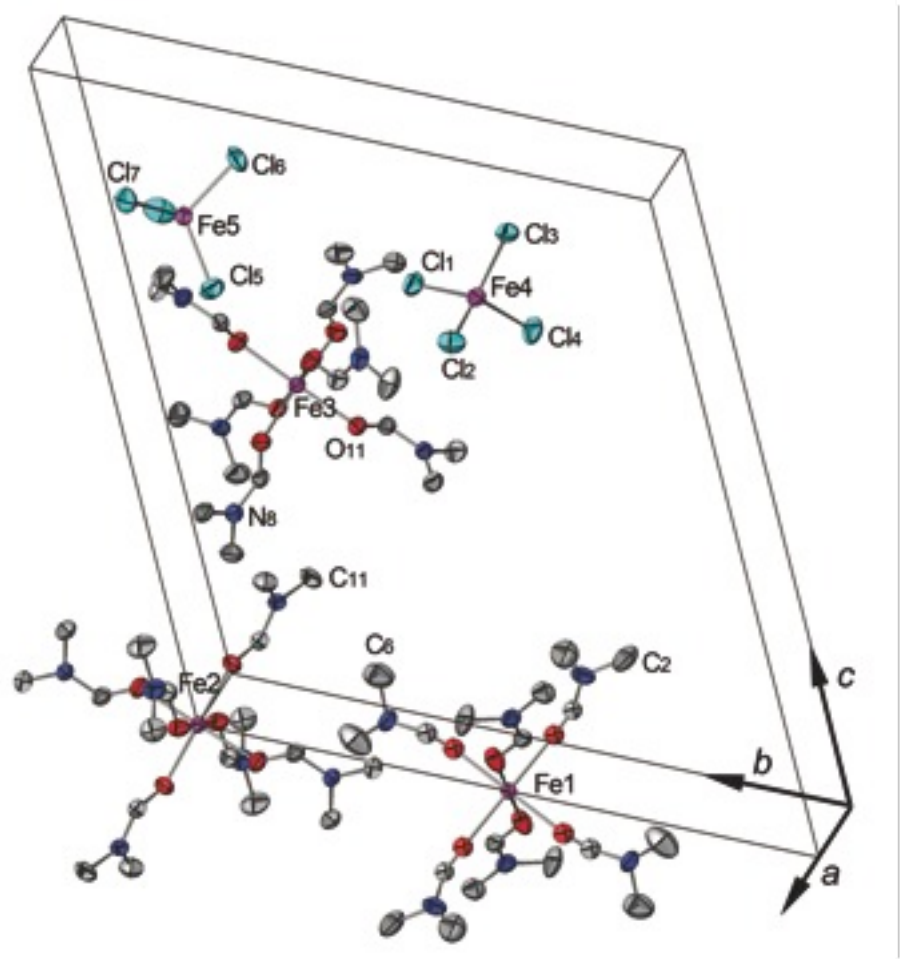
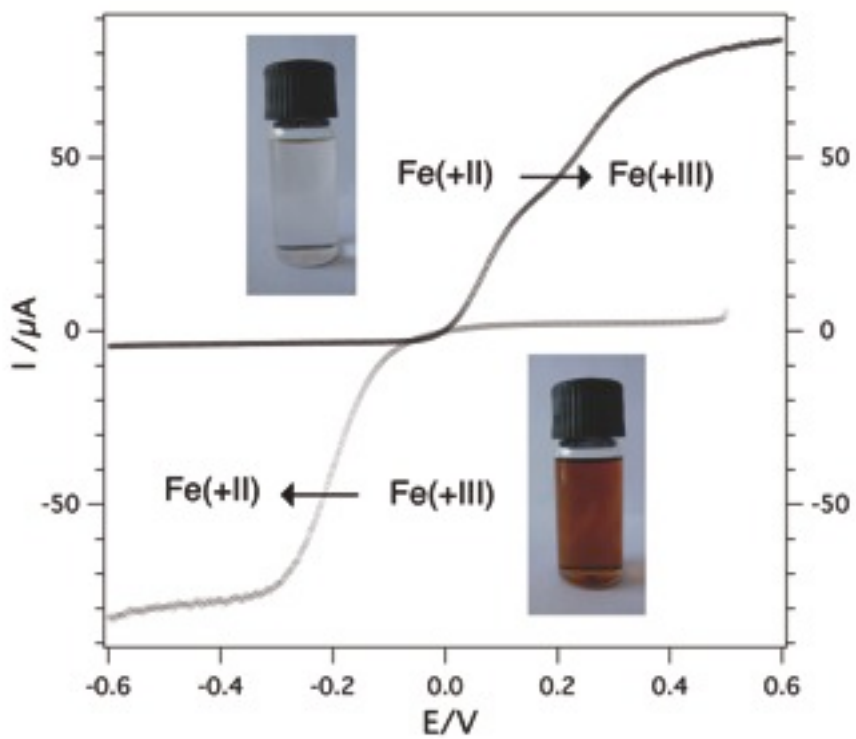
# Another application of photo reduction

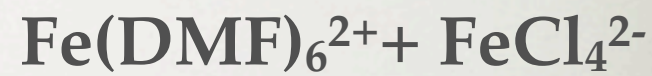
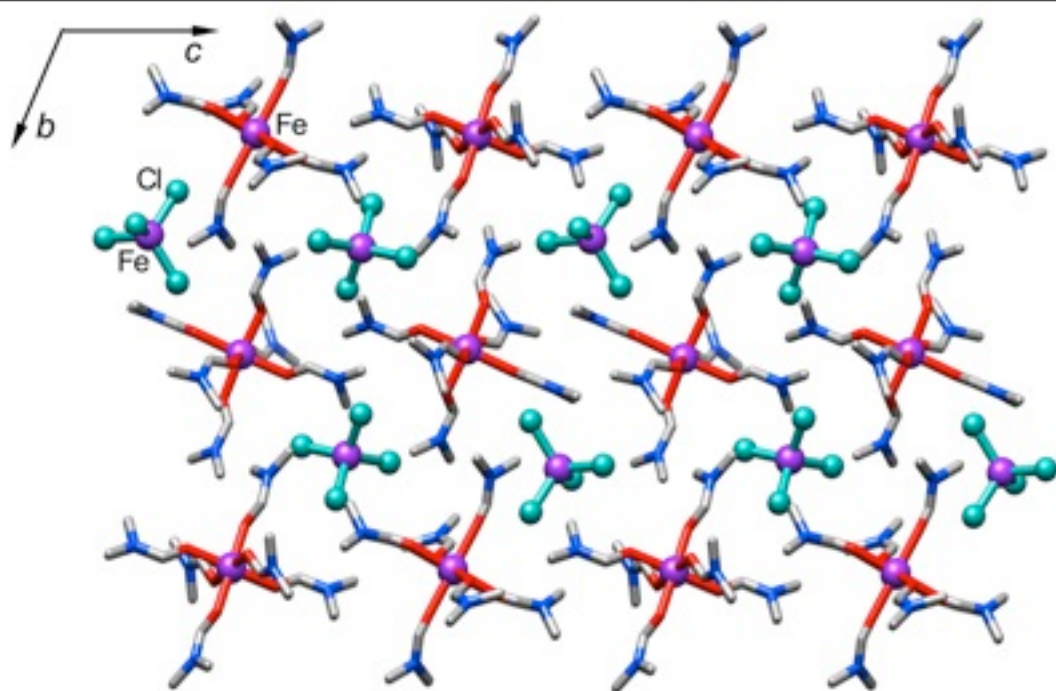




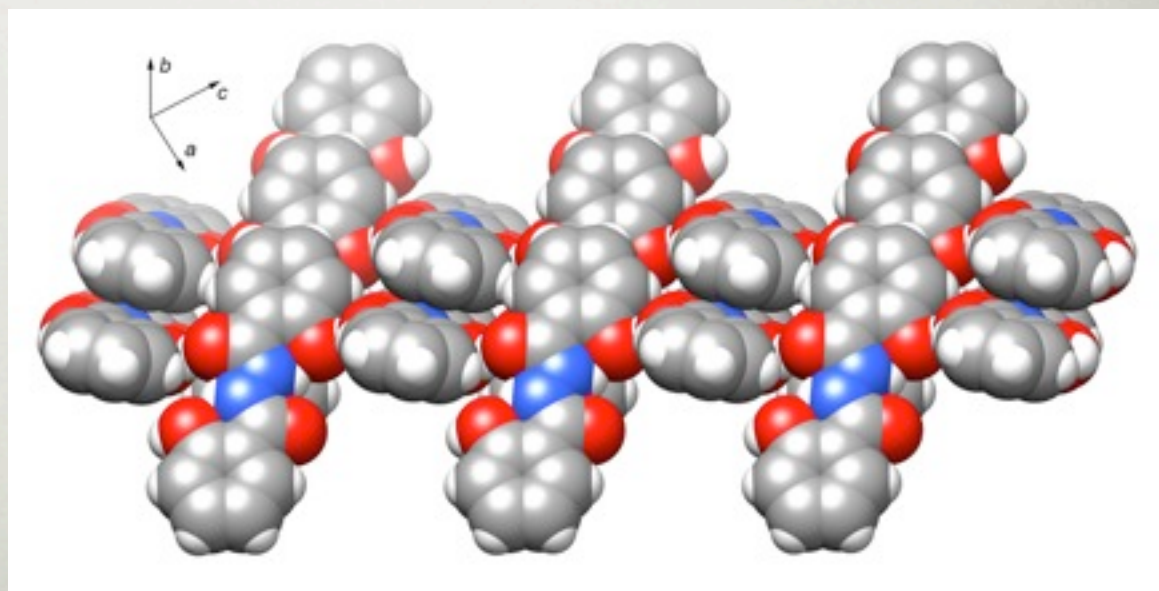








$\text{H}_4\text{L}$

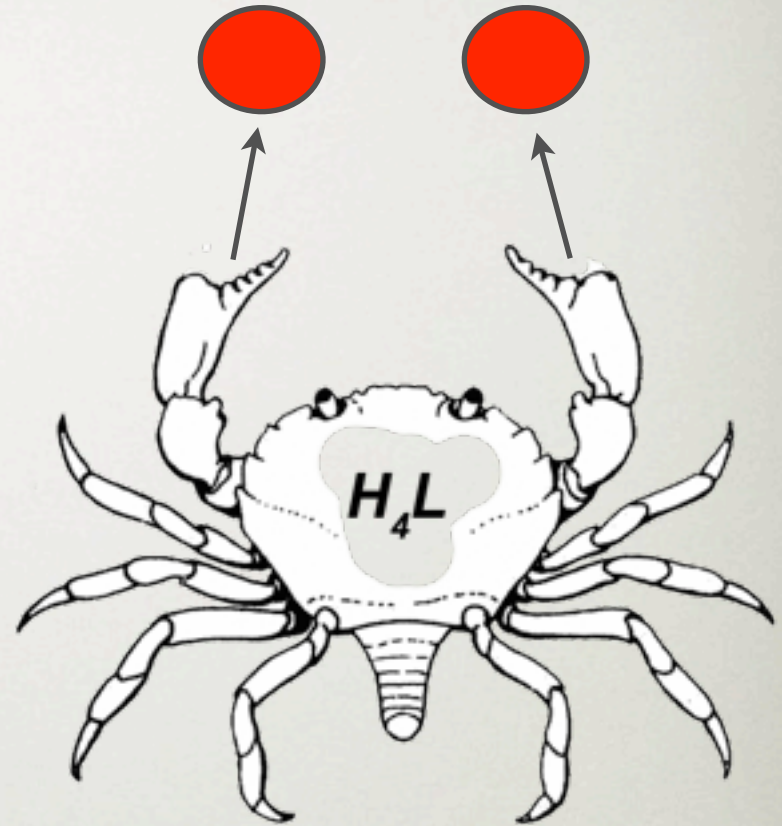




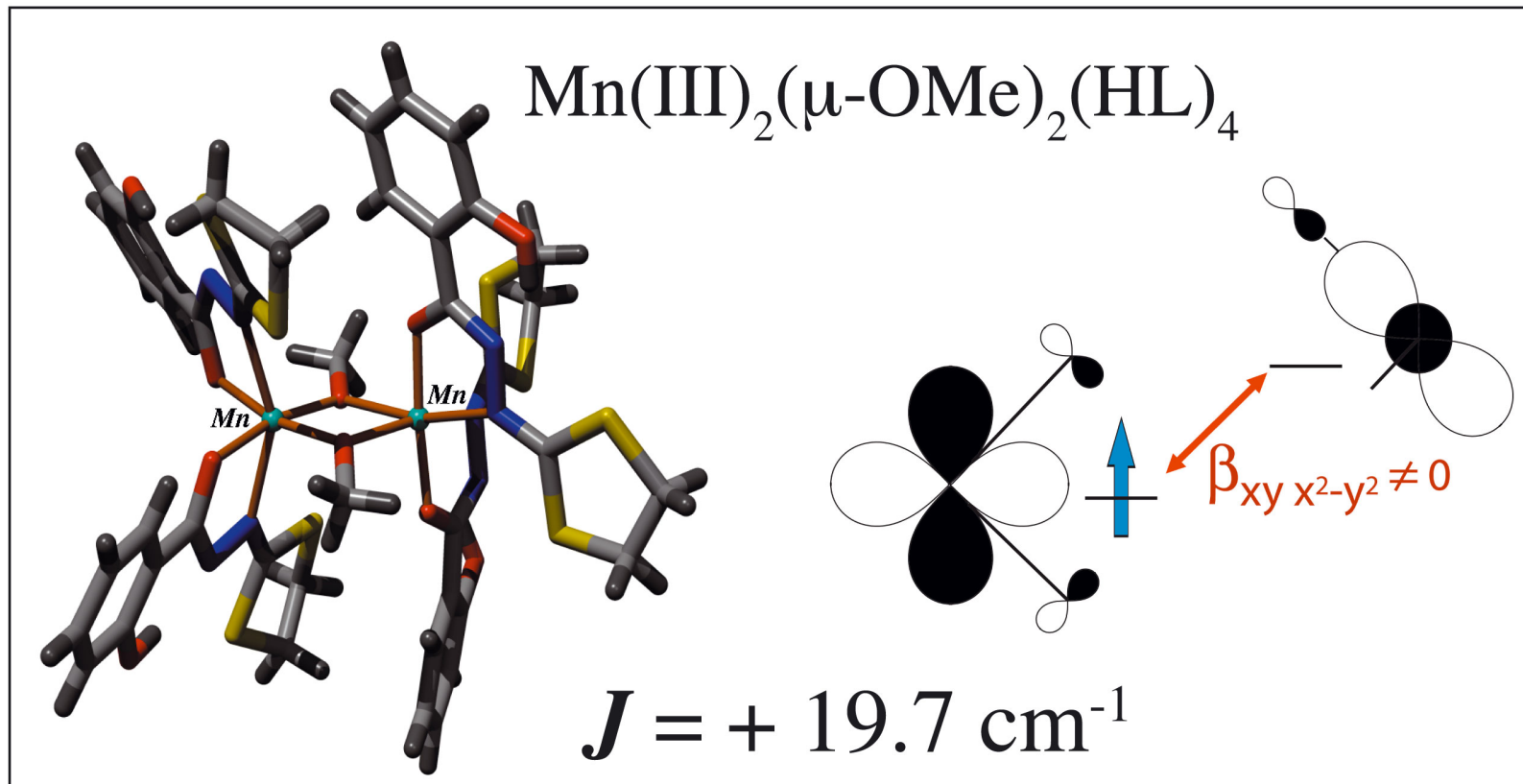
DARK



LIGHT



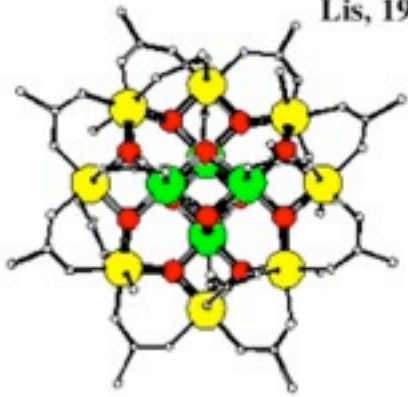
# Molecular magnetism



# Single-molecule magnets (SMM)

## Giant spins

Lis, 1980

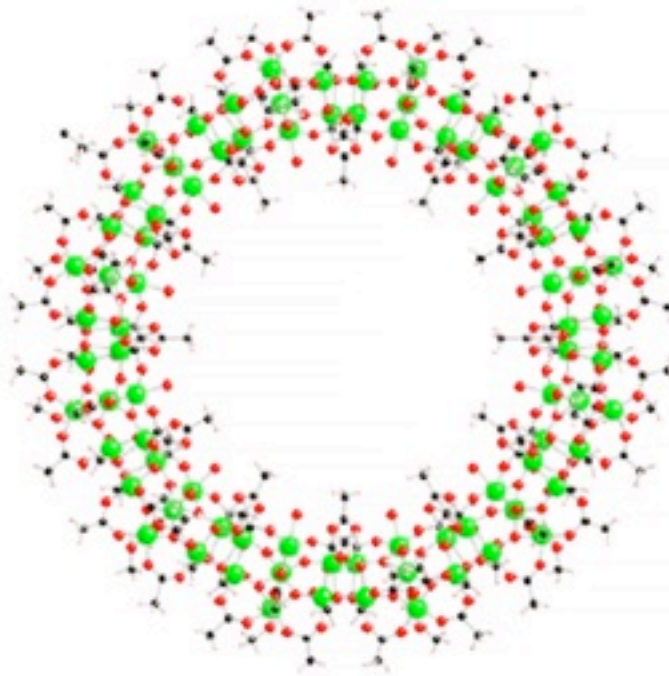


$\text{Mn}_{12}$   $S = 10$

$\text{Ni}_{12}$   $S = 12$

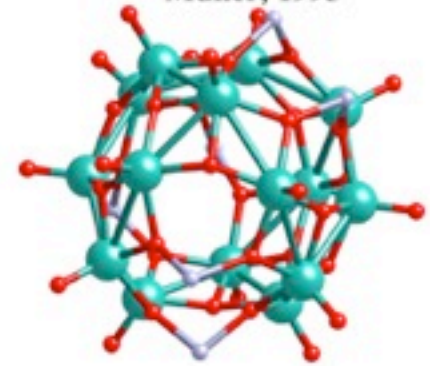


Winpenny, 1999



Christou, 2004

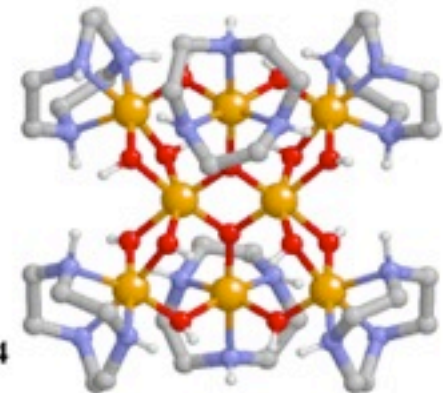
Müller, 1993



$\text{V}_{15}$   $S = 1/2$

$\text{Mn}_{84}$   
 $S \approx 6$

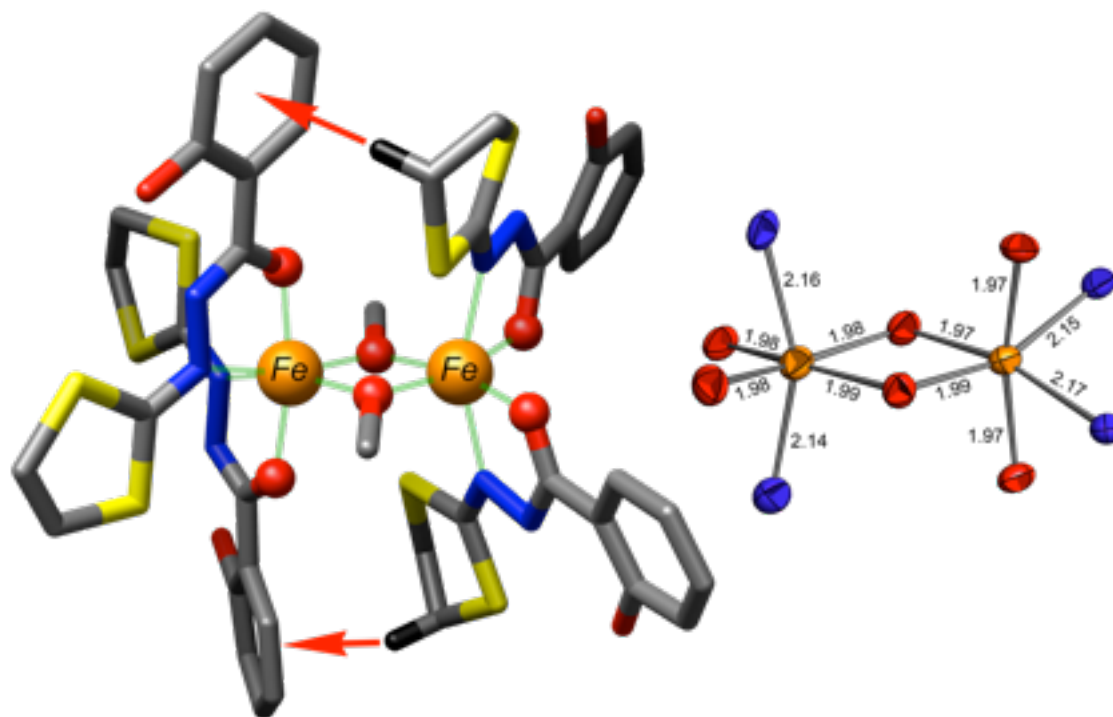
$\text{Fe}_8$   $S = 10$



Wiegart, 1984

2004 : starting point : paramagnetic dimers

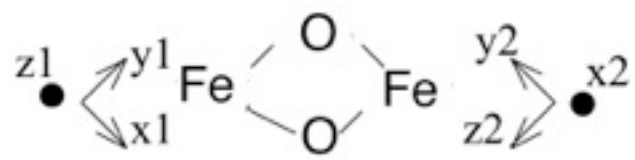
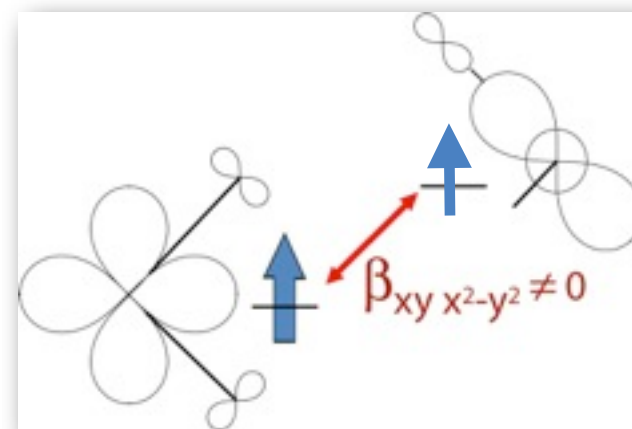
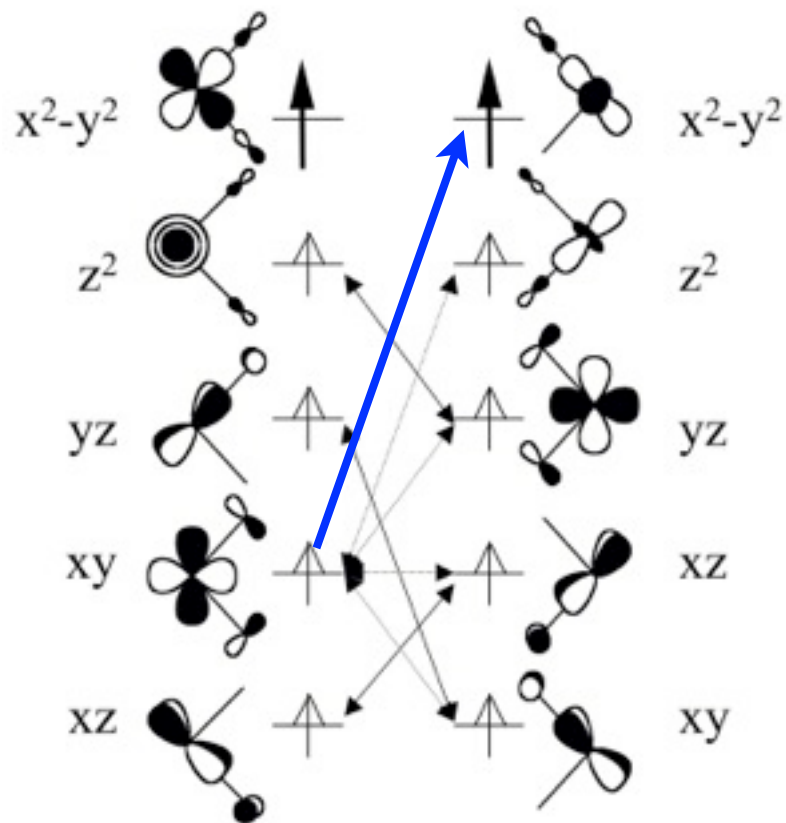
Iron(III) dimer



**Synthesis and Magnetic Properties of New Mono- and Binuclear Iron Complexes with Salicyloylhydrazono Dithiolane Ligand,**

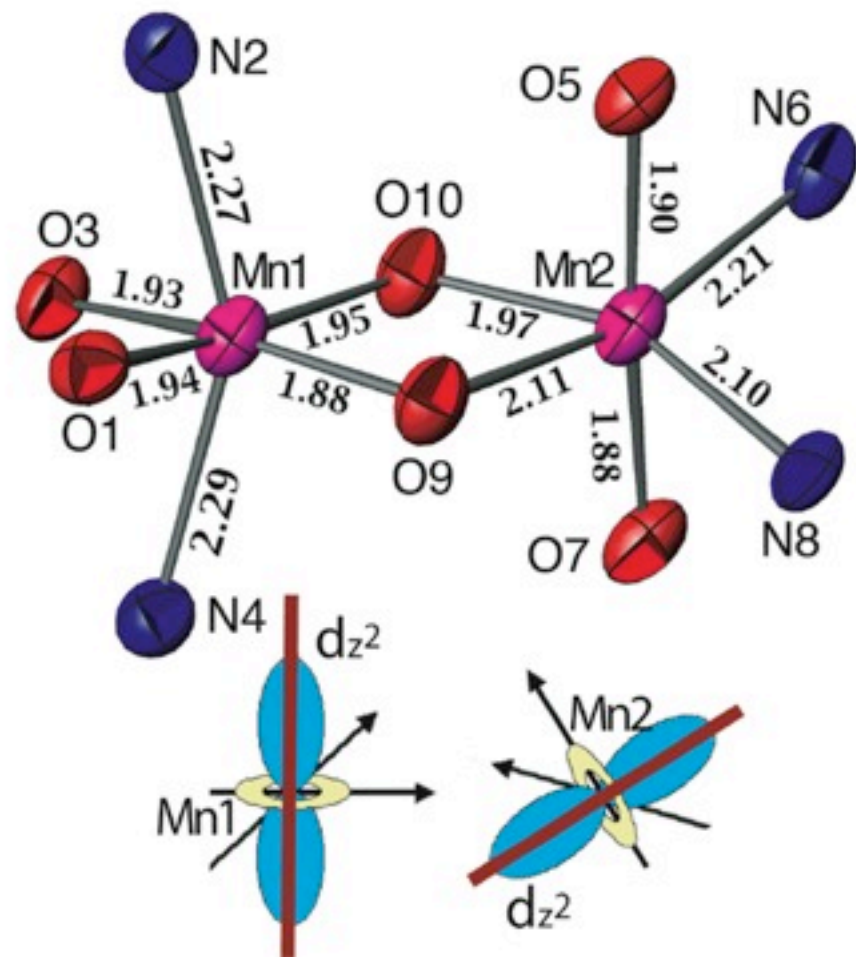
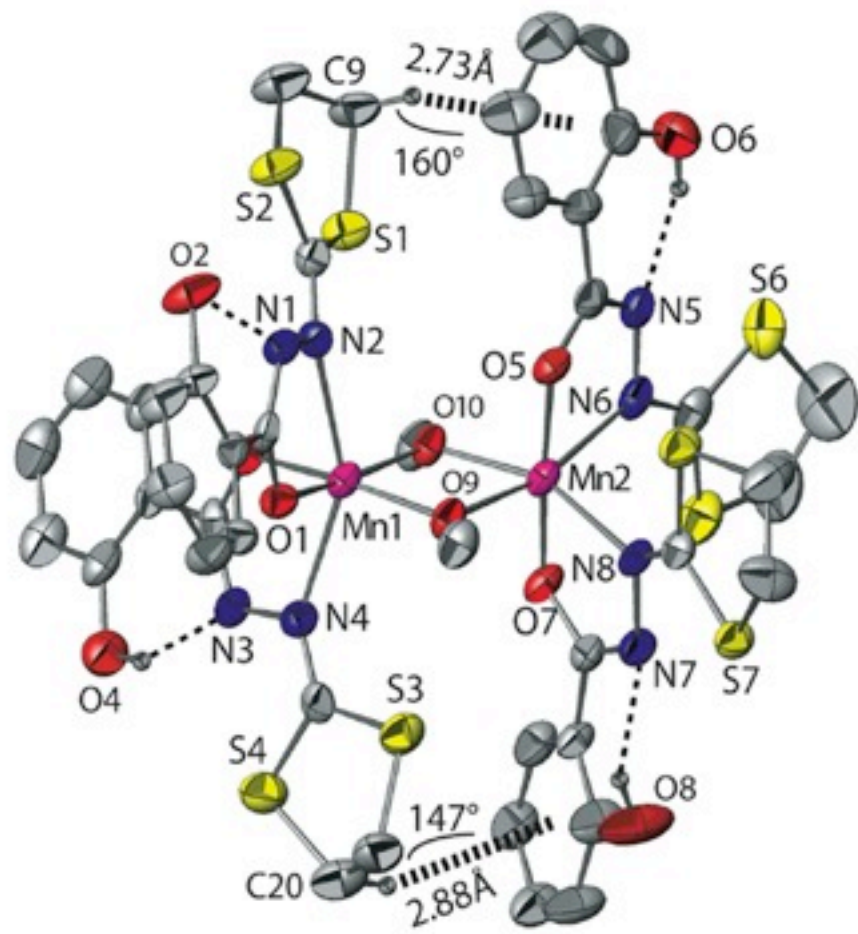
Bousslimani, N.; Clément, N.; Rogez, G.; Turek, P.; Bernard, M.; Dagorne, S.; Martel, D.; Cong, H. N.; Welter, R.  
*Inorg. Chem.*; (Article); 2008; 47(17); 7623-7630.

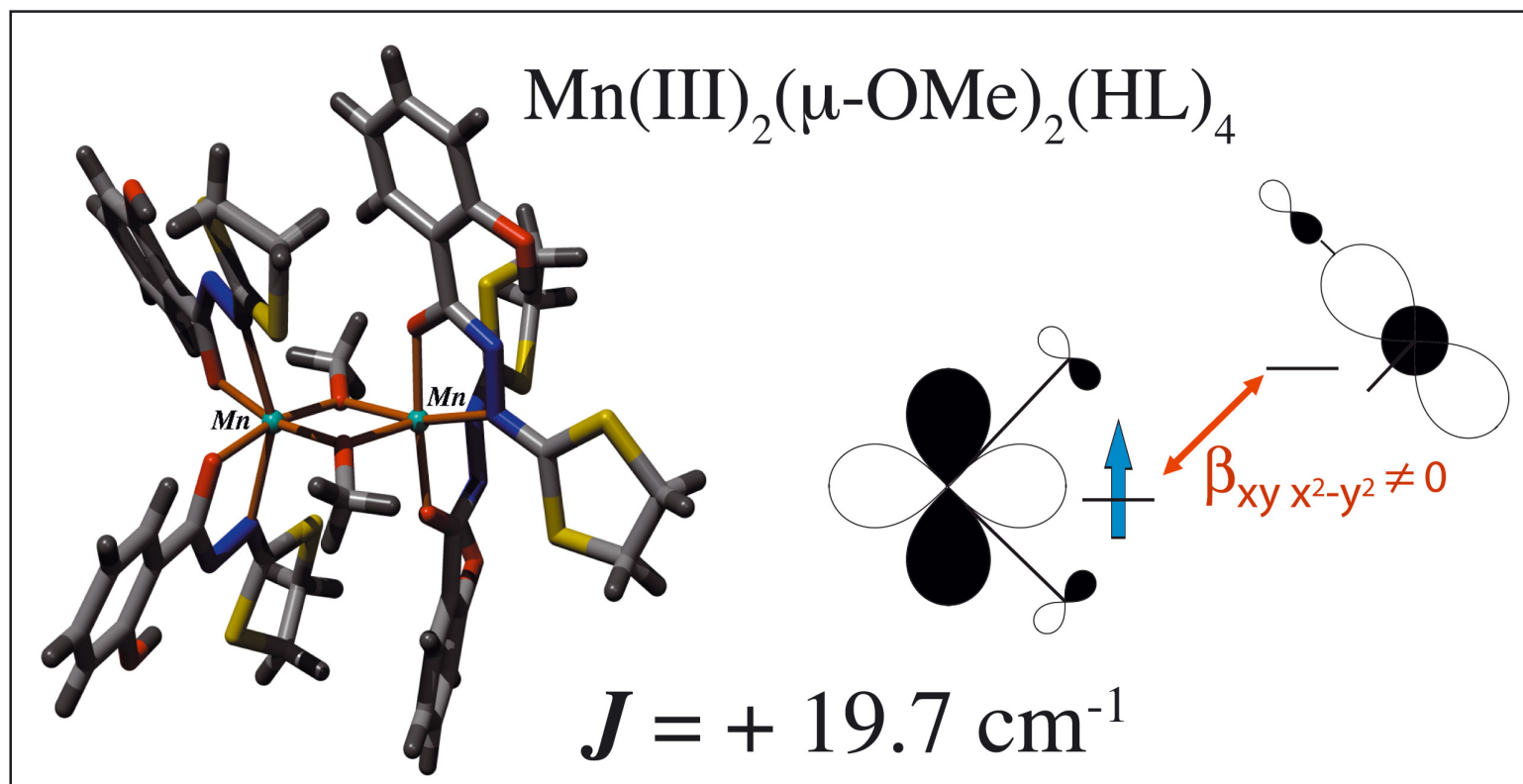
*$Fe(III)_2(\mu-O Me)_2(HL_2)_4$  complex  
(Electronic configuration)*



**Antiferro : -30 cm<sup>-1</sup>**

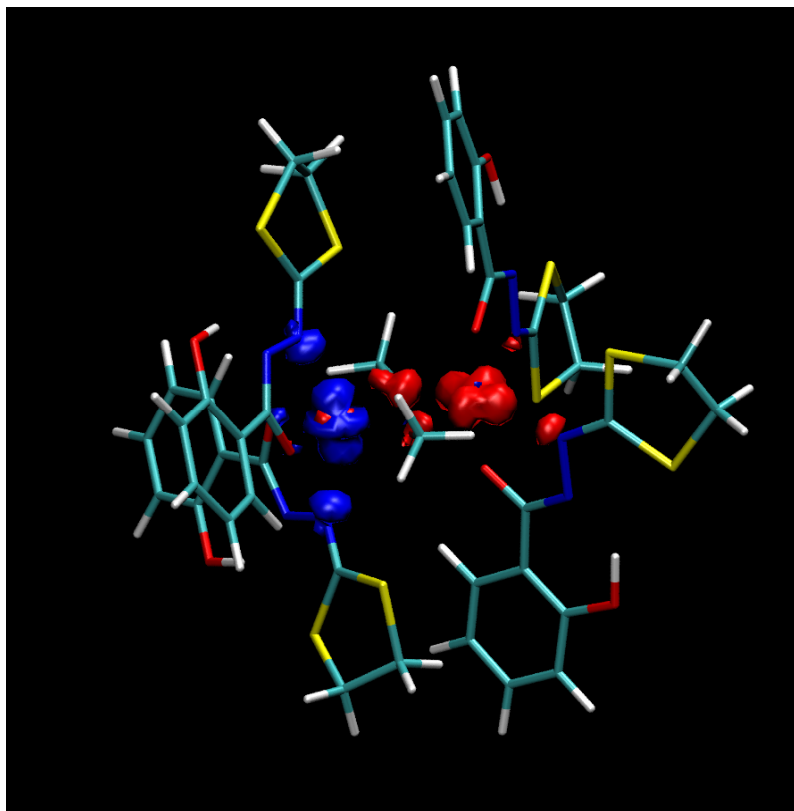






Strongest ferromagnetic interaction to date for  
 $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$  dimers !

*Mn(III)<sub>2</sub>(μ-OMe)<sub>2</sub>(HL<sub>2</sub>)<sub>4</sub> complex*  
*(DFT calculations)*



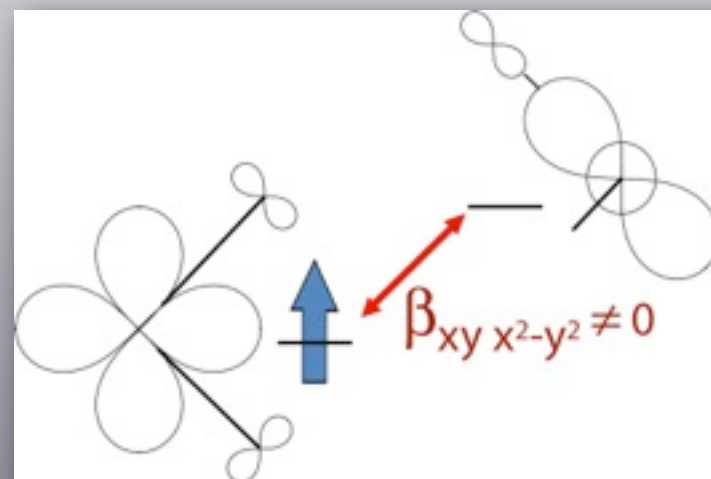
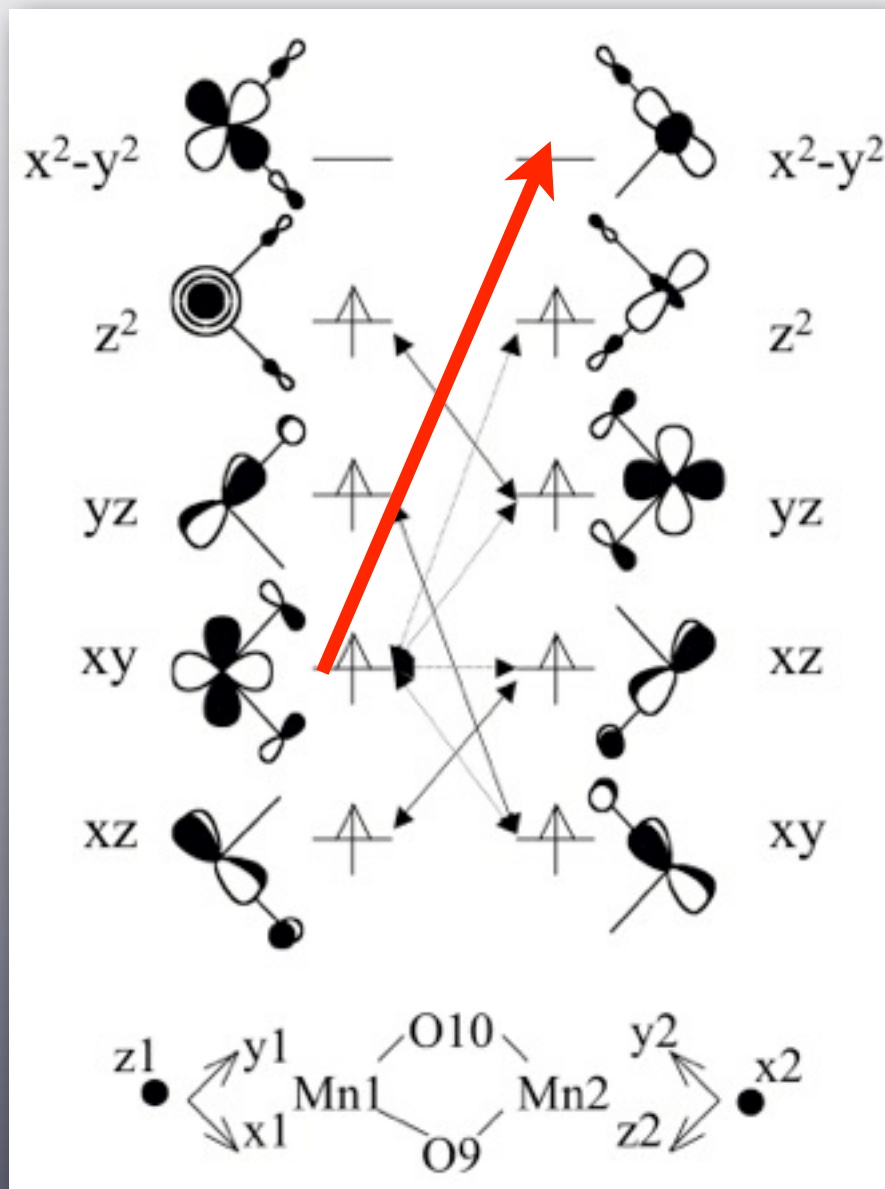
Magnetic orbitals in *Mn(III)<sub>2</sub>(μ-OMe)<sub>2</sub>(HL<sup>(2)</sup>)<sub>4</sub>*  
*alpha HOMO (blue) and HOMO-1 (red)*

$$J = +18,2 \text{ cm}^{-1}$$

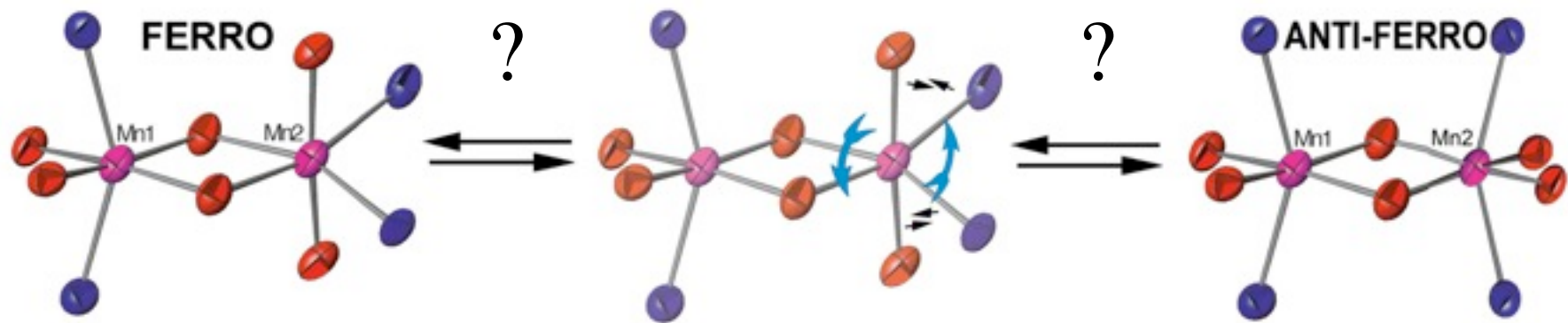
$$(D = -0.35 \text{ cm}^{-1}, E/|D| = 0.19)$$

R. Welter et al., J. AM. CHEM. SOC. 2006, 128, 3140-3141

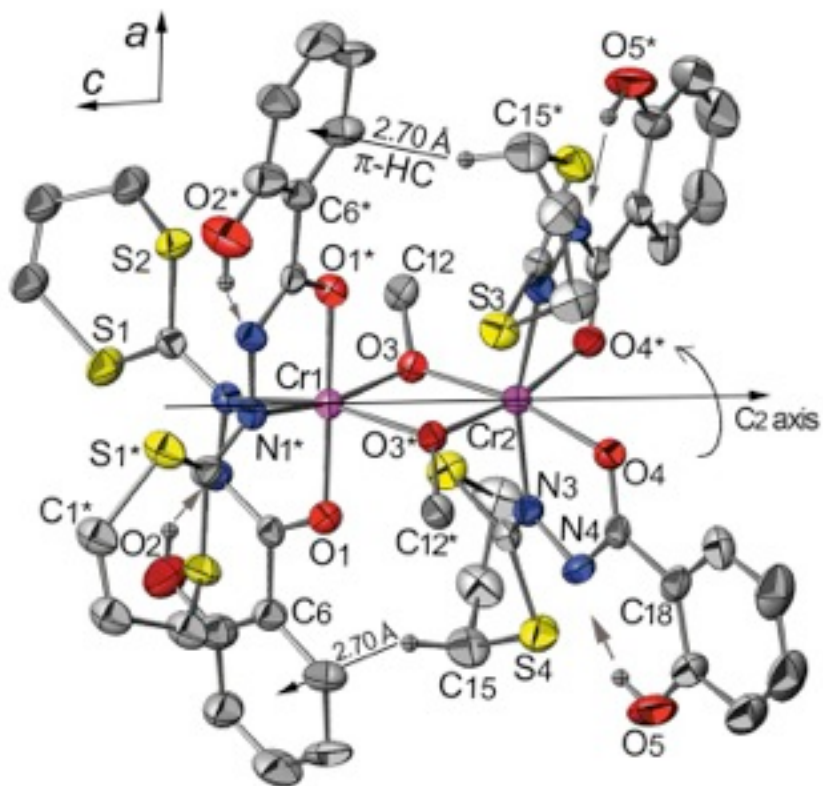
*$Mn(III)_2(\mu\text{-OMe})_2(\text{HL}_2)_4$  complex*  
*(Electronic configuration)*





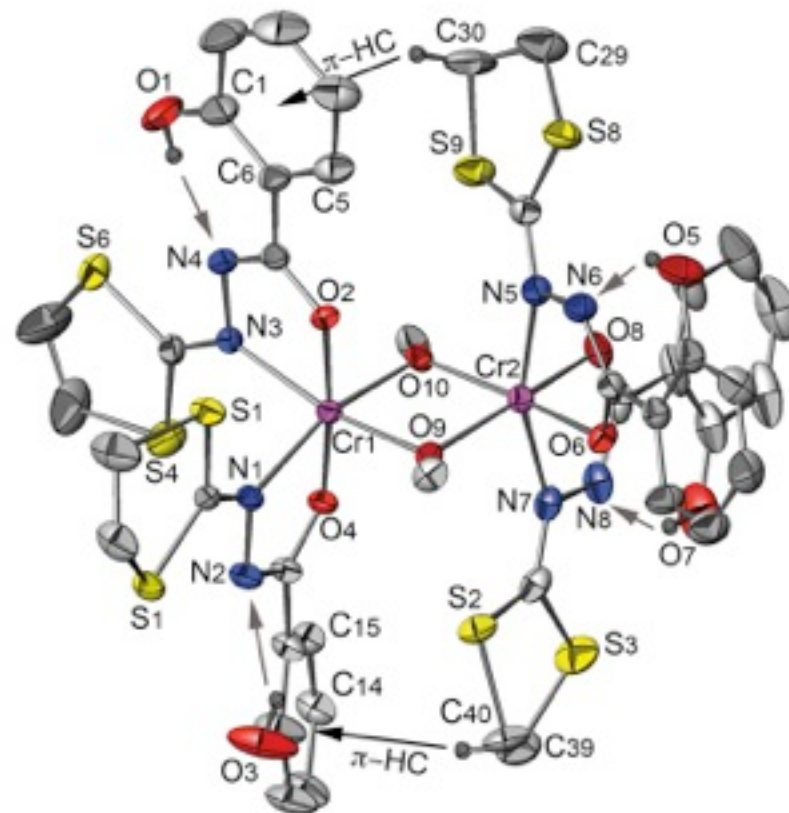


Symmetric = AF



First example

Asymmetric = Ferro ?



Same structure as Mn2 with strong ferro coupling

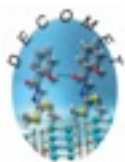
*Novel Cr-III dinuclear complexes supported by salicyloylhydrazone dithiolane and dithiane ligands: Synthesis, stability, crystal structures and magnetic properties*

Clement Nicolas, Toussaint Clement, Rogez Guillaume, Loose Claudia, Kortus Jens, BreLOT Lydia, Choua Sylvie, Dagonne Samuel, Turek Philippe, Welter Richard.

*Dalton Trans. (2010) 39, 19, 4579-4585*

## Acknowledgments

Laboratoire 'Densité Electronique et COordination METallique'  
**DECOMET** ( UMR CNRS-7177 )



B.Malaman - I. Ijaali - V.Klosek - G.Venturini - A.Vernière - N.Hansen<sup>†</sup>,  
K. Halich, P. Braunstein, N. Bouslimani, A et C Beghidja, N. Clément,  
K. Cheaib, D. Specklin, C. Toussaint, M. Guth, D. Welsch, D. Martel,...



