# *Molecular Nanomagnets*

**E. Coronado**

- **Polyoxometalate clusters**

- **SMMs in different environments**

Instituto
de Ciencia Molecular

Universitat de València

# Outline

I. Introduction to POMs

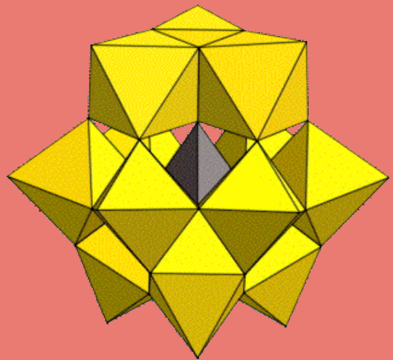
II. SMMs and Quantum tunnelling in lanthanide POMs

III. SMMs into superconductors

# Polyoxometalates : Molecular metal-oxide anions

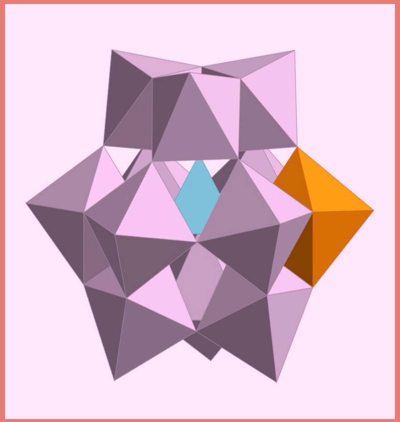
Keggin

bi-capped
Keggin



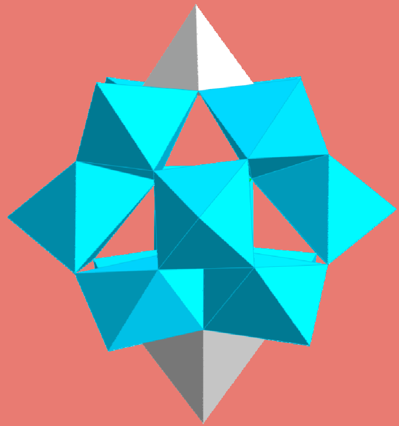
$XW_{12}$

$XMo_{12}$



$XW_{11}M$

$XMo_{11}M$



$PMo_{12}(VO)_2$

**Structural/Chemical versatility:**

**Soluble Metal-oxide cluster anions with defined topologies**

**Electronic versatilities:**

**Magnetic Exchange and/or Electron Transfer**

**Magnetic anisotropy**

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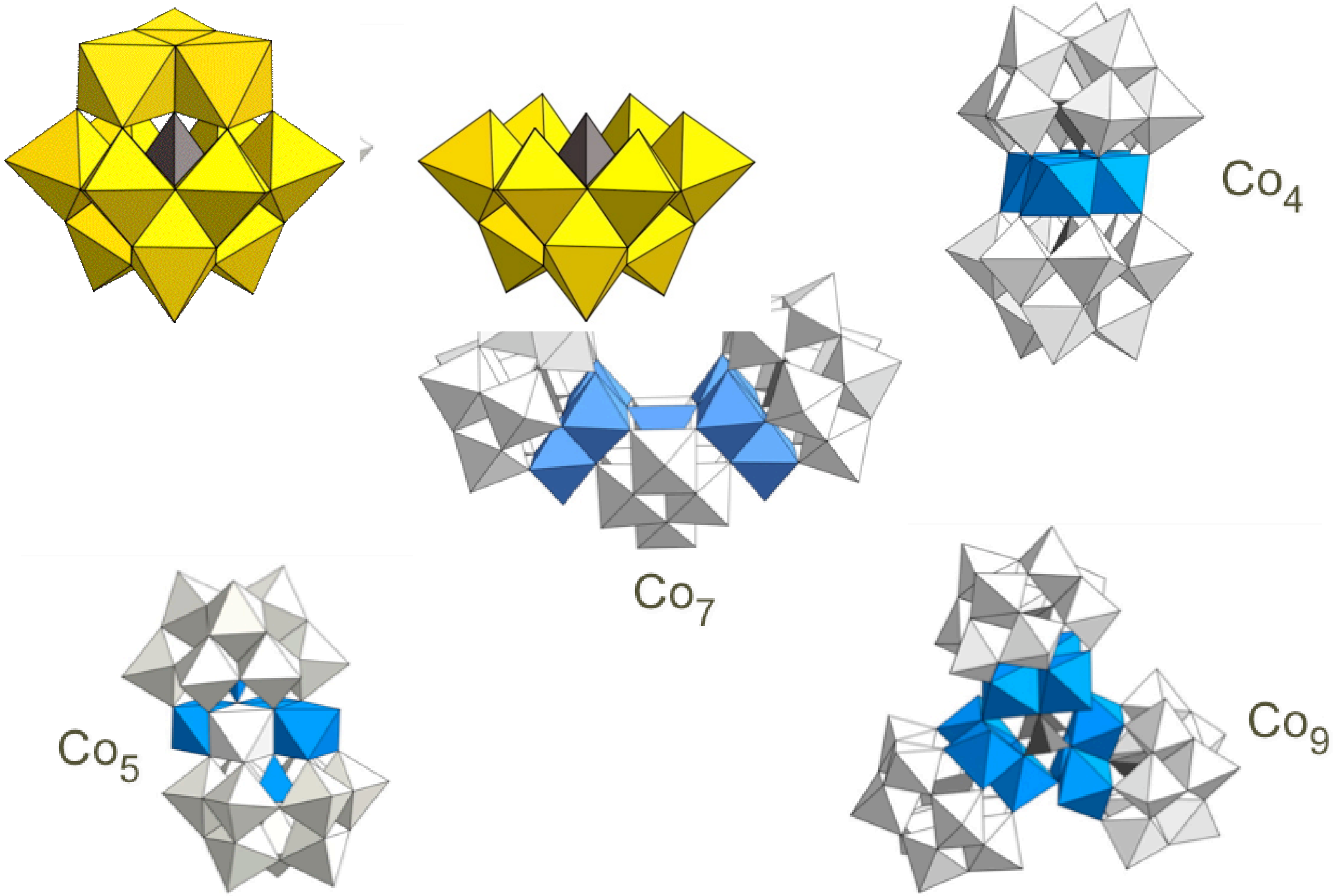
# Magnetic clusters encapsulated by POMs




J. M. Clemente-Juan, E. Coronado, *Coord. Chem. Rev.* **1999**, *193-195*, 361

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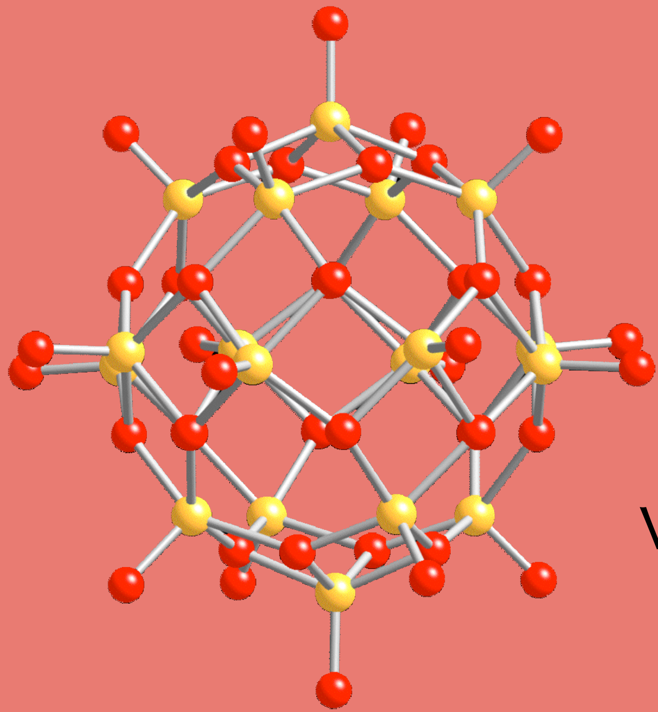
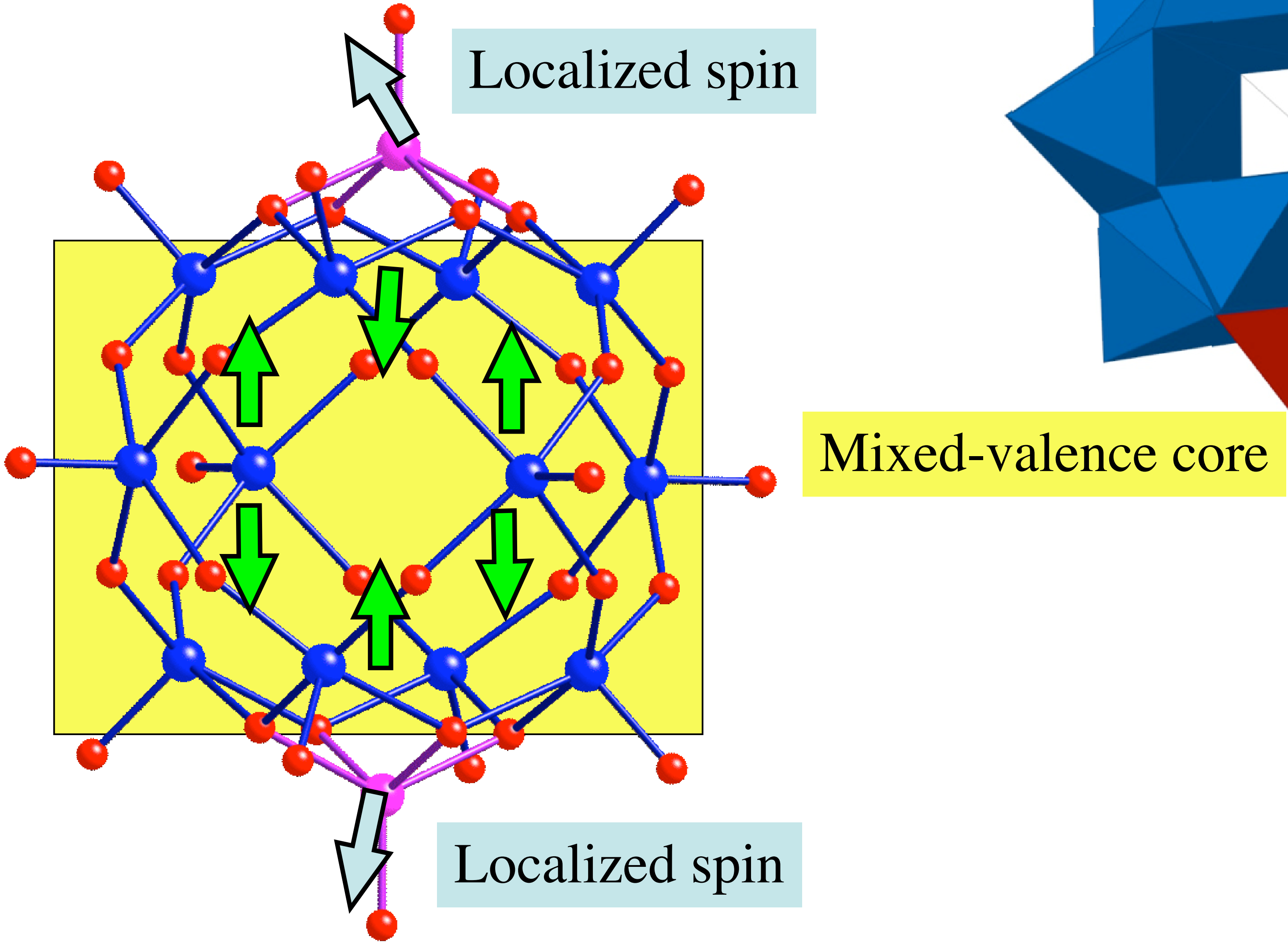
# Magnetic clusters of POMs

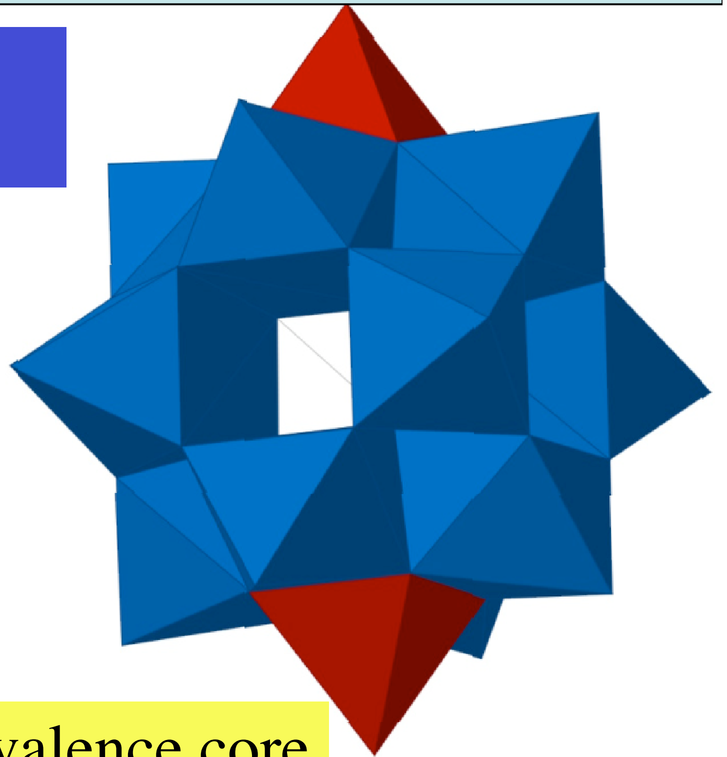


$V_{18}$

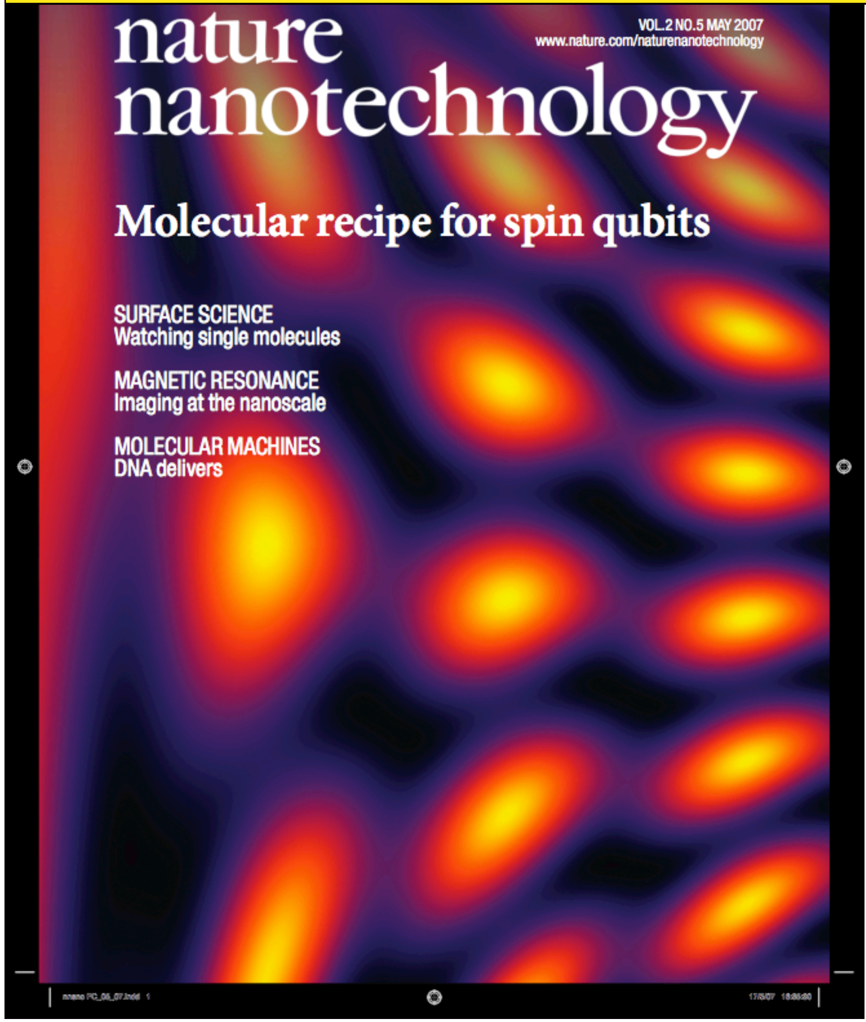
# Magnetic mixed-valence POMs

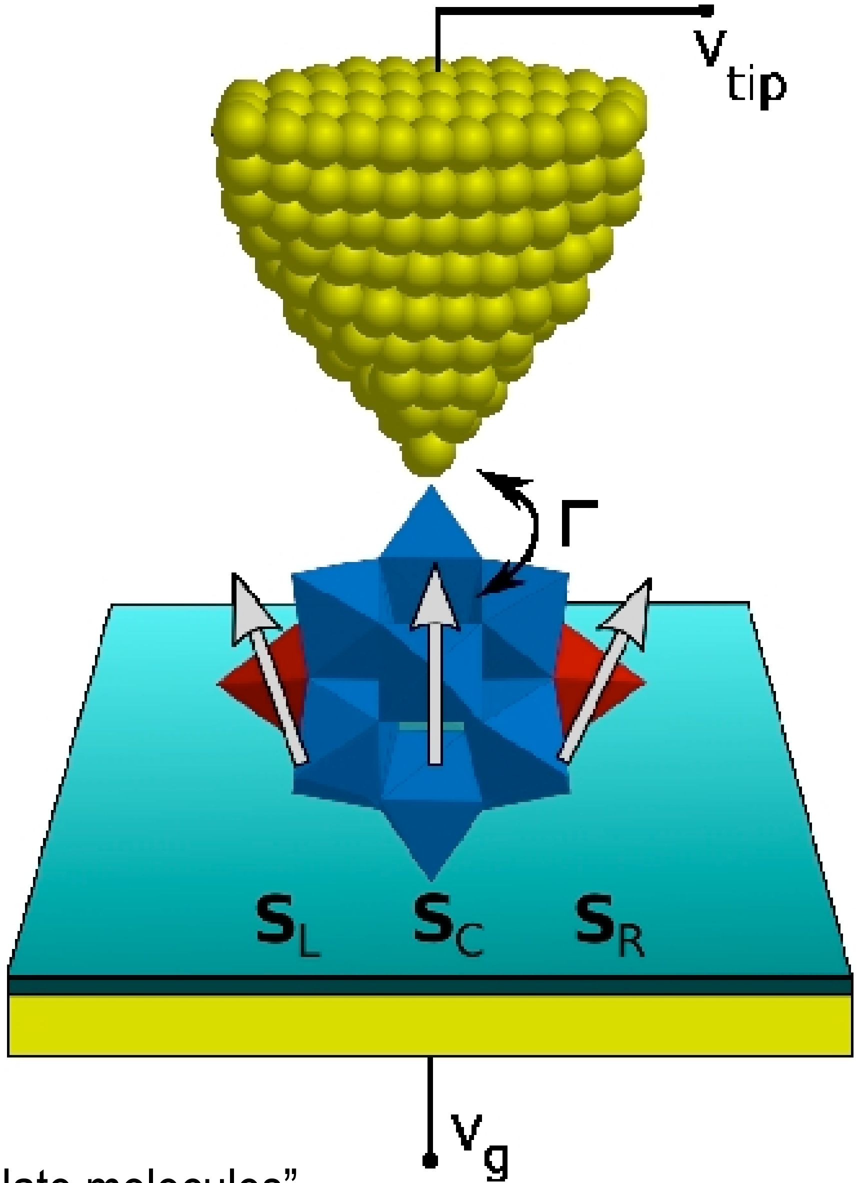
## $[PMo_{12}O_{40}(VO)_2]^{5-}$



# Applications: Quantum computing

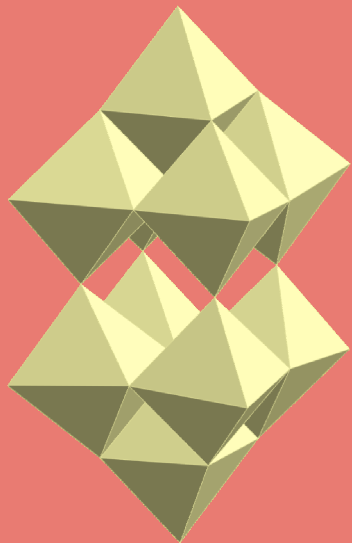


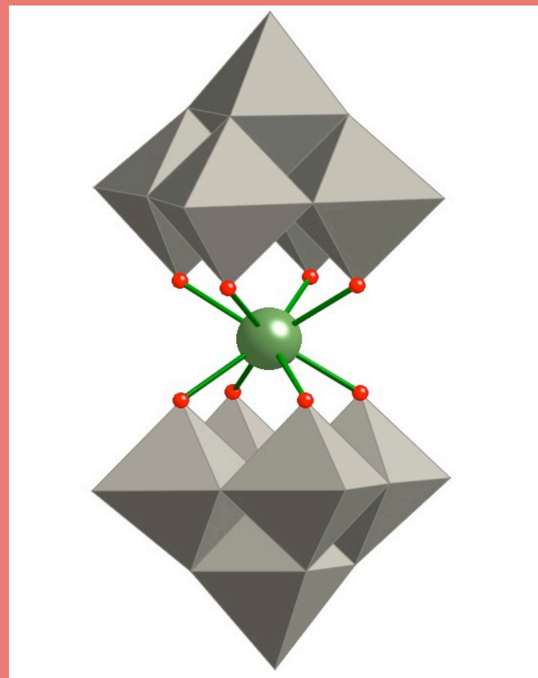

**Magnetic Molecular clusters as Qubits**

J. Lehmann, A. Gaita-Ariño, E. Coronado, D. Loss
“Spin qubits with electrically gated polyoxometalate molecules”
*Nature Nanotechnology* 2, 312-317 (2007)

# Rare-Earths encapsulated by POMs



$W_{10}$



$LnW_{10}$

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in lanthanide POMs

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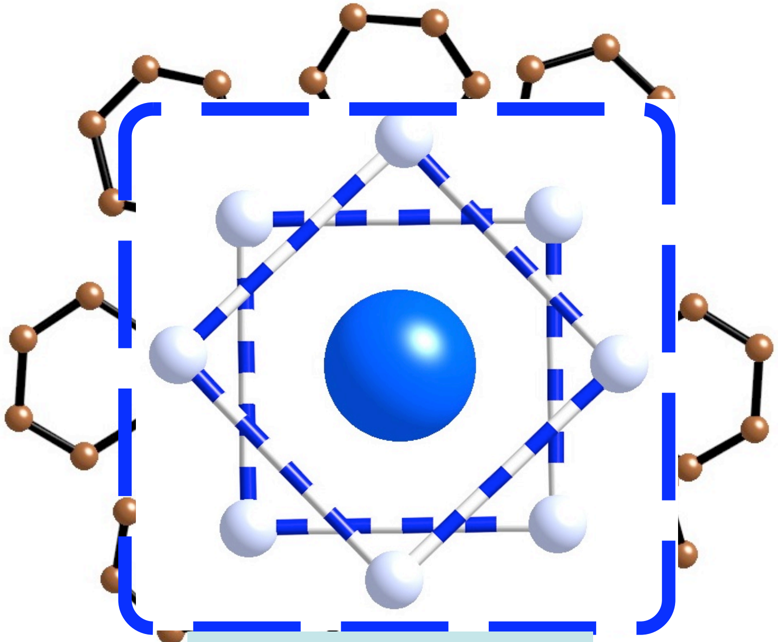
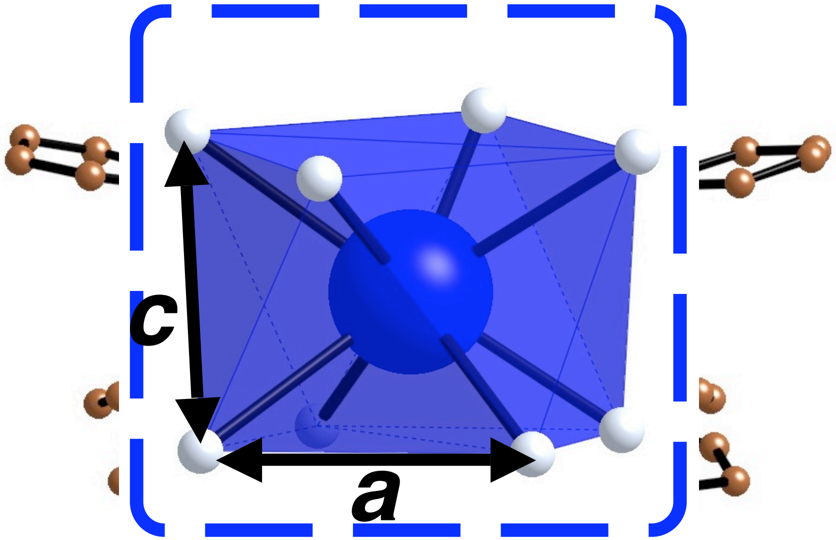
# Lanthanide bis-phtalocyanine complexes

Structural description

$[Ln^{III}(Pc)_2]^-$



$\Phi$= 43.2




$D_{4d}$ symmetry

$a$ = 2.80 Å

$c$ = 2.76 Å

Koike *et. al Inorg. Chem.* **1996,** *35*, 5798-5804.

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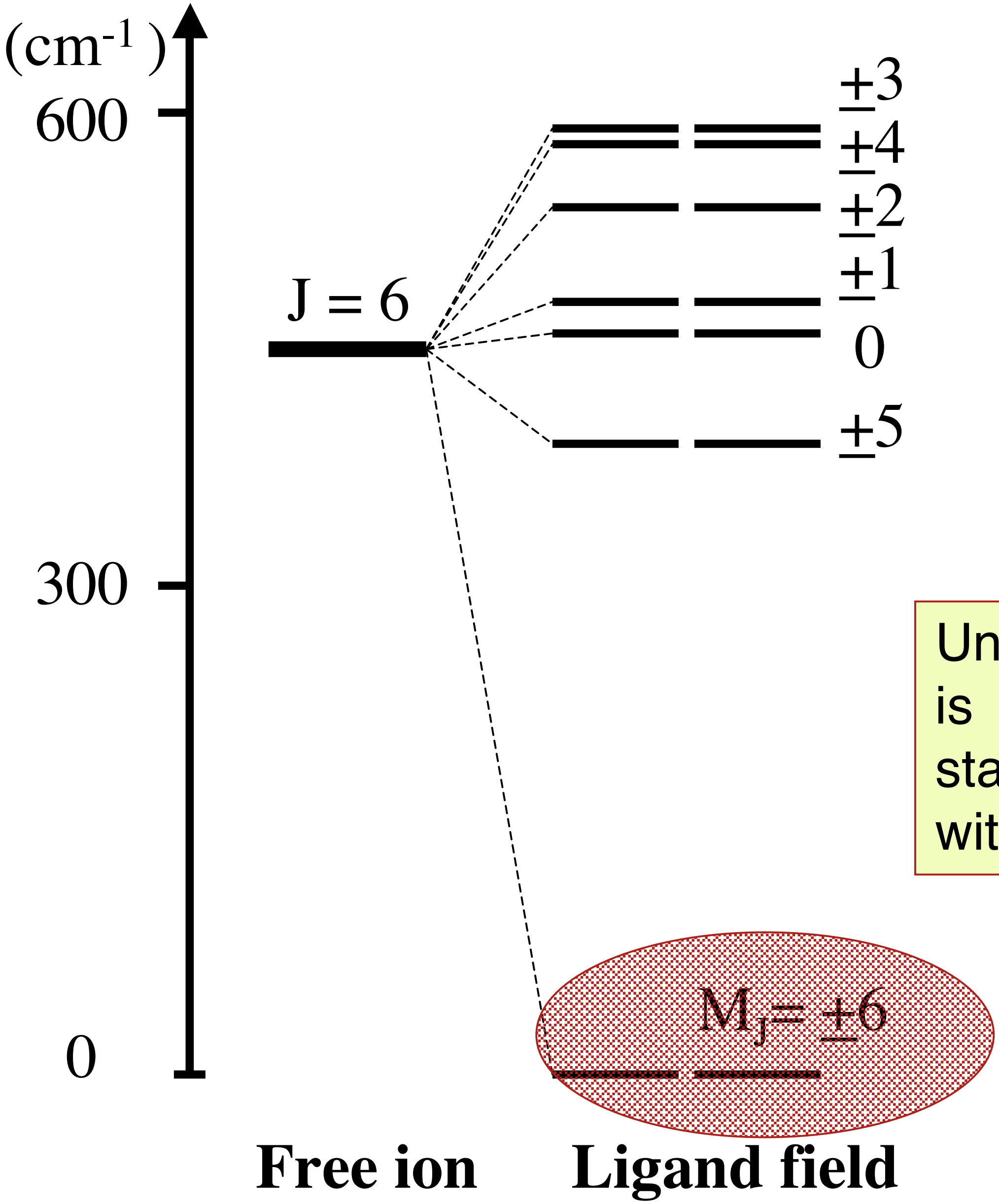
# Lanthanide bis-phtalocyanine complexes

Energy levels




$[Tb^{III}(Pc)_2]^-$

Uniaxial magnetic anisotropy is achieved thanks to the stabilization of the sublevel with largest $M_J$

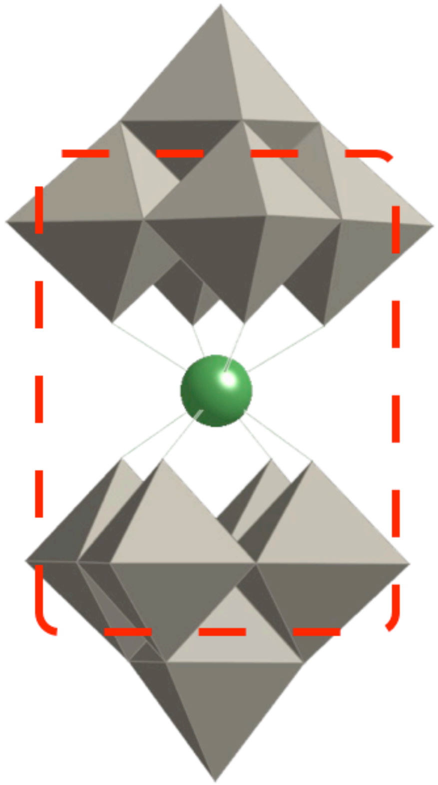
Also for Dy and Ho

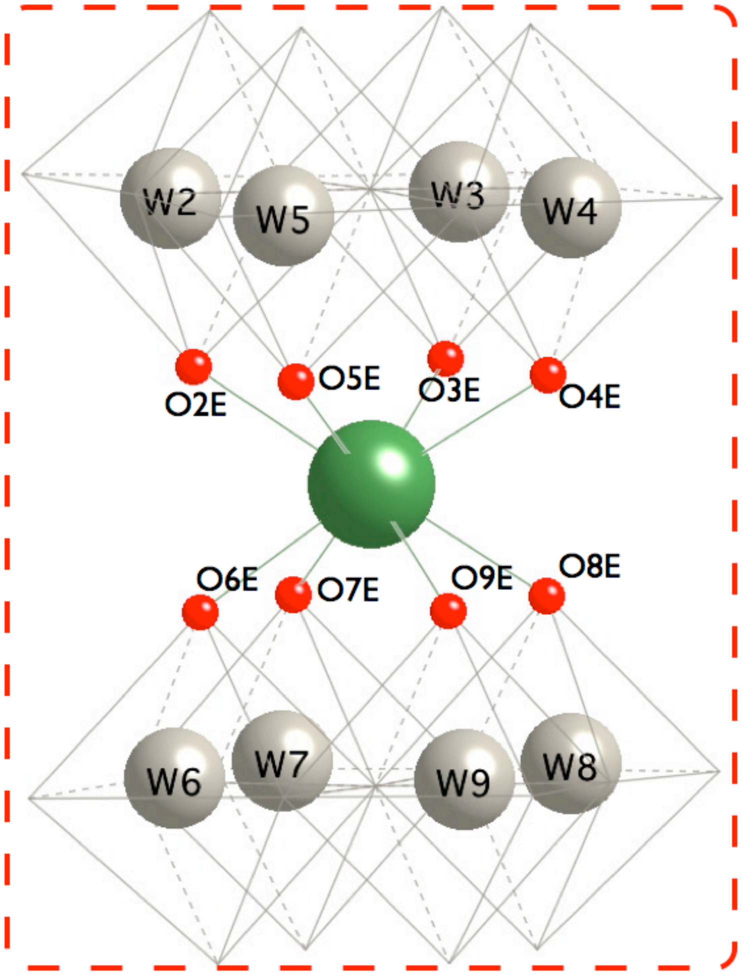
# Lanthanide polyoxometalate (POM) complexes

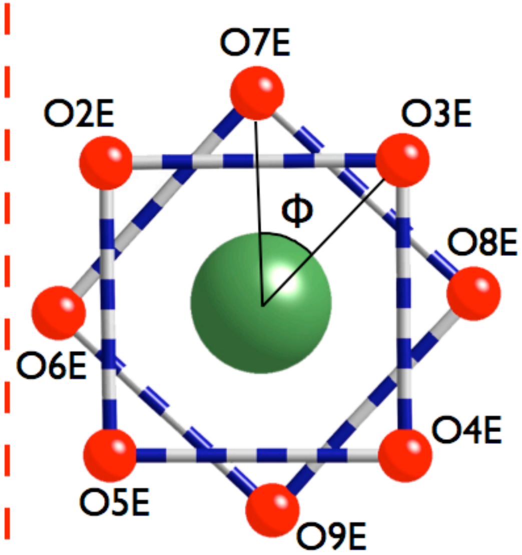
Structural description

## $[Ln^{III}(POM)_2]^{n-}$

**$[Ln^{III}(W_{10}O_{36})]Na_9.xH_2O$ ($Ln^{III}$ = Tb, Dy, Ho, Er)**



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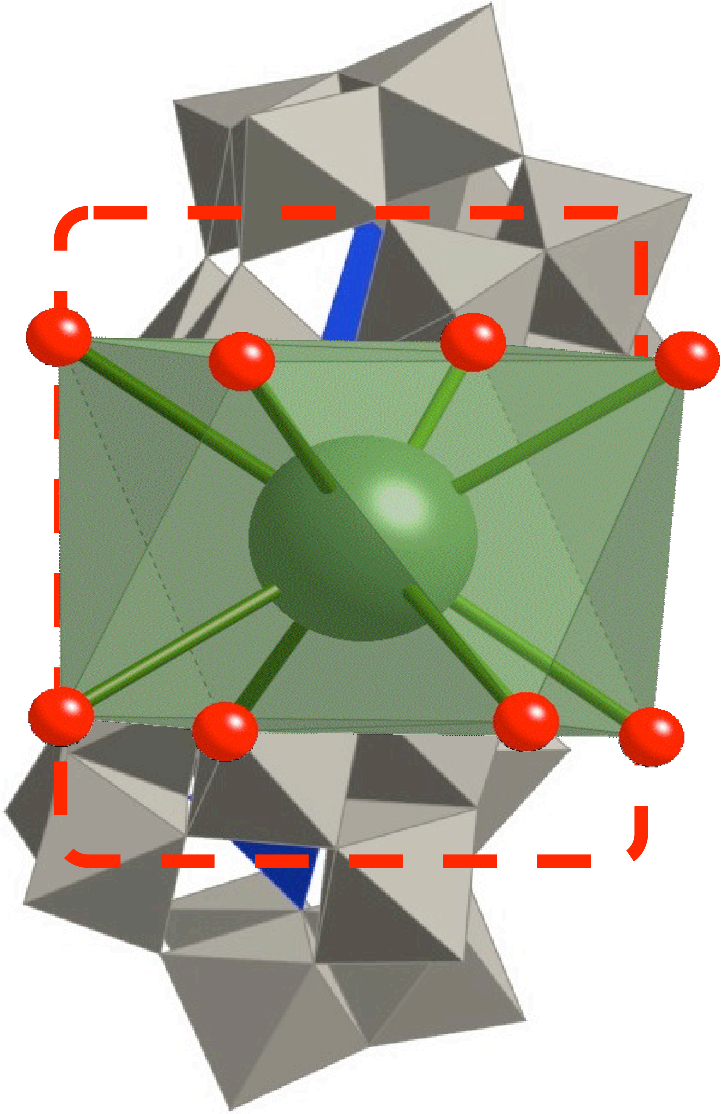
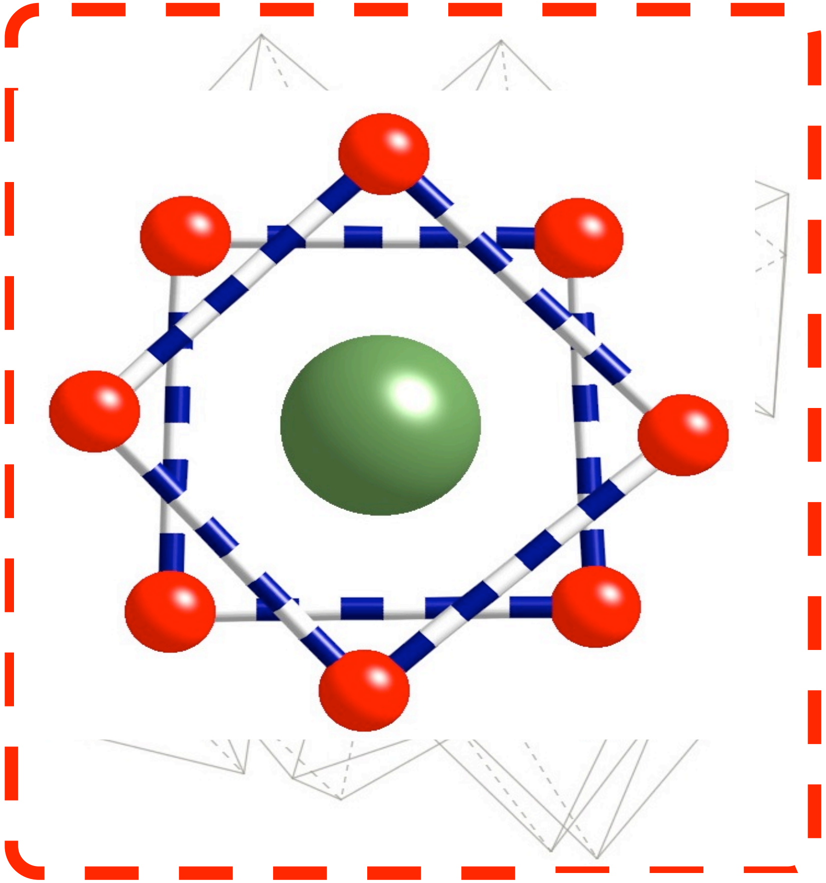
# Lanthanide polyoxometalate (POM) complexes

Structural description

## $[Ln^{III}(SiW_{11}O_{39})_2]K_{13}\_xH_2O$ ($Ln^{III}$ = Dy, Ho, Er, Tm, Yb)





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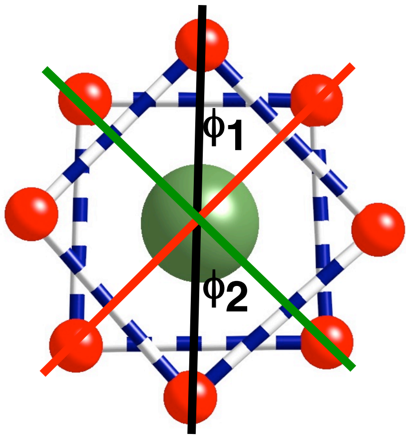
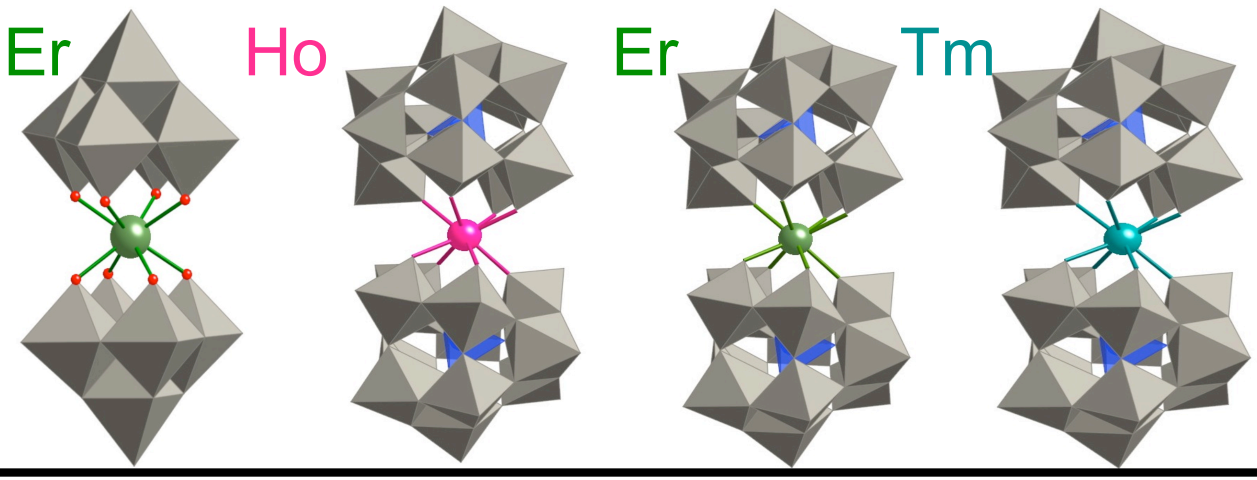
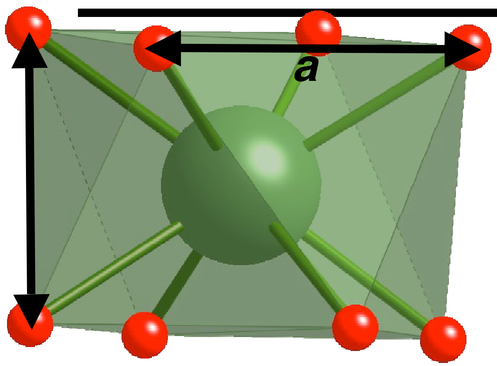
# $[Ln^{III}(W_{10}O_{36})]^{9-}$ and $[Ln^{III}(SiW_{11}O_{39})_2]^{13-}$ families

## Structural Parameters




| | | | | |
|---|---|---|---|---|
| $\phi_1$ | 47,6 | 46,1 | 43,1 | 45,2 |
| $\phi_2$ | 44,2 | 41,1 | 45,5 | 46,0 |
| ***a*** **(Å)** | 2,86(5) | 2,80(4) | 2,82(8) | 2,84(3) |
| ***c*** **(Å)** | 2,47(1) | 2,39(5) | 2,48(5) | 2,46(6) |

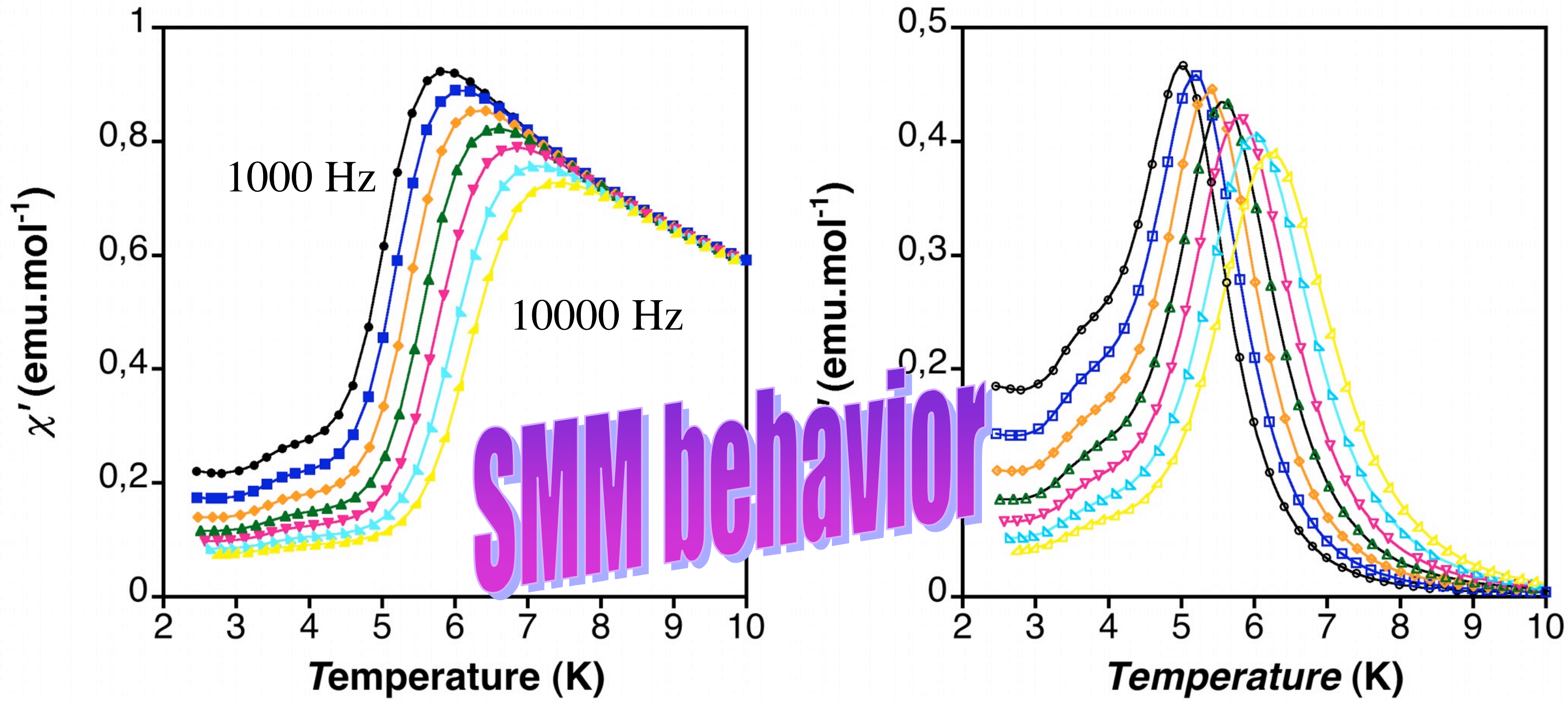



**Compression of the antiprism**

**(vs. elongation in the phtalocyanine family)**

# $[Er(W_{10}O_{36})]Na_9.nH_2O$

Magnetic characterization




*AC magnetic susceptibility at 1000, 1467, 2154, 3162, 4641, 6813 and 10000 Hz*

***Frequency-dependent superparamagnetic blocking***

***Slow magnetic relaxation***

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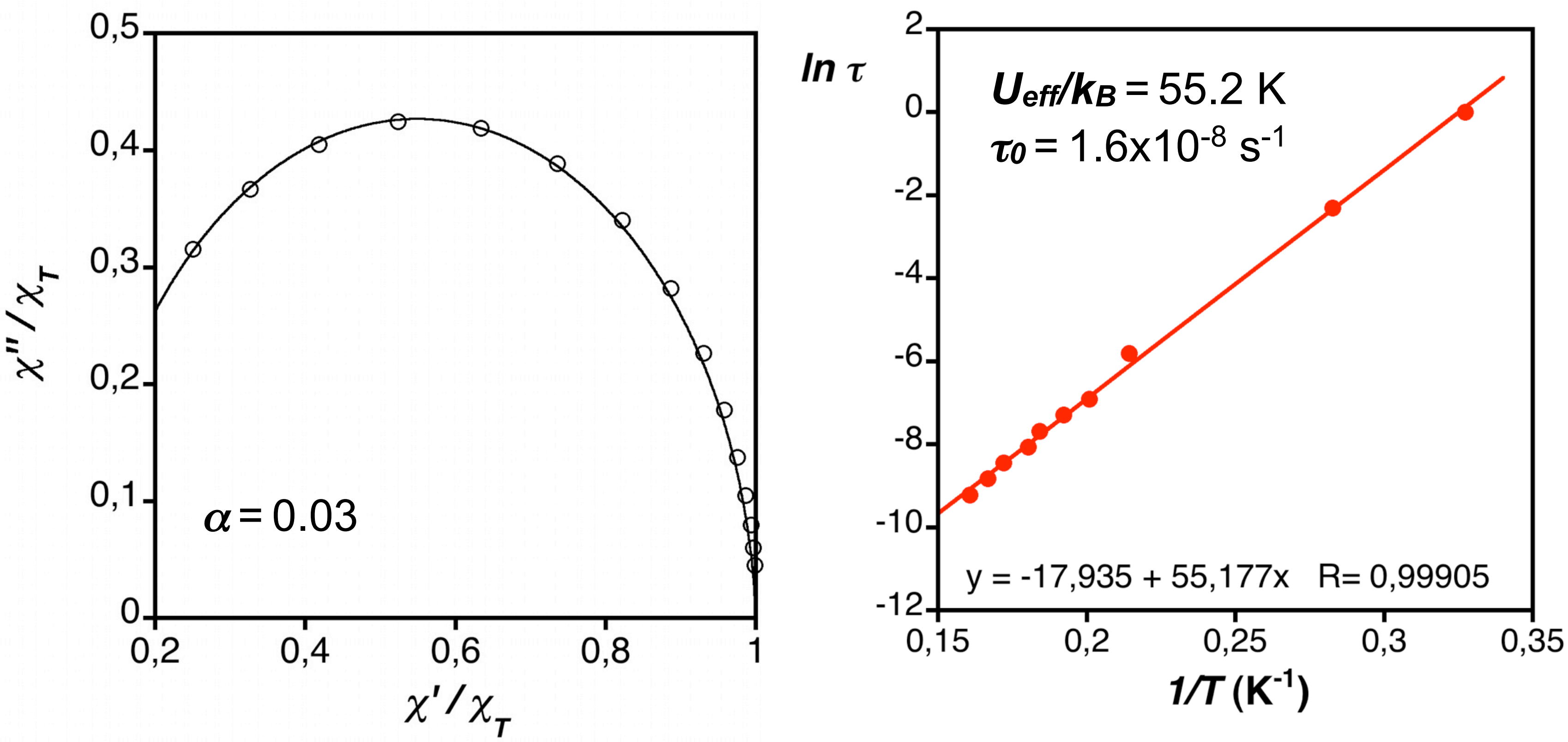
Magnetic characterization

# $[Er(W_{10}O_{36})]Na_9.nH_2O$




Argand plot at 5 K (*left*). Experimental data best fitting to Arrhenius law for the frequencies 1-10000 Hz (*right*).

E. Coronado et al. *JACS* **2008**, *130*, 8874

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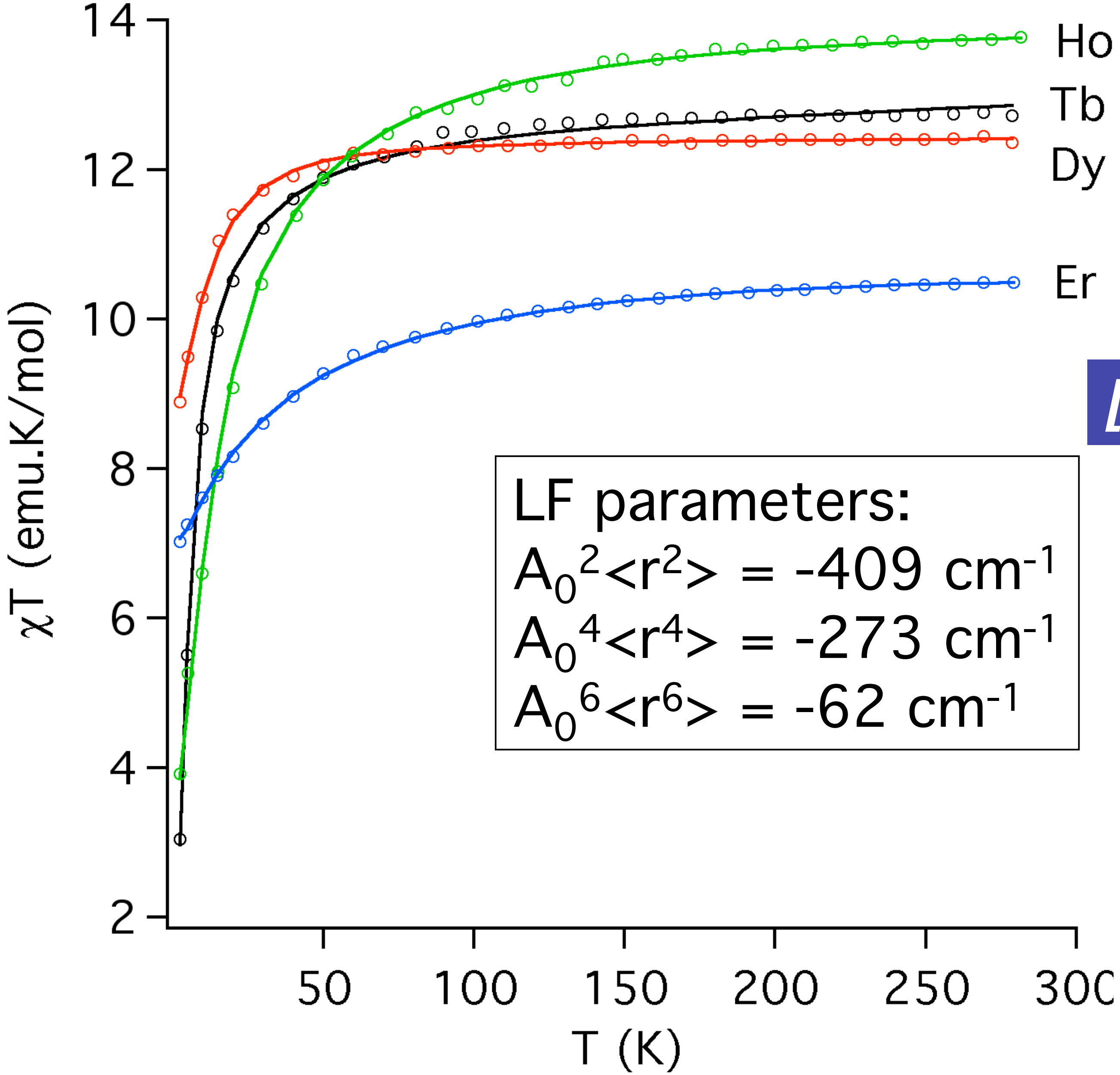
## $[Ln(W_{10}O_{36})]Na_9.nH_2O$

# Ligand field parameters




$[Ln^{III}(Pc)_2]^-$

+

−

+

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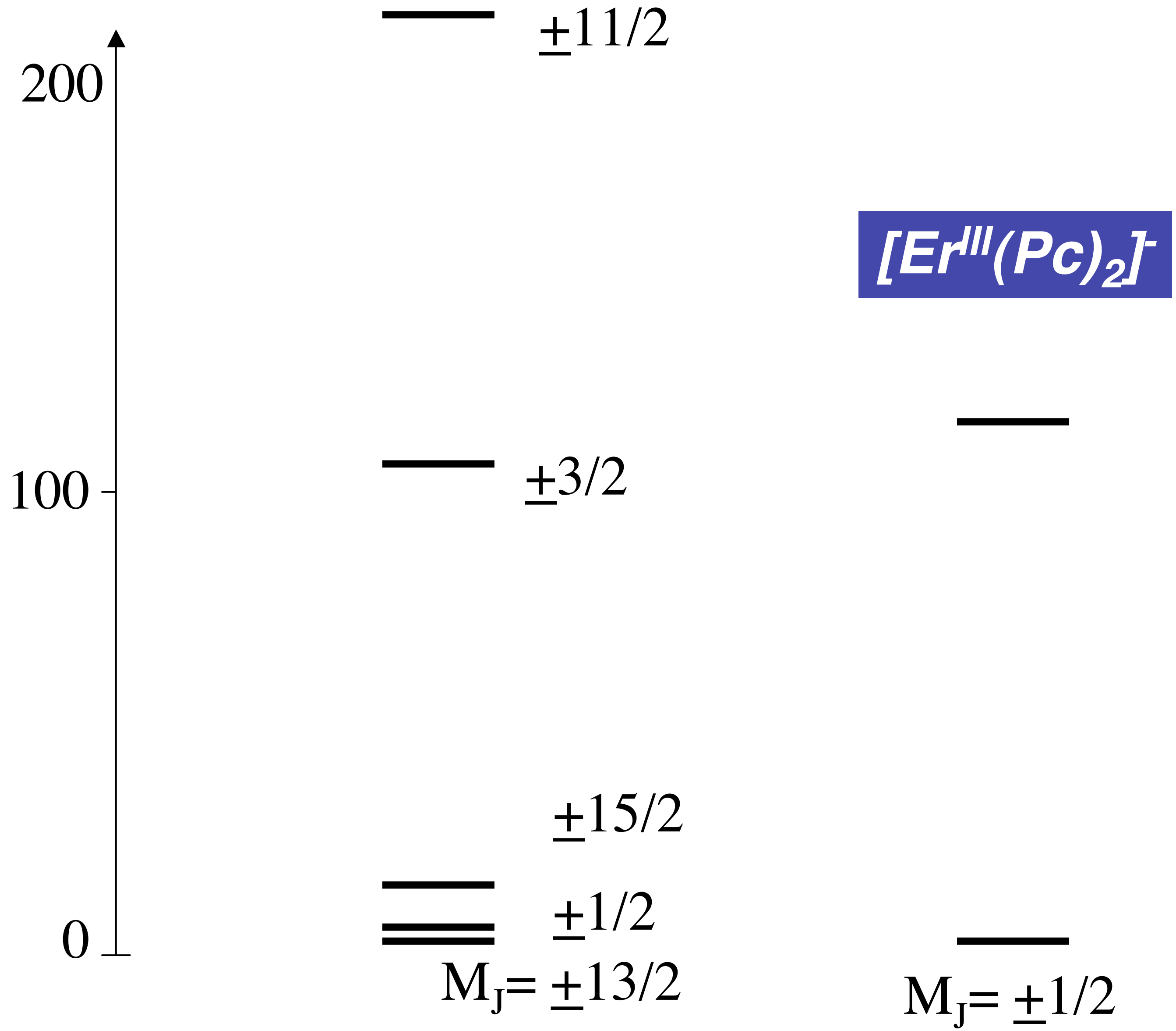
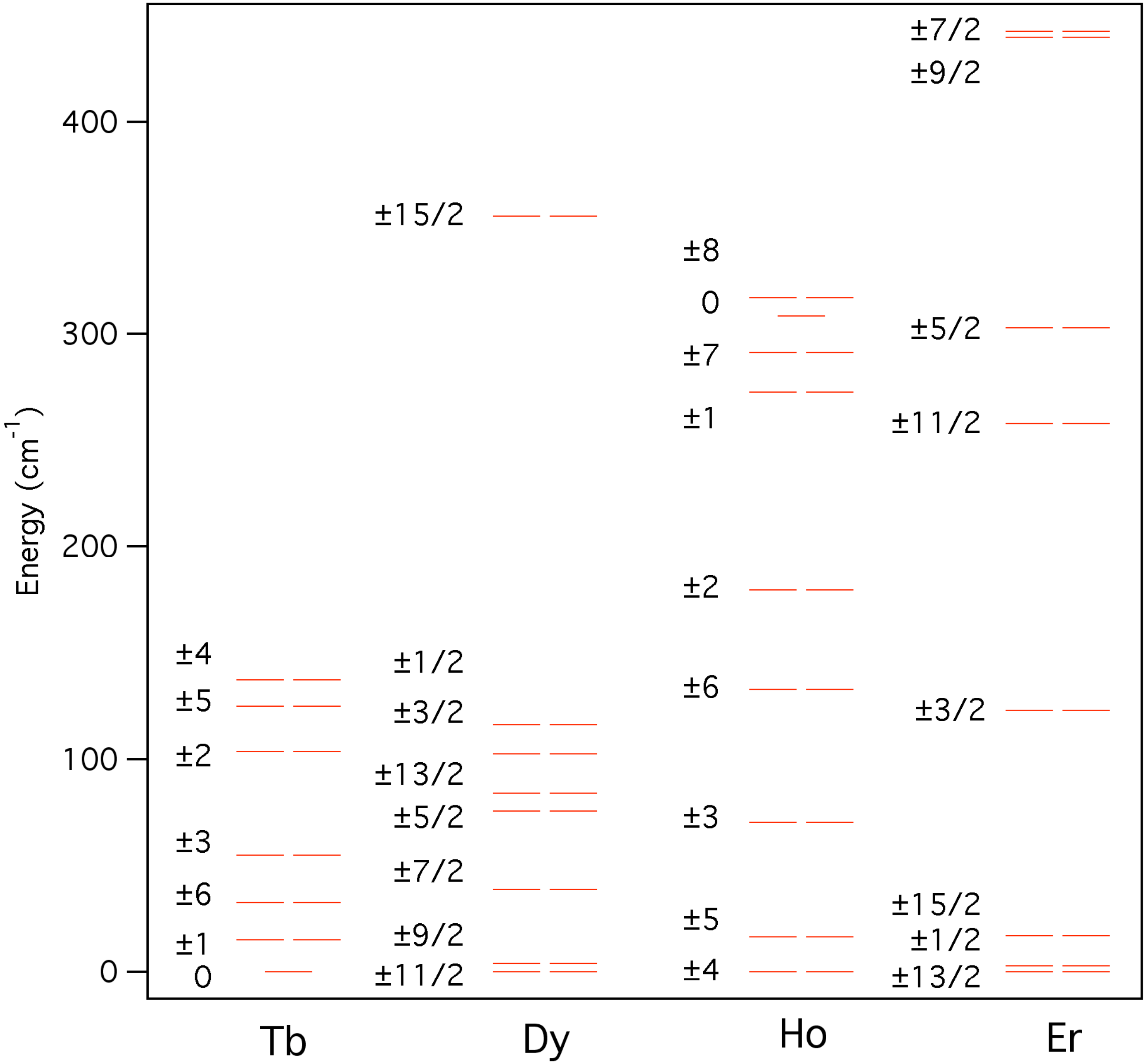
# $[Er(W_{10}O_{36})]Na_9.nH_2O$

Energy levels



# $[Ln(W_{10}O_{36})]Na_9.nH_2O$

## Energy levels

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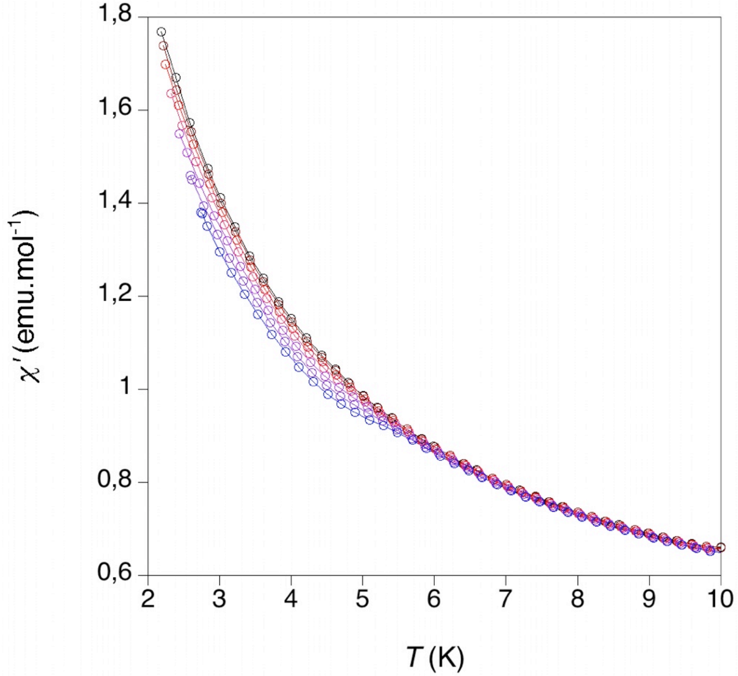
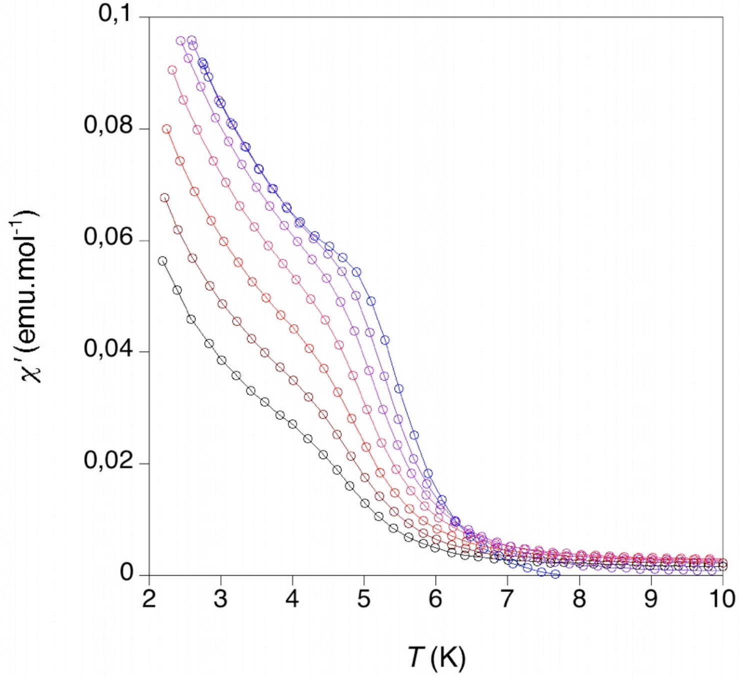
# $[Ho(W_{10}O_{36})]Na_9.nH_2O$

## Magnetic characterization




AC magnetic susceptibility at 1000, 1467, 2154, 3162, 4641, 6813 and 10000 Hz

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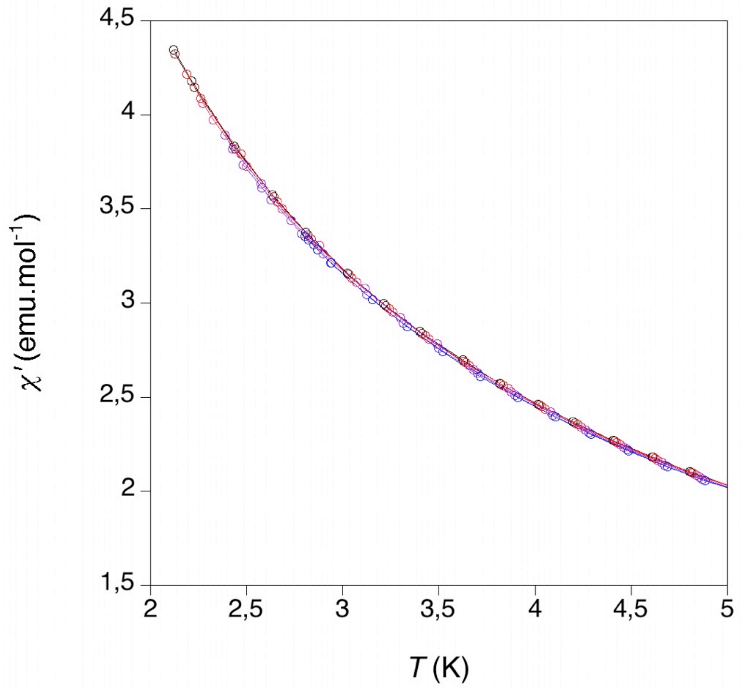
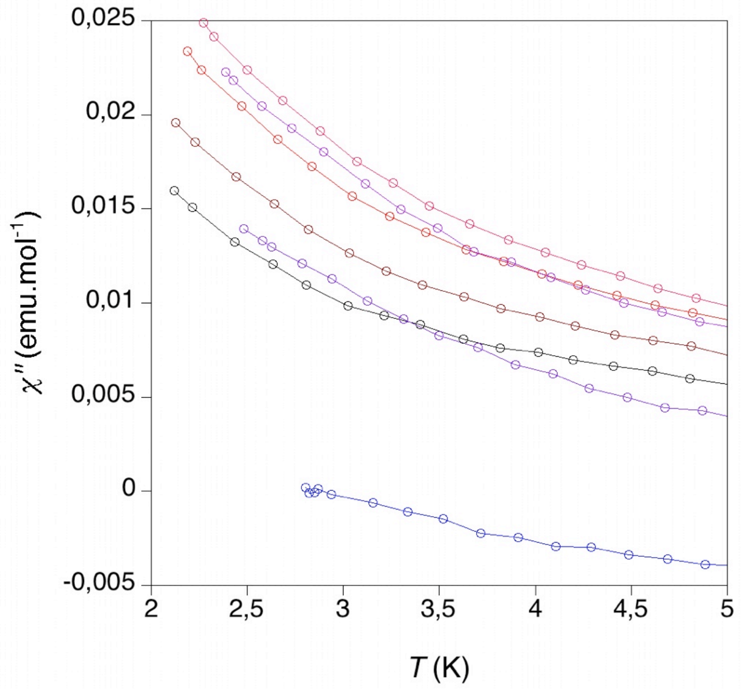
# $[Dy(W_{10}O_{36})]Na_9.nH_2O$

## Magnetic characterization




*AC magnetic susceptibility at 1000, 1467, 2154, 3162, 4641, 6813 and 10000 Hz*

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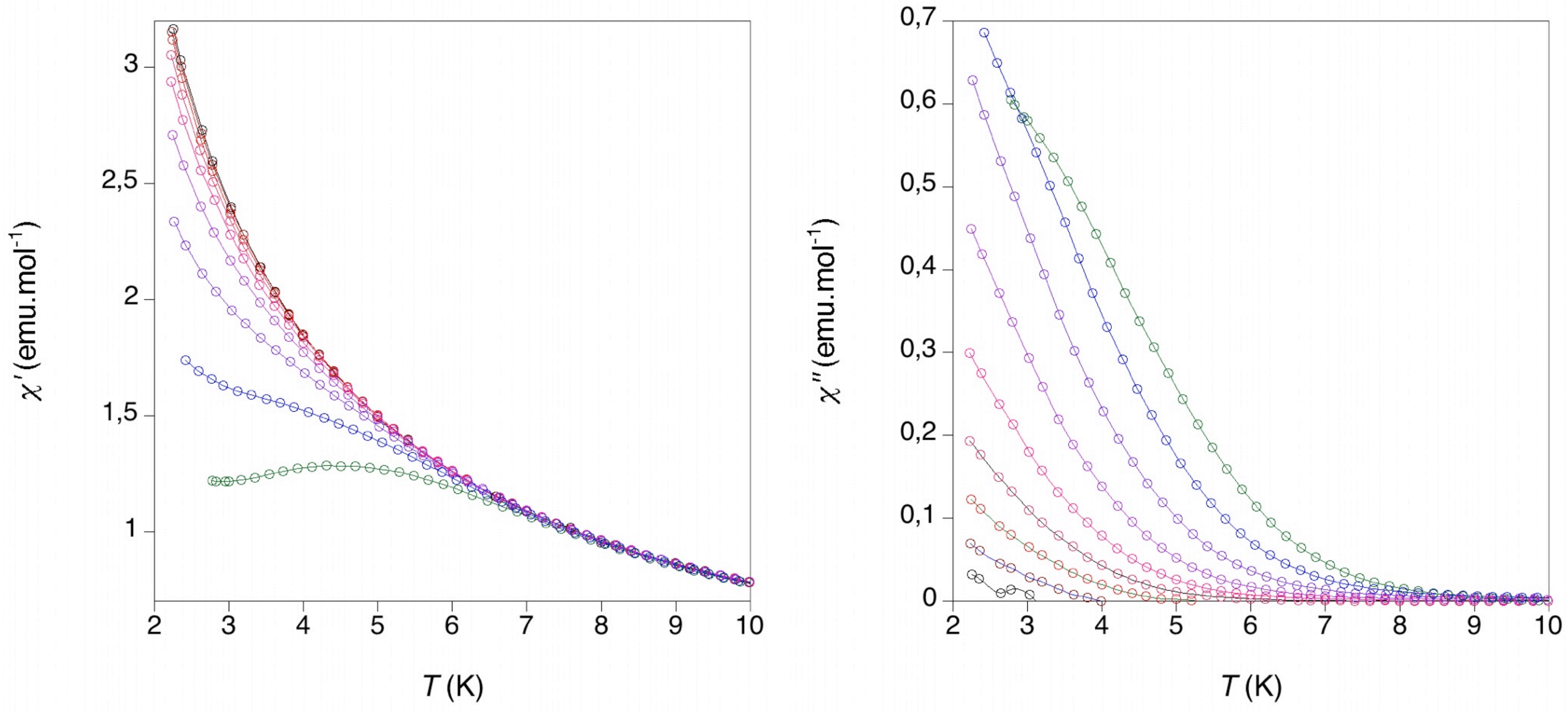
# Magnetic characterization

## $Er(SiW_{11}O_{39})_2]K_{13}.nH_2O$




AC magnetic susceptibility at 1000, 1467, 2154, 3162, 4641, 6813 and 10000 Hz

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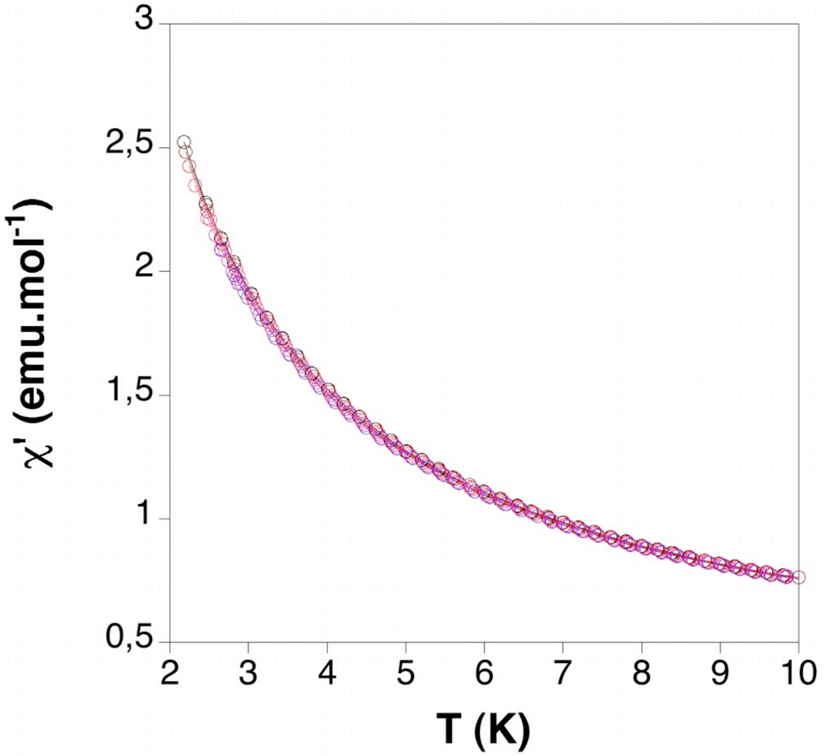
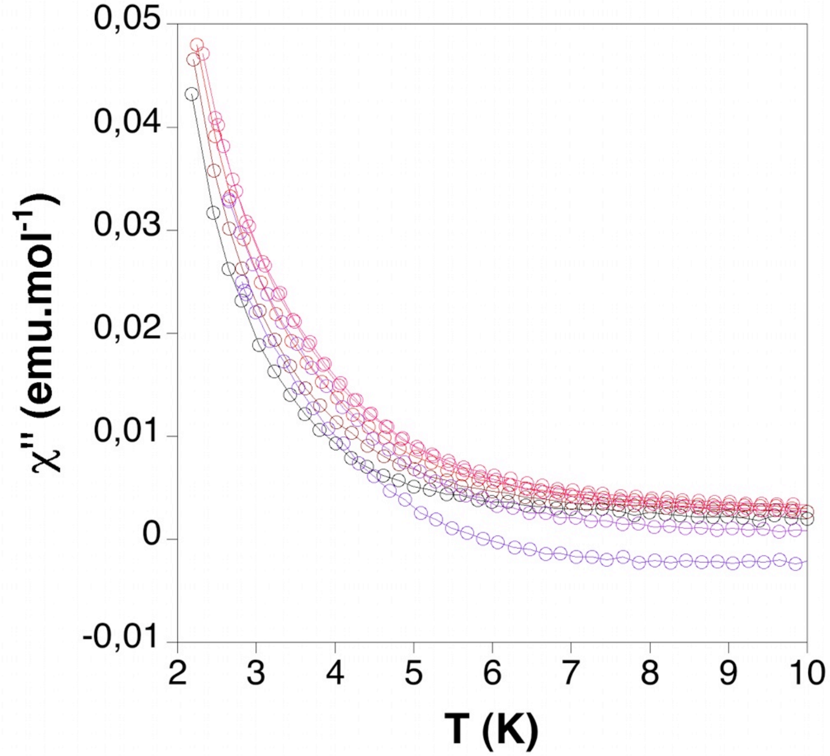
# $[Ho(SiW_{11}O_{39})_2]K_{13}.nH_2O$

## Magnetic characterization




AC magnetic susceptibility at 1000, 1467, 2154, 3162, 4641, 6813 and 10000 Hz

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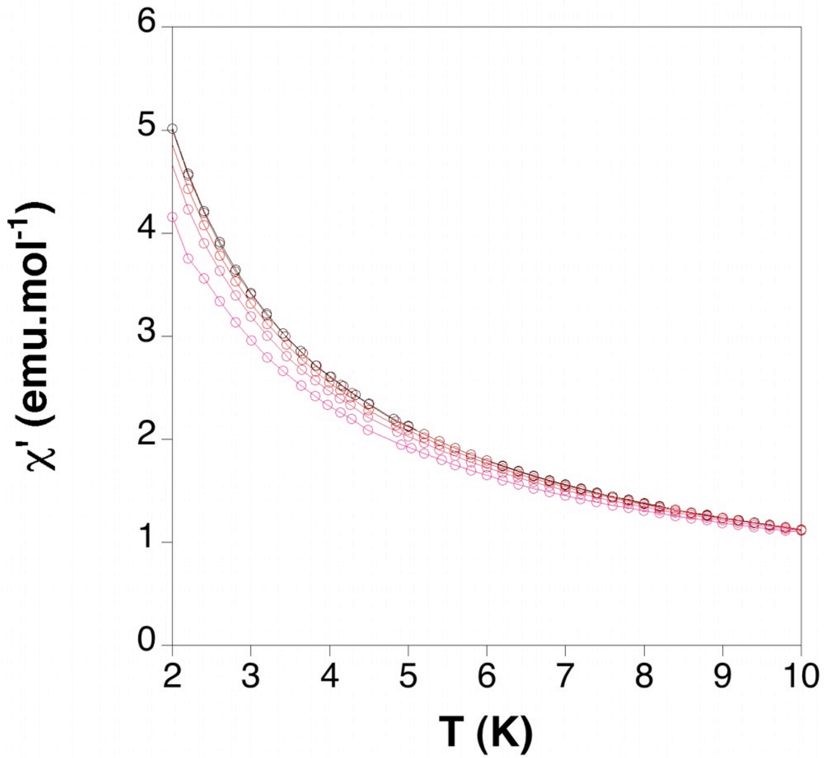
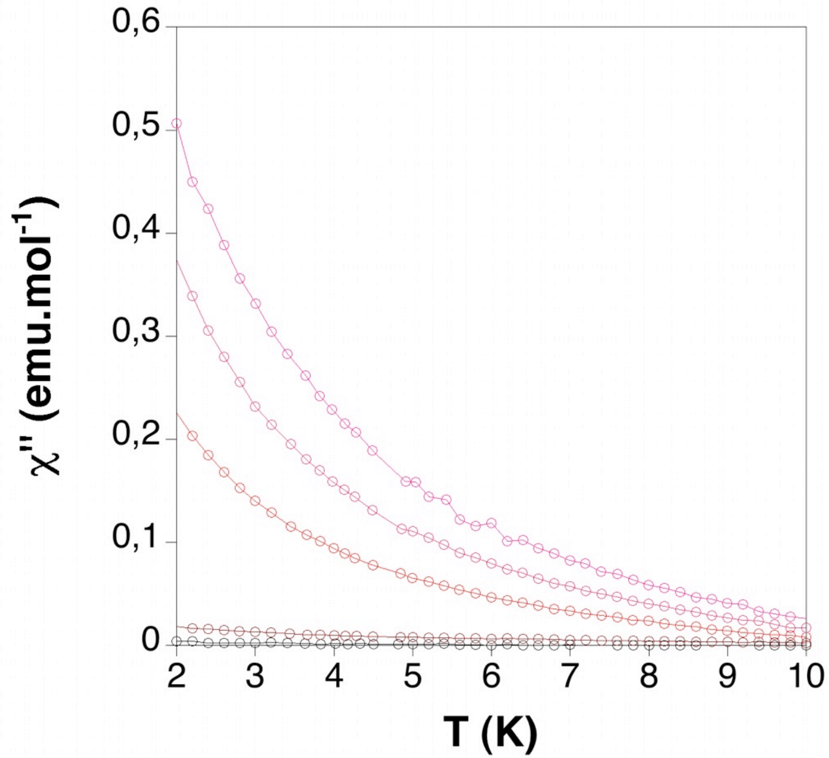
# $[Dy(SiW_{11}O_{39})_2]K_{13}.nH_2O$

**Magnetic characterization**




*AC magnetic susceptibility at 1000, 1467, 2154, 3162, 4641, 6813 and 10000 Hz*

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I. Introduction to POMs

II. SMMs and Quantum tunnelling
in lanthanide POMs

*collaboration with Fernando Luis*

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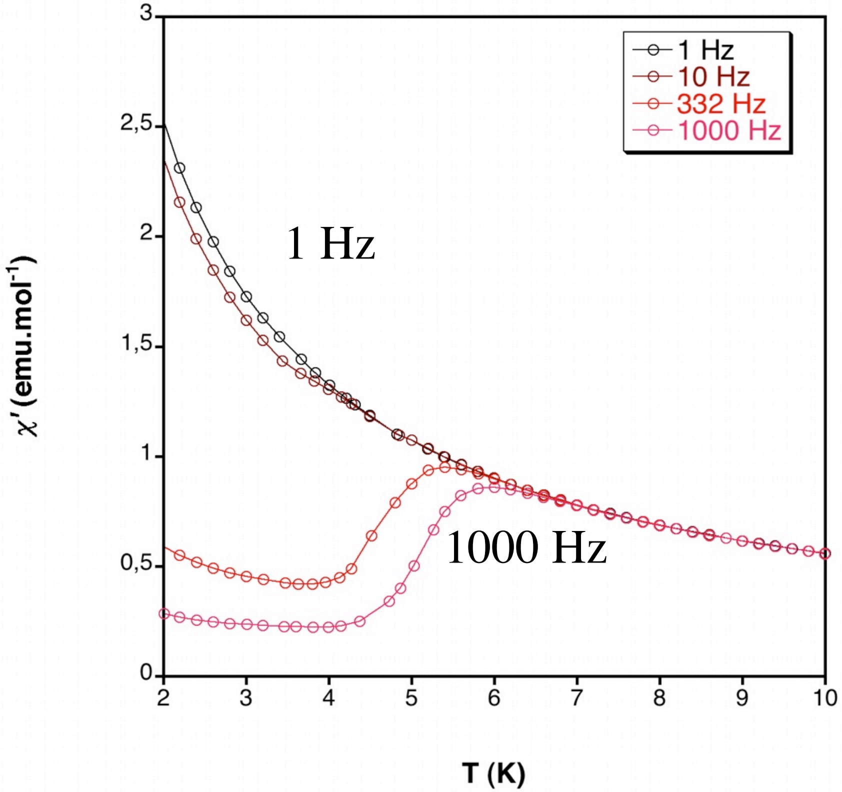
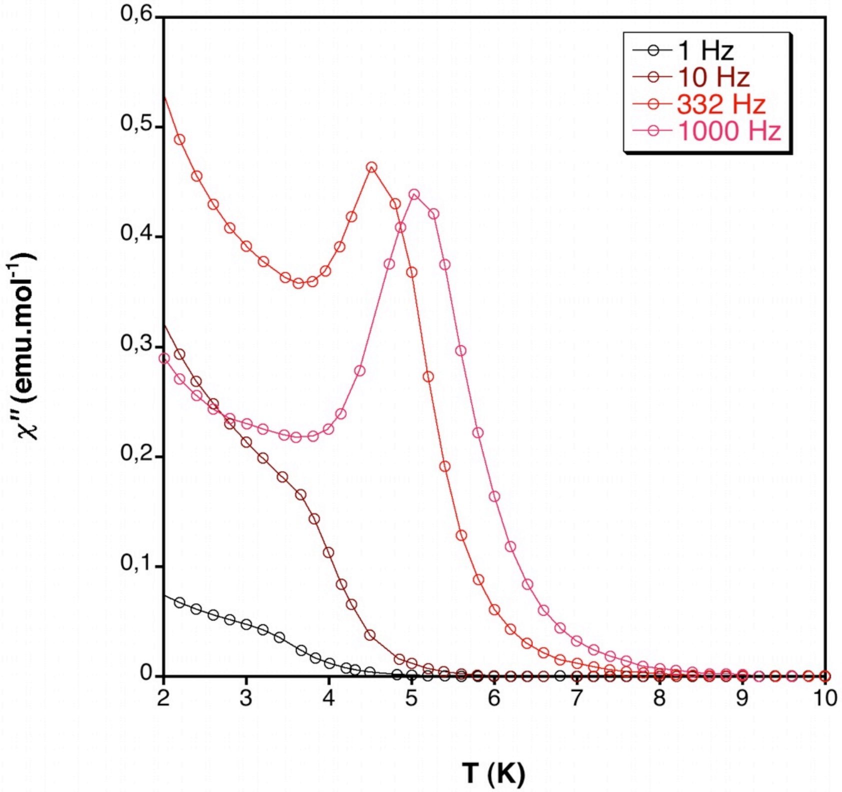
# $[Er(W_{10}O_{36})]Na_9.nH_2O$

## Exotic magnetic behavior




AC magnetic susceptibility at 1, 10, 332 and 1000 Hz.

***Divergence in χ' and χ'' below the blocking T***

***Fast magnetic relaxation at low frequencies***

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**Divergence in χ' and χ'' below the blocking T**

***ORIGIN: VERY FAST QUANTUM TUNNELLING OF THE MAGNETIZATION via THE GROUND STATE***

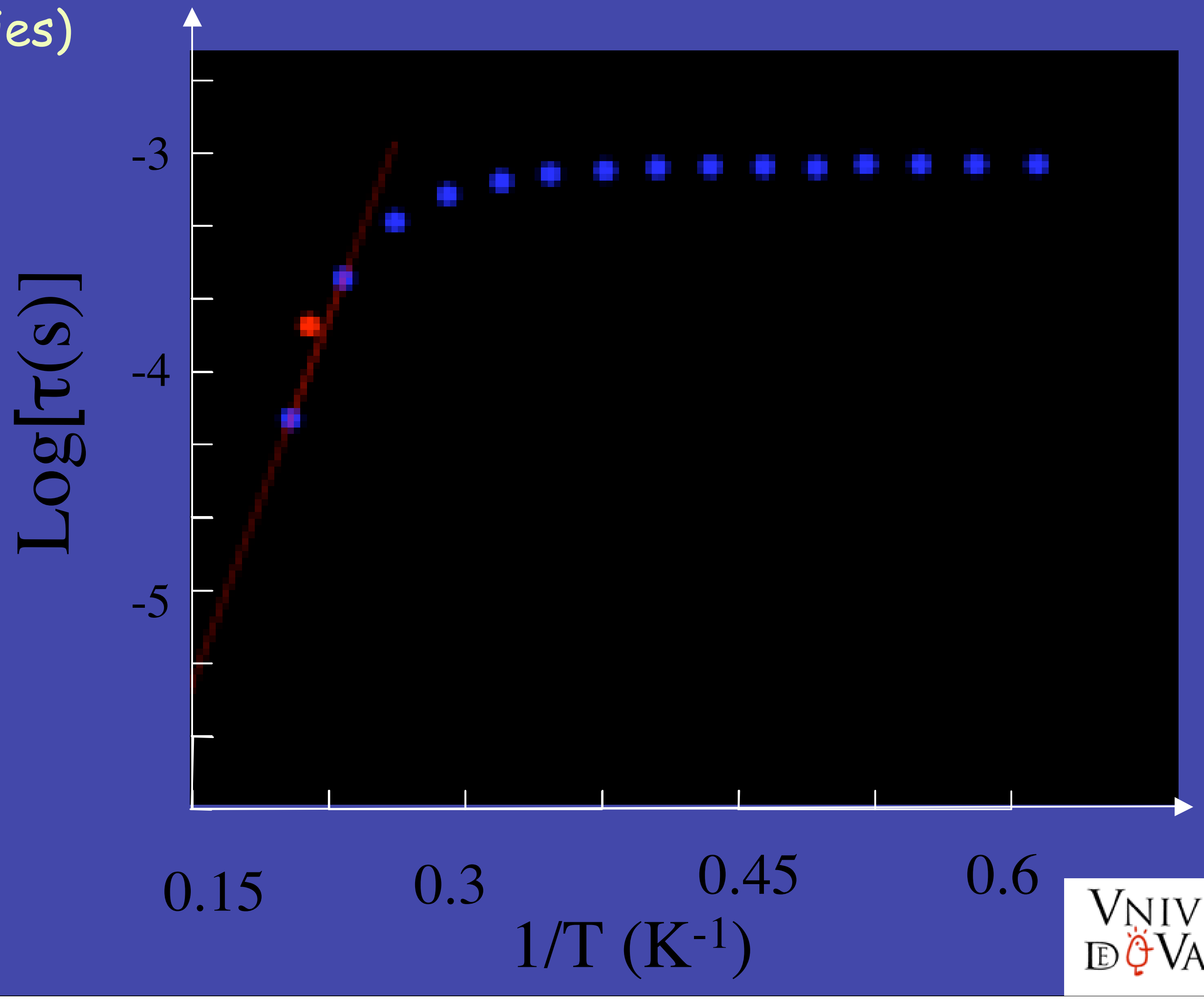
***Susceptibility fully blocked only when the time scale of the experiment***
***$(1/2\pi\nu) \ll$ tunnelling time***
***(at $\nu > 10000$ Hz)***

***Susceptibility unblocked (even at T = 0) when***
***$(1/2\pi\nu) >$ tunnelling time***
***(at $\nu > 10$ Hz)***

magnetic behavior

## $[Er(W_{10}O_{36})]Na_9.nH_2O$

Quantum tunnelling regime below 4.4 K with a relaxation time of *ca* 1 ms. (from the study of the *ac* susceptibilities as a function of frequencies)

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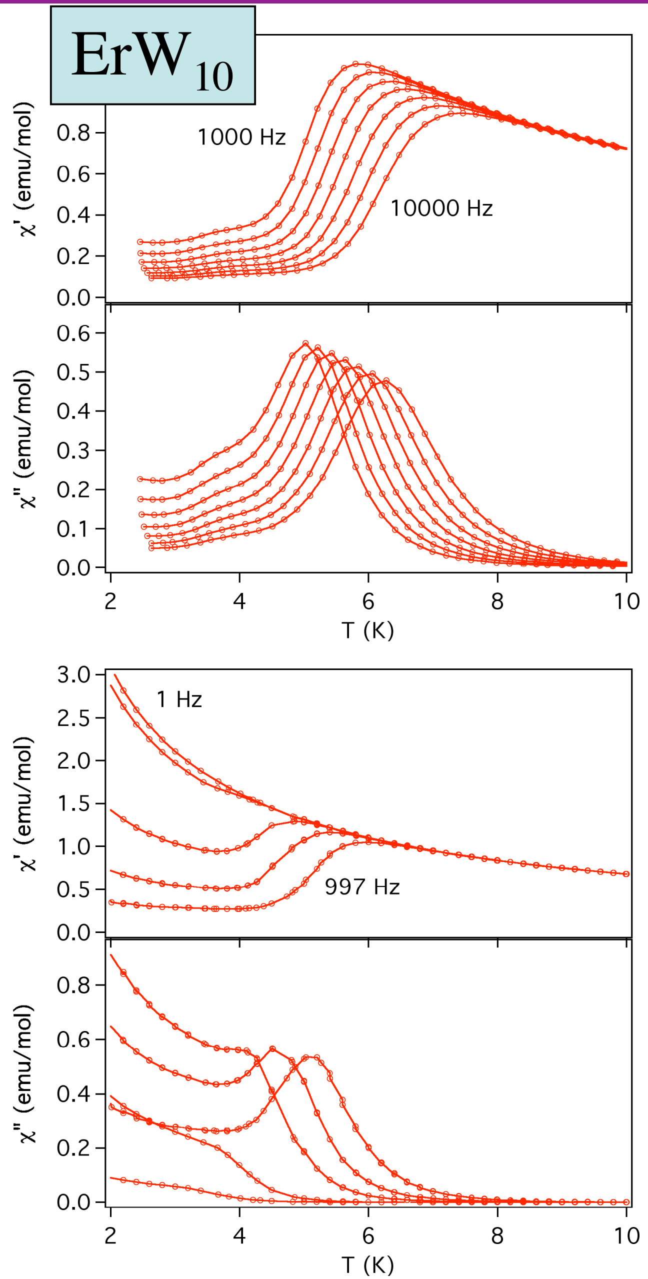
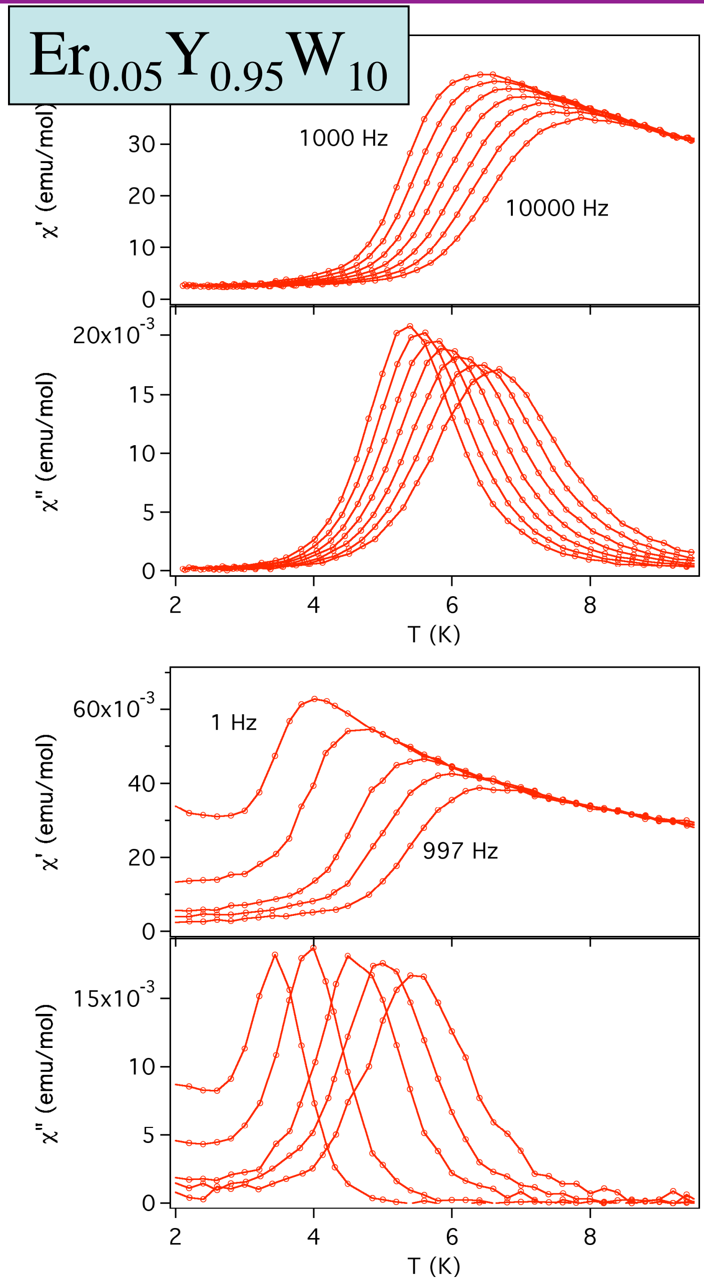
# $[Er(W_{10}O_{36})]Na_9.nH_2O$

## MAGNETIC DIPOLAR EFFECTS

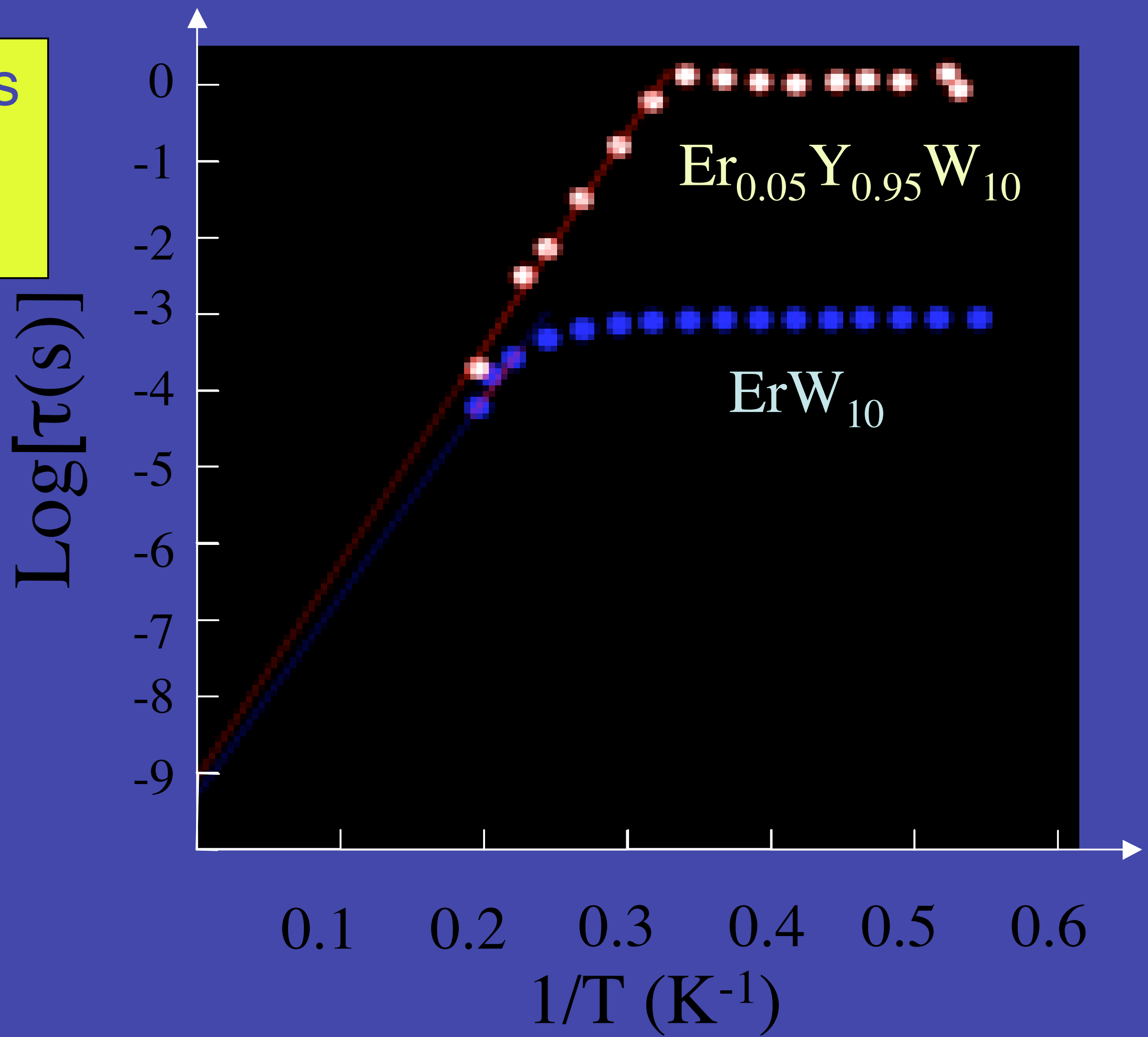


## $[Er(W_{10}O_{36})]Na_9.nH_2O$

MAGNETIC DIPOLAR EFFECTS

Dipole interactions open a "window" for the tunnelling

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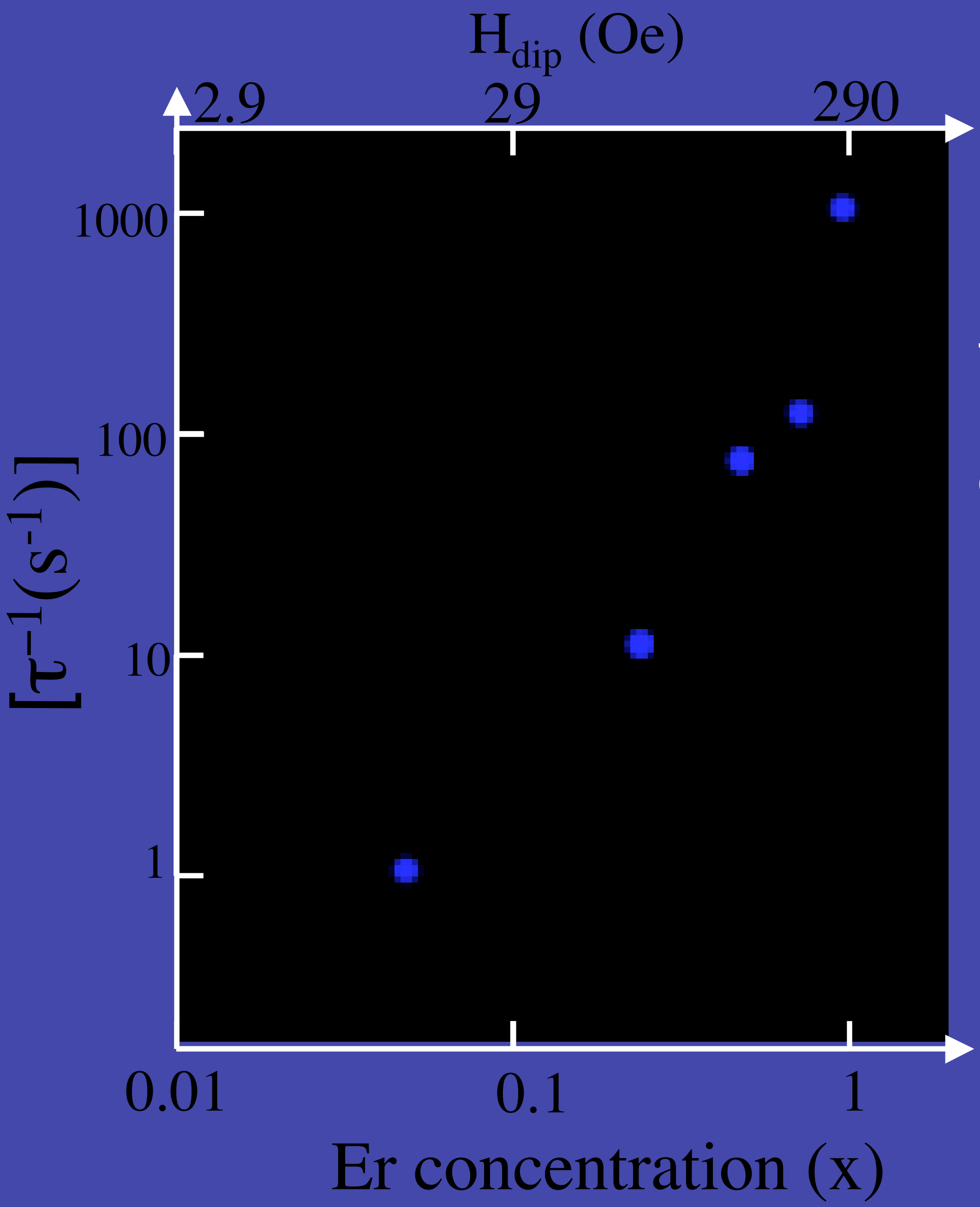
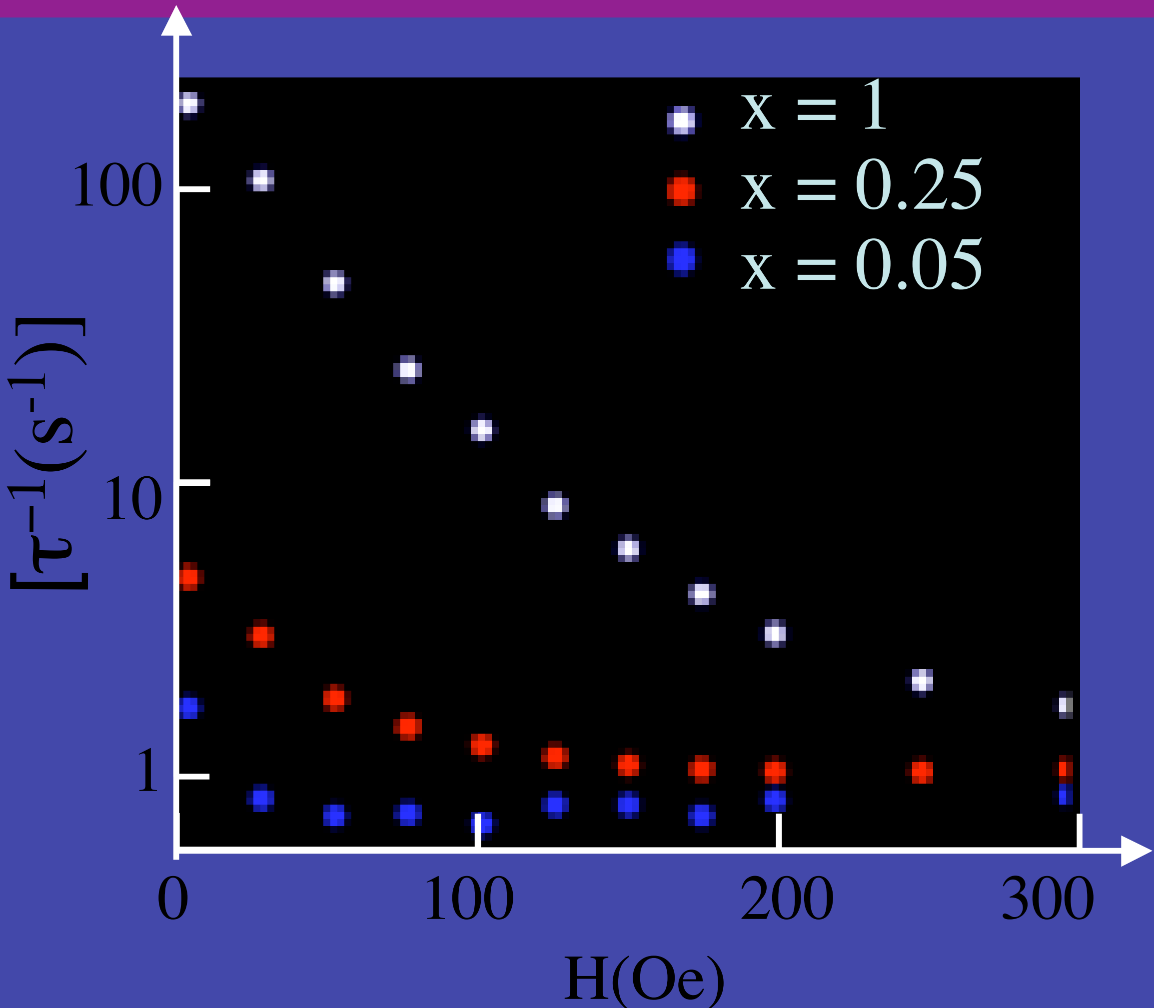
# MAGNETIC DIPOLAR EFFECTS




The spin-lattice relaxation rate is largely enhanced by dipole-dipole interactions acting as an "effective" magnetic field

EXTERNAL MAGNETIC FIELD EFFECTS

## $[Er(W_{10}O_{36})]Na_9.nH_2O$




The spin-lattice relaxation rate is rapiply surpressed by application of external magnetic fields

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# $[Er(W_{10}O_{36})]Na_9.nH_2O$

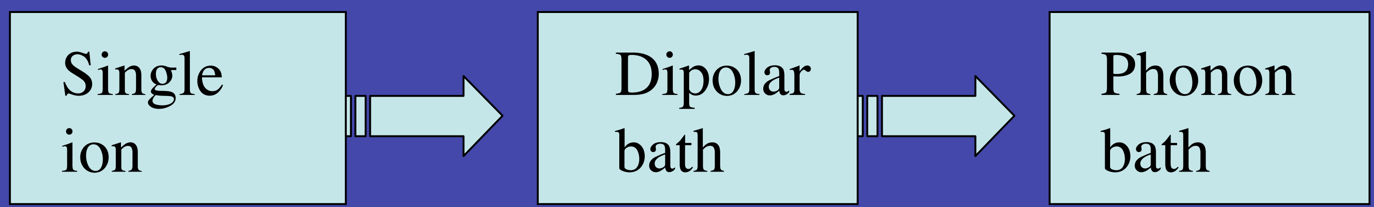
## CONCLUSION

The relaxation in the quantum tunnelling regime is very sensitive to extremely weak environmental magnetic fields (**dipolar and external**)

However these two fields produce opposite effects in the spin-lattice relaxation.

MODEL: Dipolar-mediated quantum spin-lattice relaxation.

For sufficiently low magnetic fields spins transfer their energy to the “dipolar bath” via quantum tunnelling processes

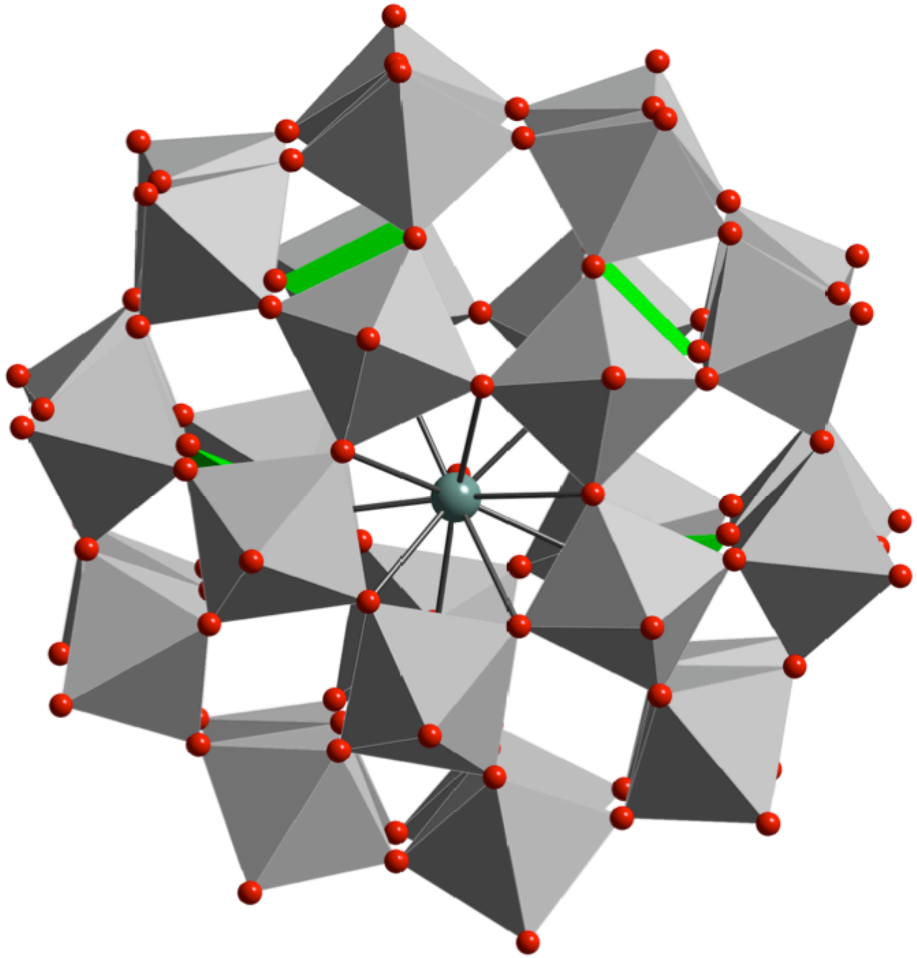


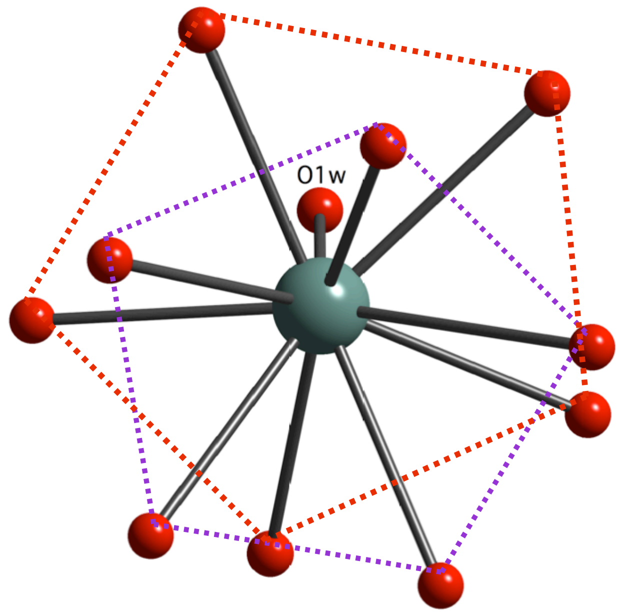
# Lanthanide polyoxometalate (POM) complexes

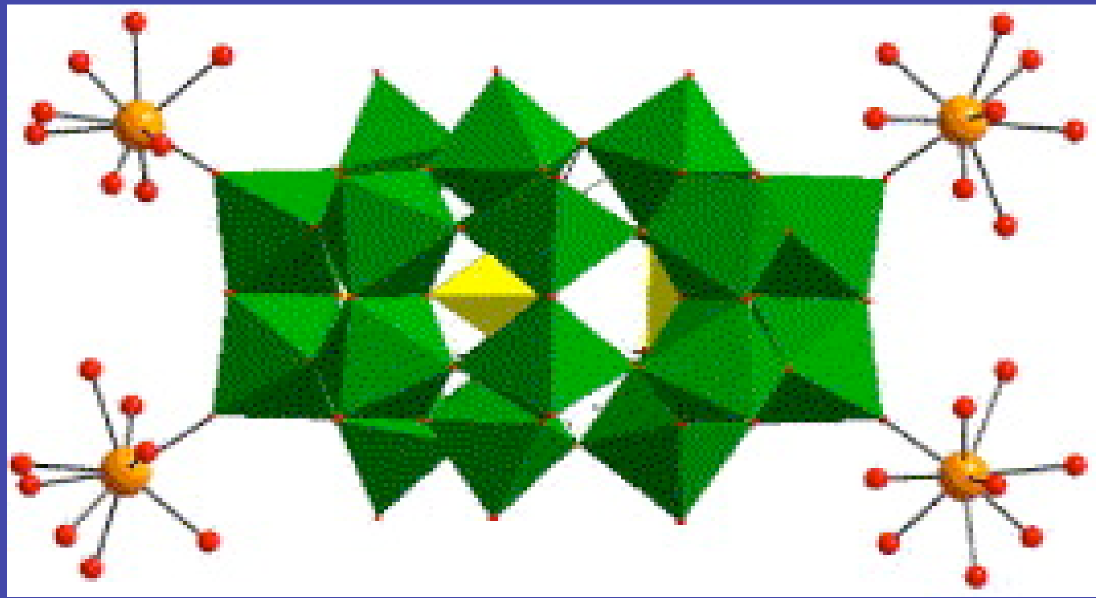
Structural description

## BIGGER CLUSTERS; OTHER CRYSTAL FIELD SYMMETRIES

**Preyssler anion** $[Ln(P_5W_{30}O_{110})]^{n-}$







Adding magnetic moments around SMMs : Single Lanthanide clusters surrounded by magnetic ions (Gd)

## POTENTIAL OF LANTHANIDE-POMs

SMMs based on single-metal ions

- Extremely good insulation of the rare earth (dilution is not needed).

*Even the pure magnetic sample is diluted. Possibility to study spin dynamics in crystal lattices avoiding structural disorder*

- Stability of the POM in solution and in the solid state (and in surfaces)

- Spin nuclear-free samples available

- Large single crystals available

- Highly charged anions : Electrospray techniques / Electrostatic approaches may be used for deposition on surfaces

**Ideal systems for studying quantum spin dynamics in SMMs, for applications in quantum computing, for making chemistry (hybrid materials), for processing on surfaces,…**

# *Molecular Nanomagnets*

## E. Coronado

- POLYOXOMETALATE CLUSTERS

- **SMMs in different environments**
  - On surfaces
  - Intercalated / embedded

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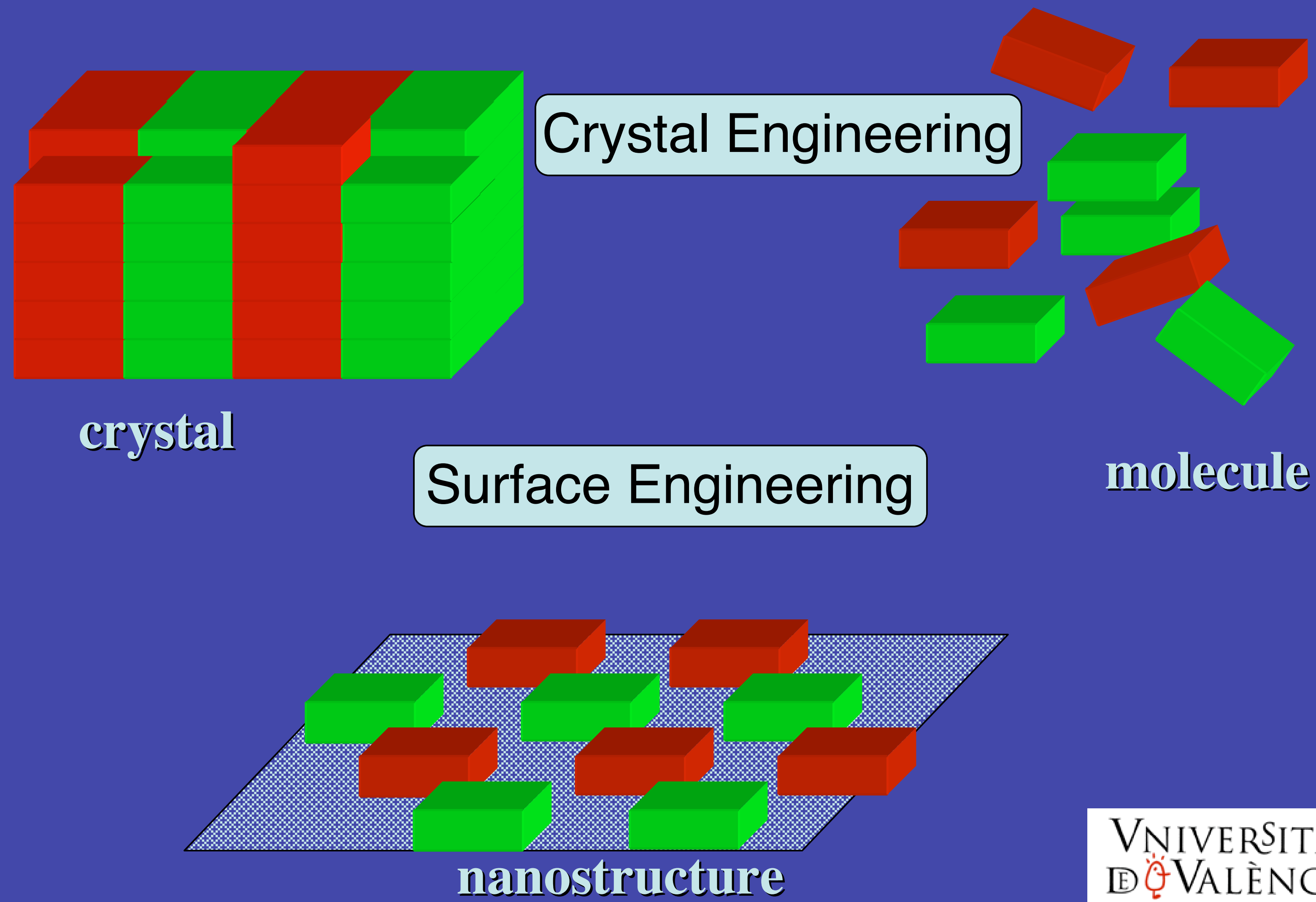


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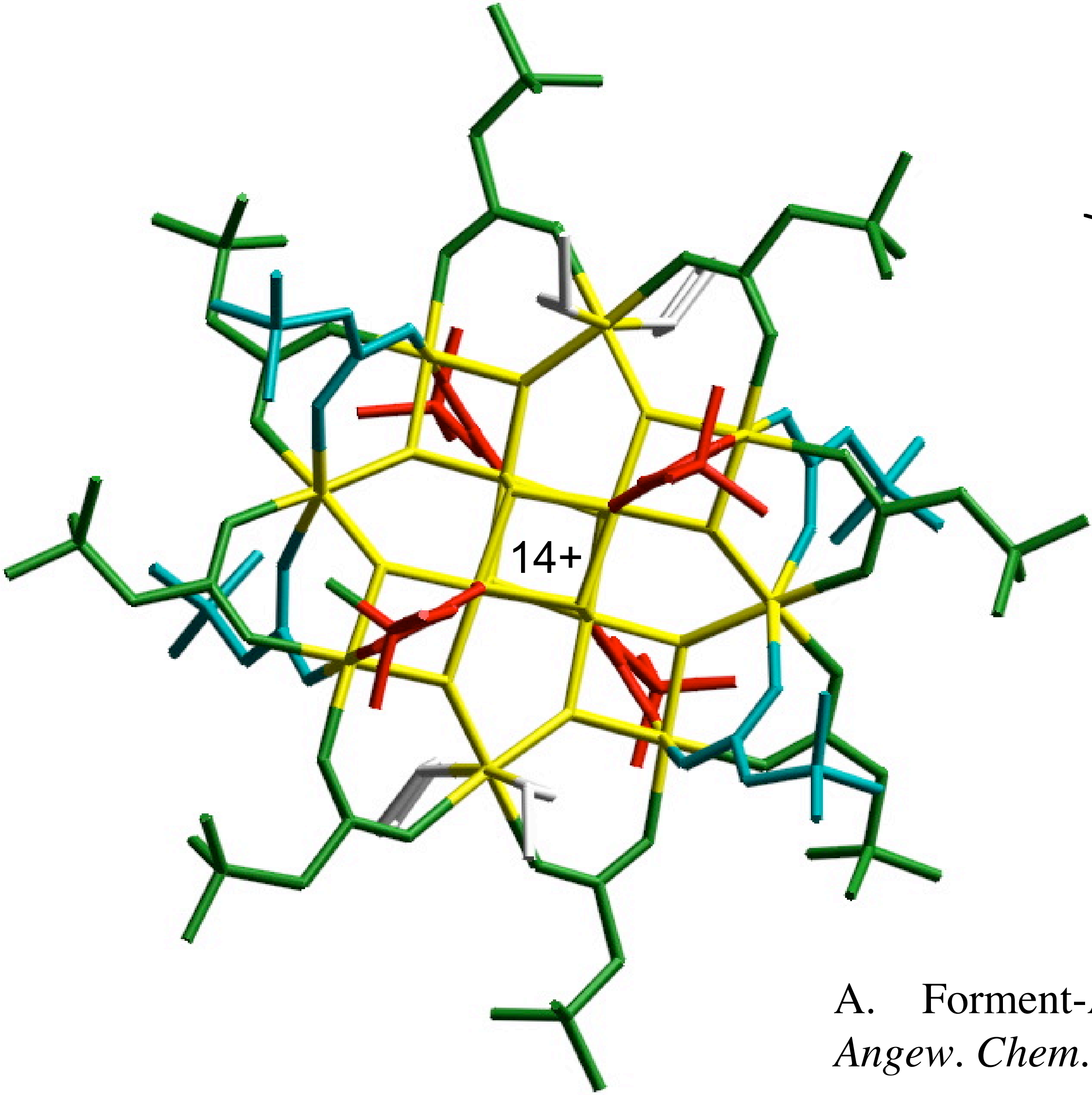
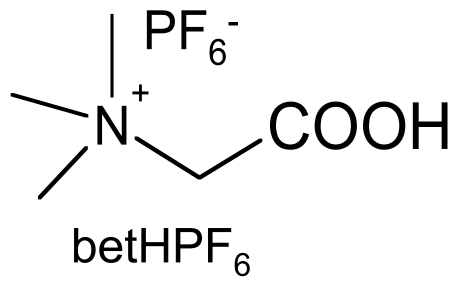
# Intercalation of Single Molecule Magnets into layered superconductors

# Cationic $Mn_{12}$ molecules



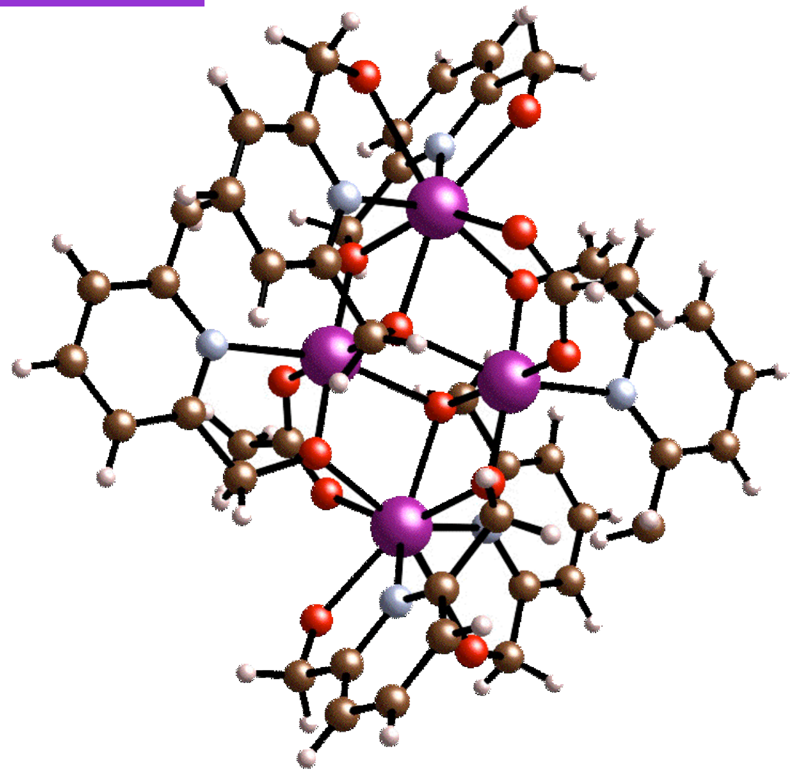



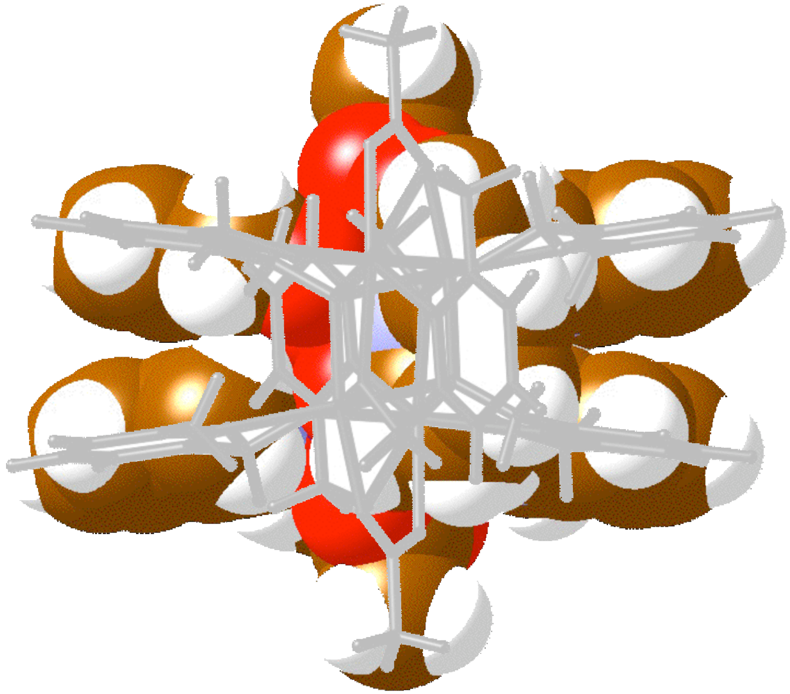

A. Forment-Aliaga et al.
*Angew. Chem. Int. Ed.* **2004**, *43*, 6152

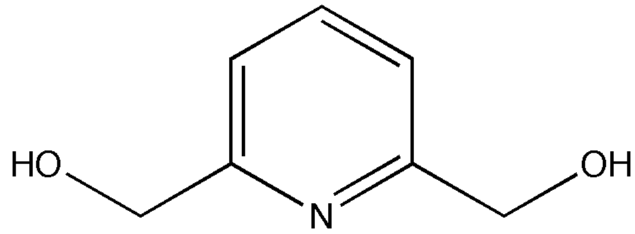
# *CATIONIC $Mn_4$ MOLECULES*

***Structural description***

**$Mn_4$** $2+$





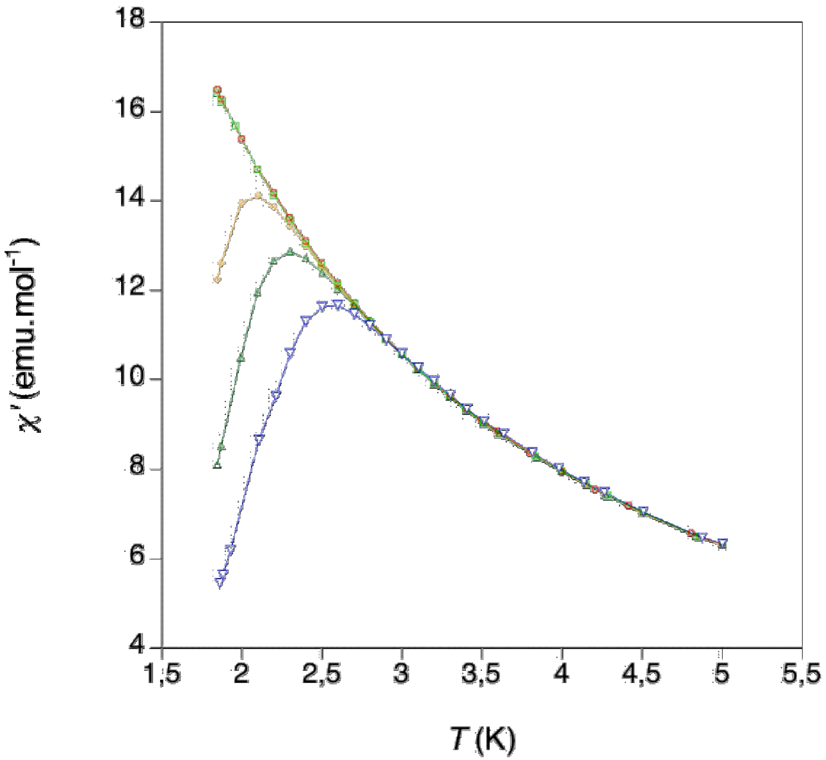


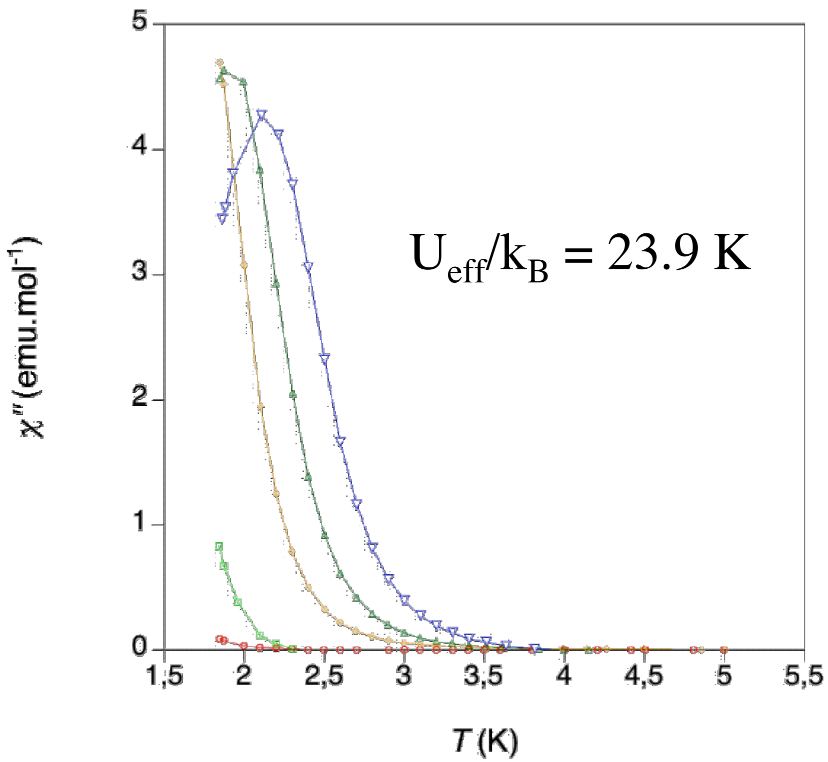

pdmH = $C_7H_9N_2$

*G. Christou; D. N. Hendrickson *et al*. *Inorganic Chemistry* **2000,** 39, (16), 3615-3623.

# CATIONIC $Mn_4$ MOLECULES

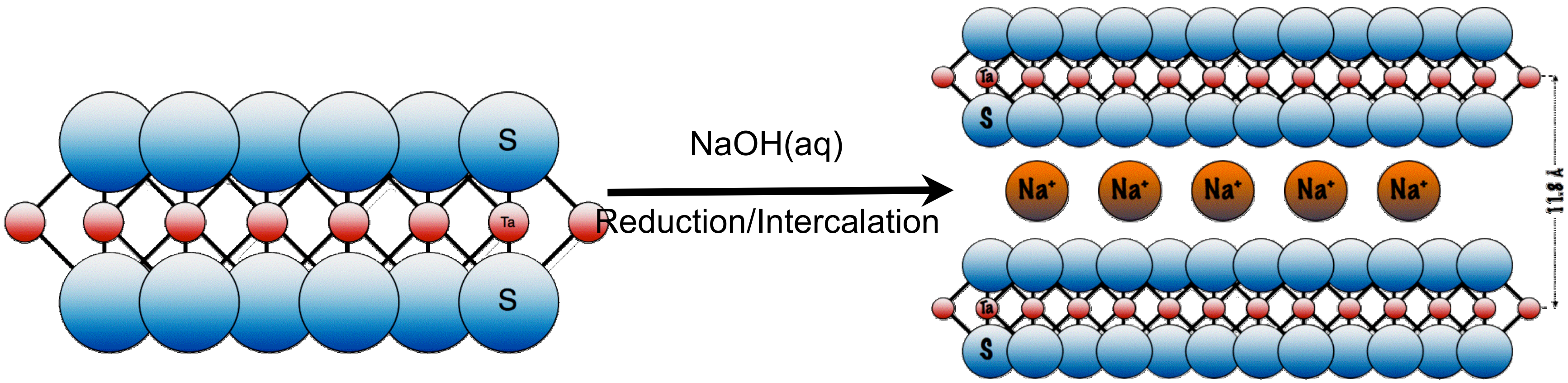
Magnetic Characterization



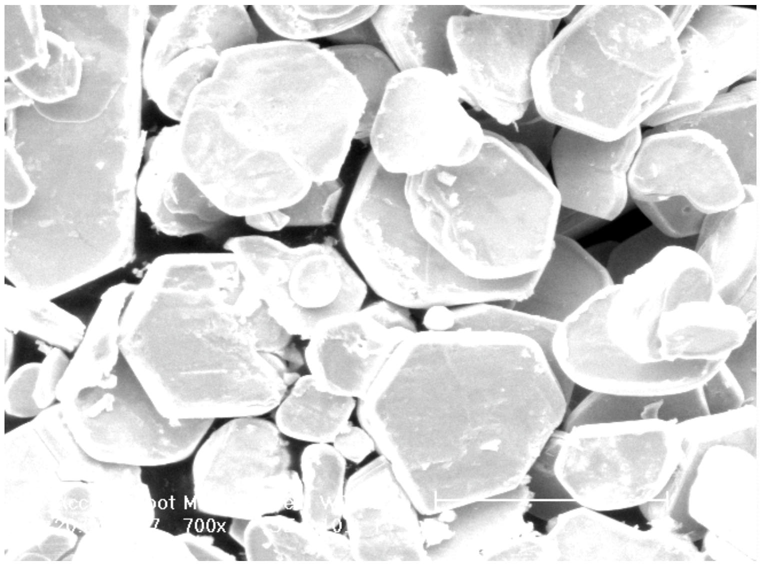



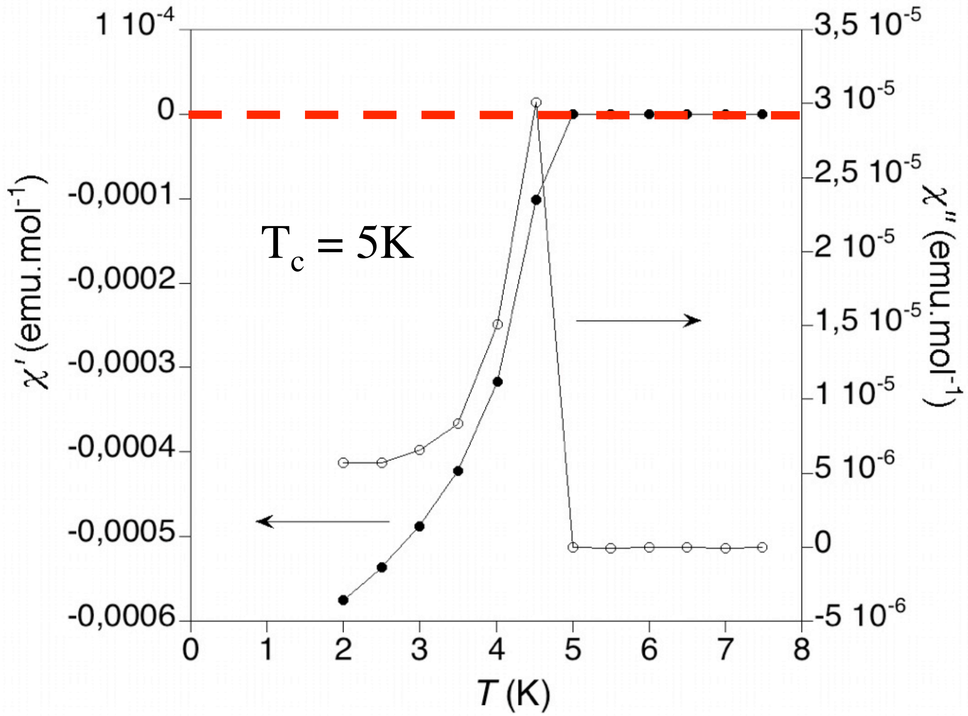

AC magnetic susceptibility at 1, 10, 332 and 1000 Hz.

# A layered superconductor



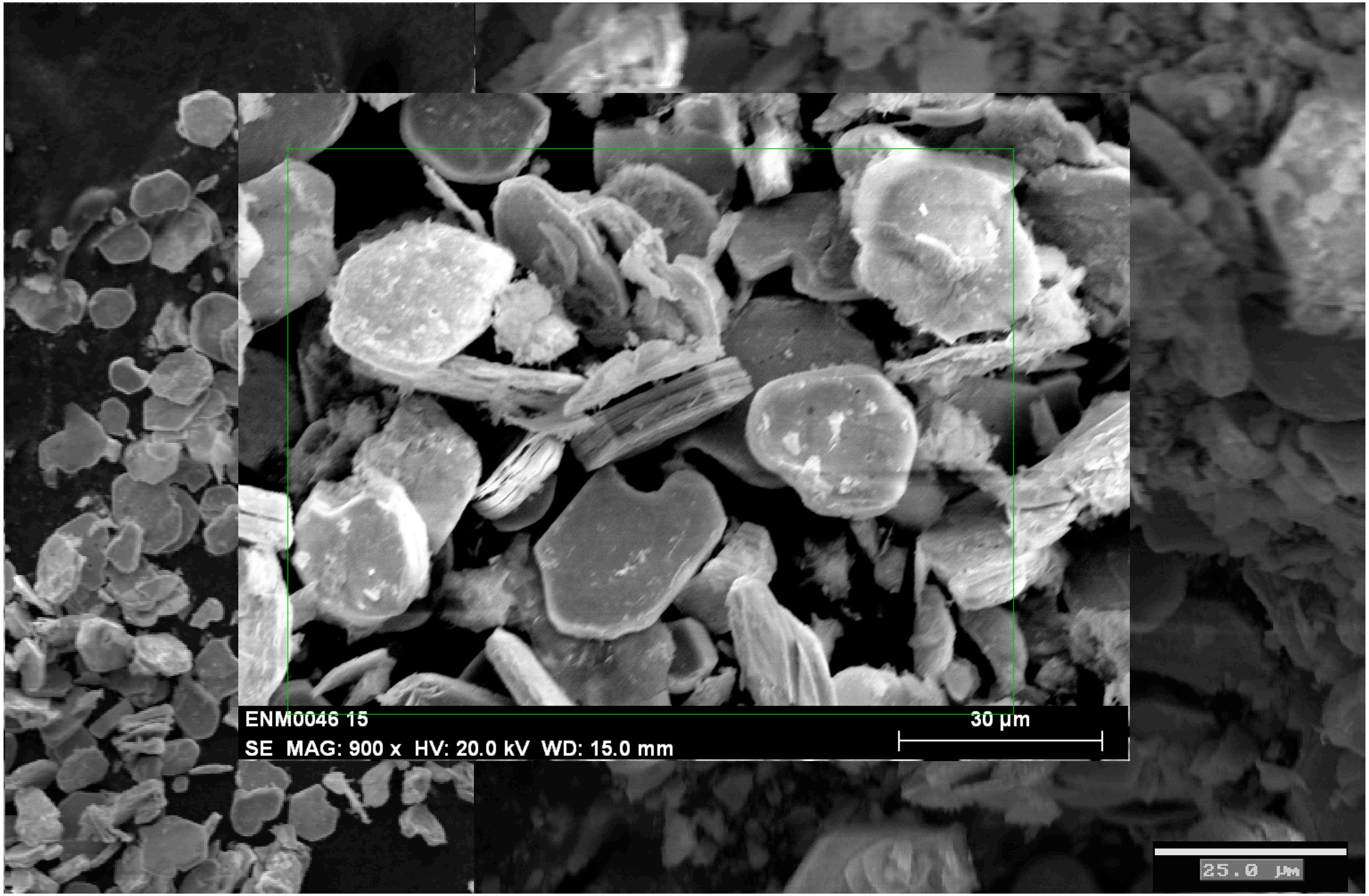

$Na_{0.33}[Ta^{III,IV}S_2]$





# *$Mn_4$ intercalated in a layered superconductor*

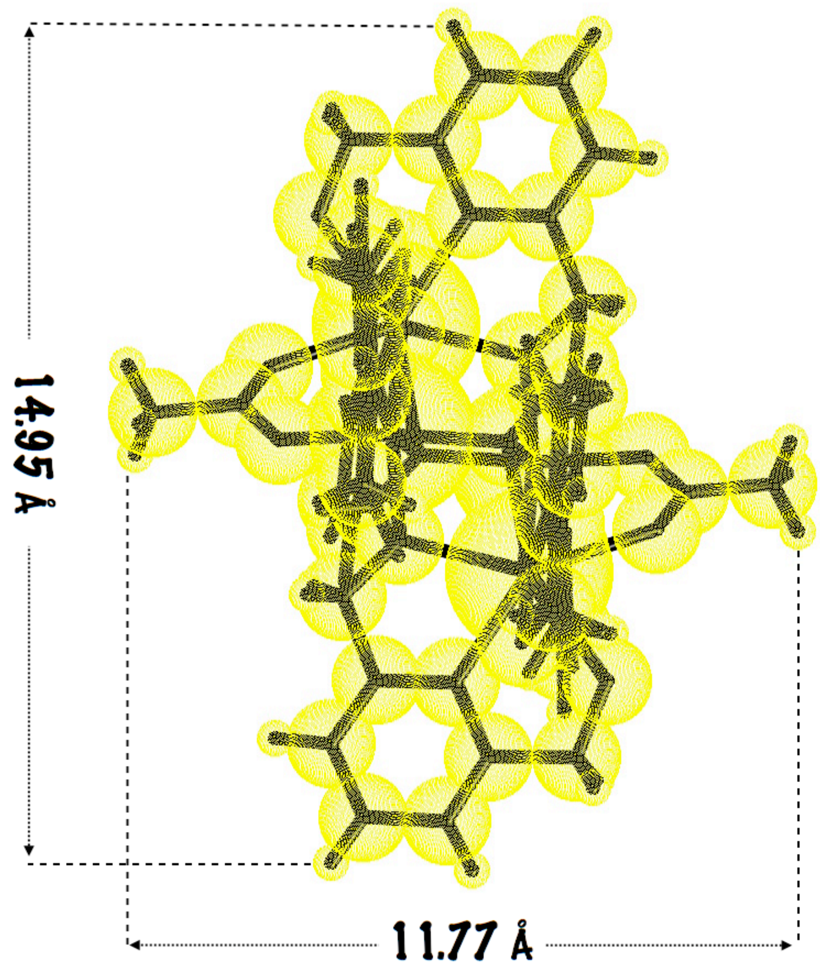
***Morphology***

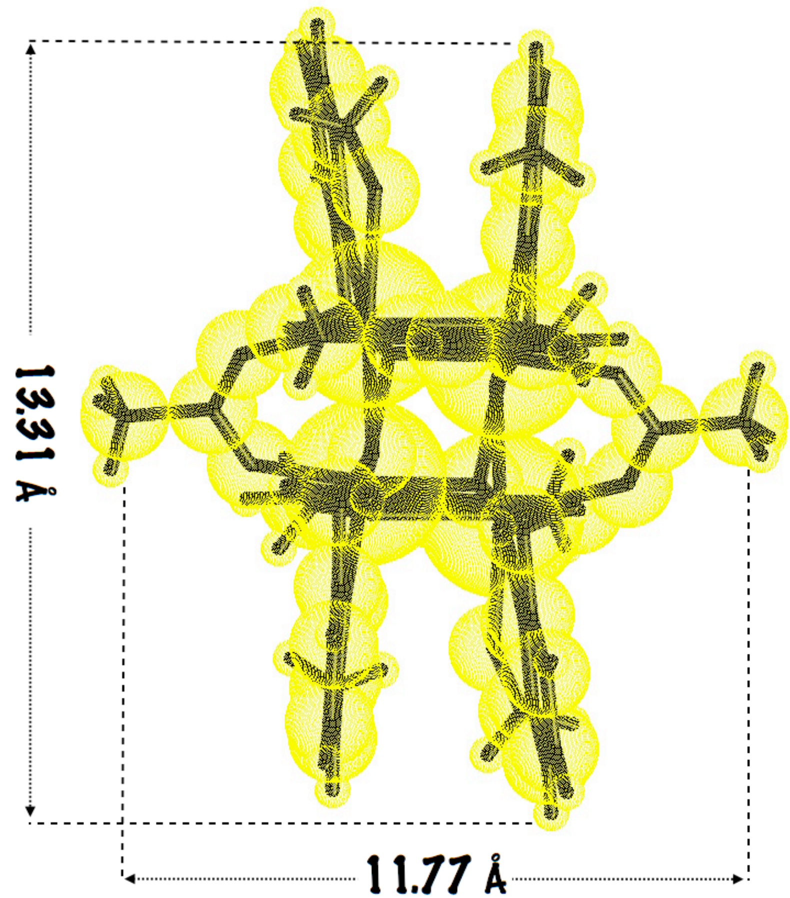



**Pictures aquired in a Hitachi S-4100 Scanning Electron Microscope**

# *$Mn_4$ intercalated in a layered superconductor*

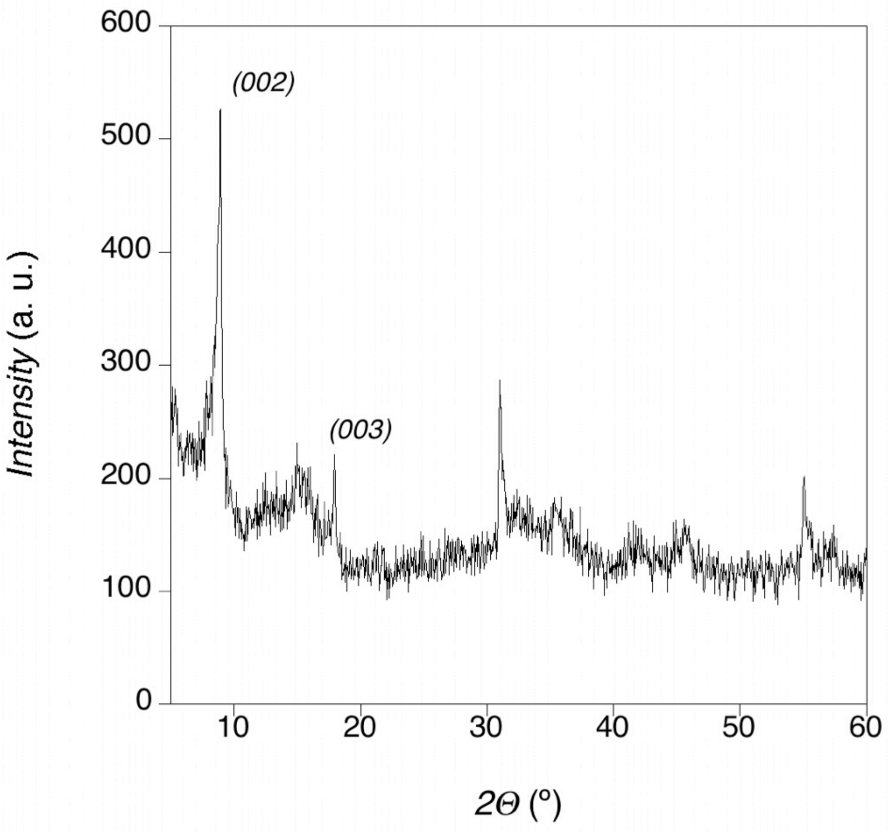
## *Dimensions*

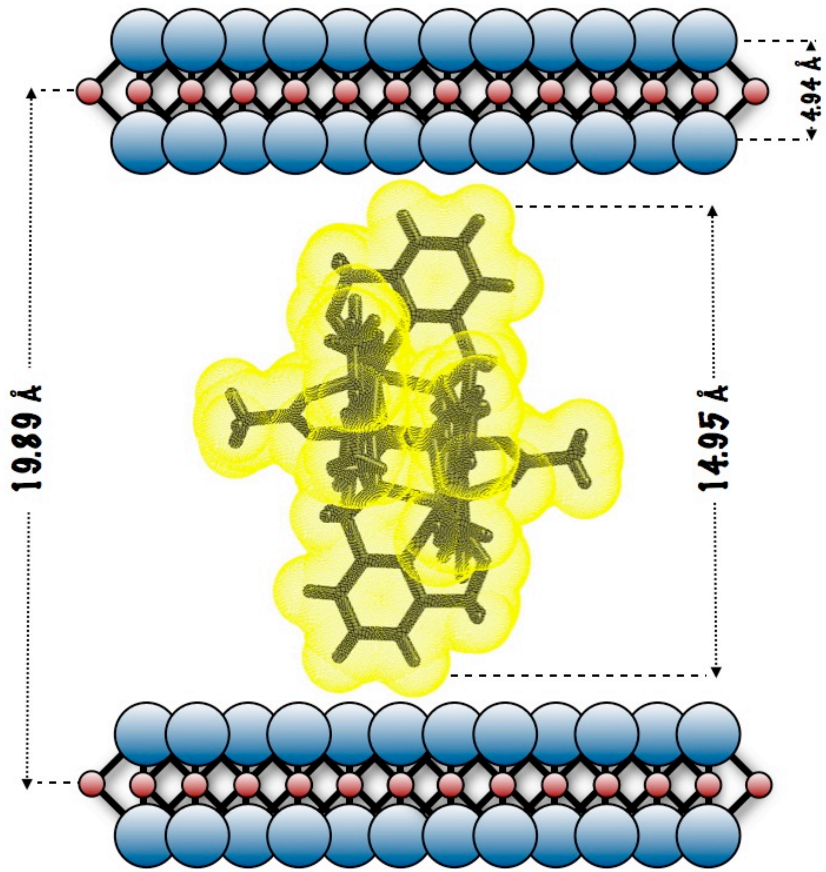


# $Mn_4$ intercalated in a layered superconductor

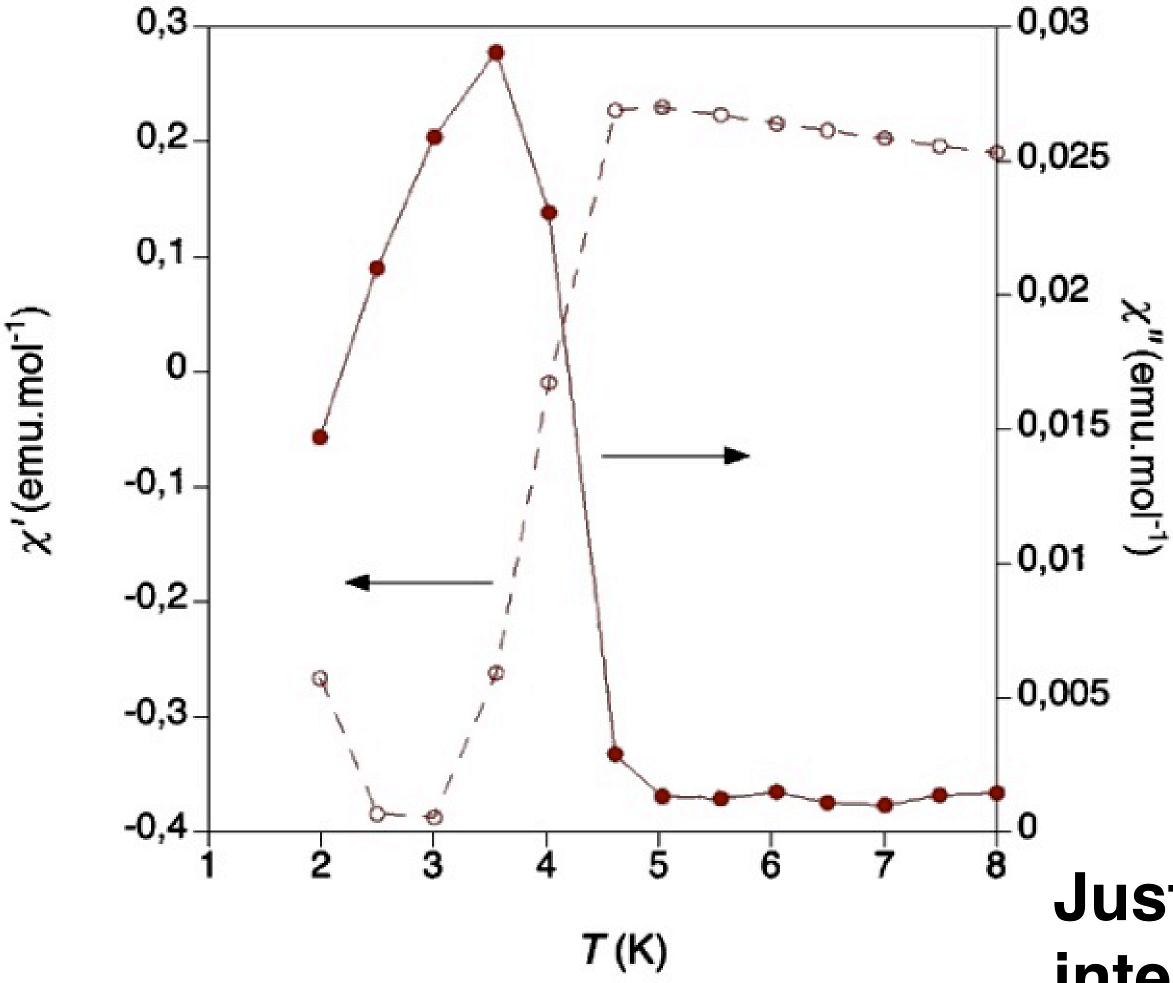
## Structure



# *$Mn_4$ intercalated in a layered superconductor*

*Physical Characterization*



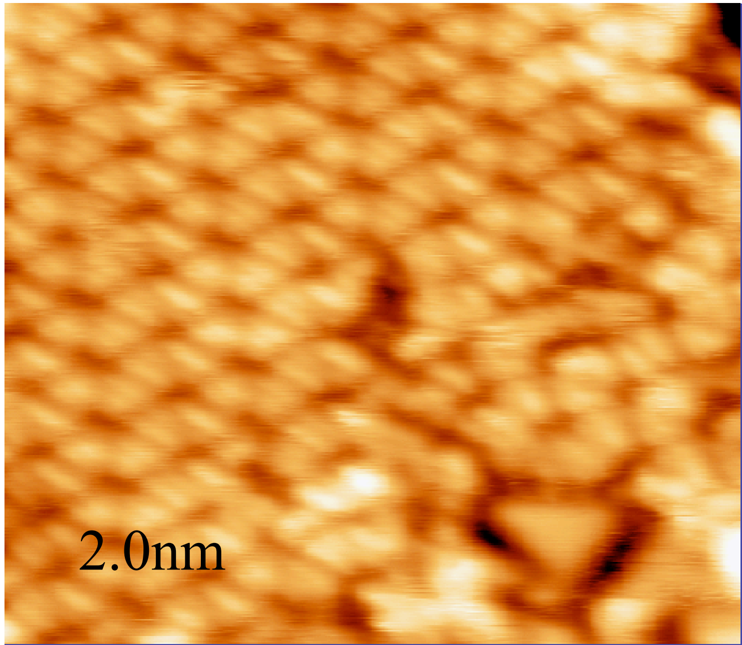

AC magnetic susceptibility of Mn4-TaS2 at 110 Hz.

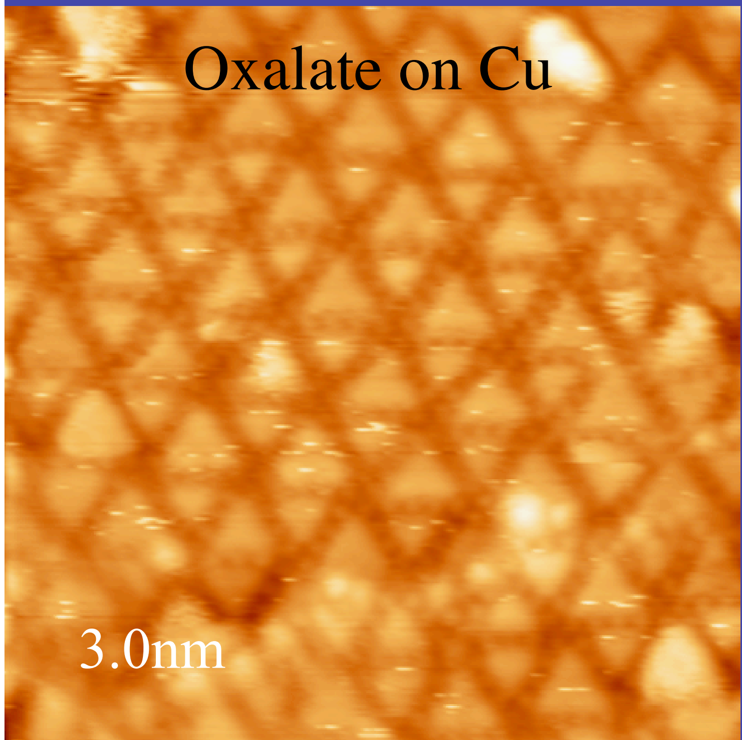
**Just coexistence or... interaction**

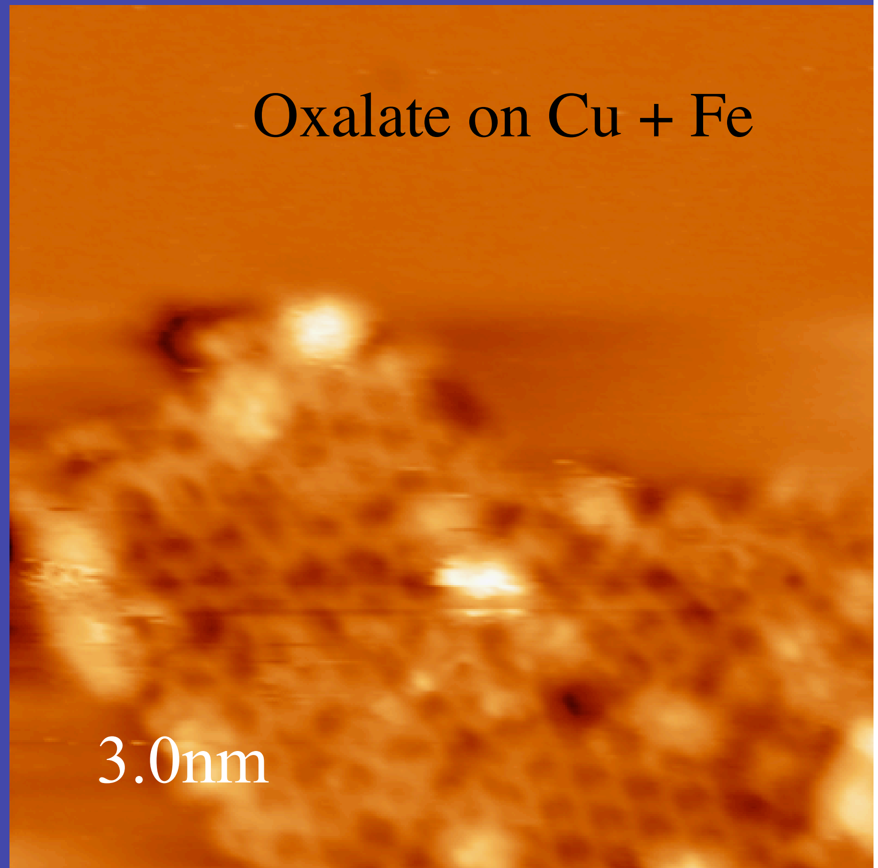
**The energy barrier is reduced by 1/2 (from 24 to 12 K): Screening of dipolar interactions by the superconductor ?????**

# MAGNETIC MONOLAYERS

## Oxalates on surfaces



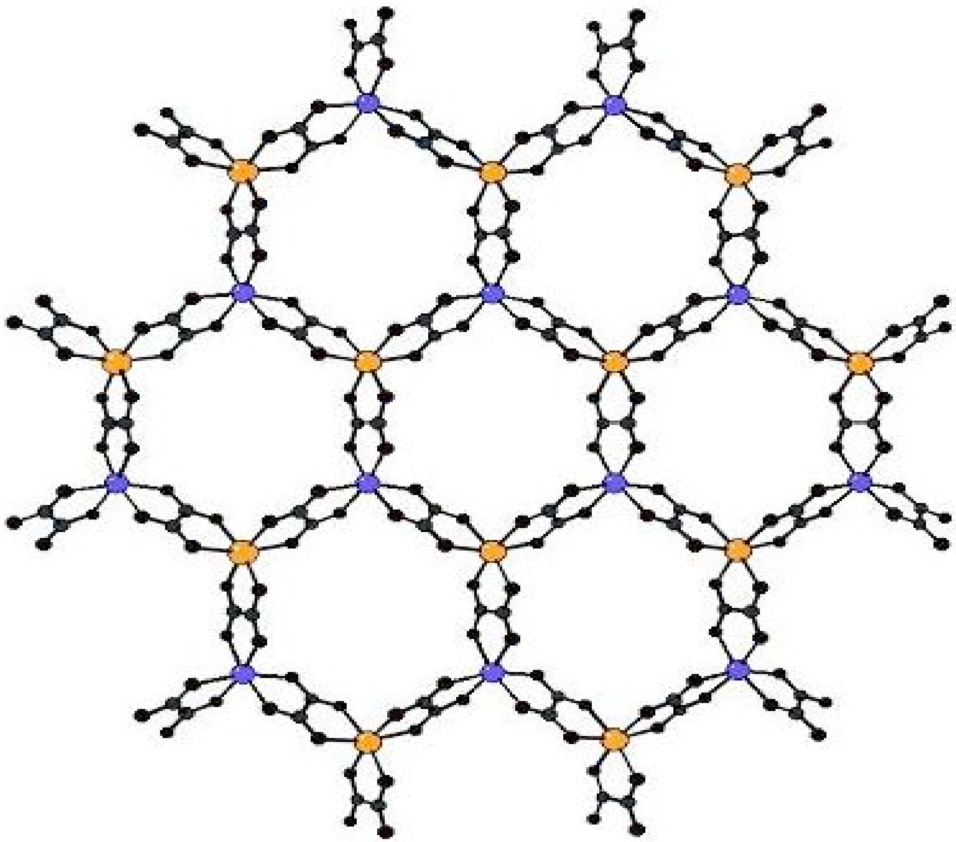




Collaboration with R. Miranda

# BIMETALLIC OXALATE LAYERS

$A[M^{II}M^{III}(ox)_3]$



**2D**