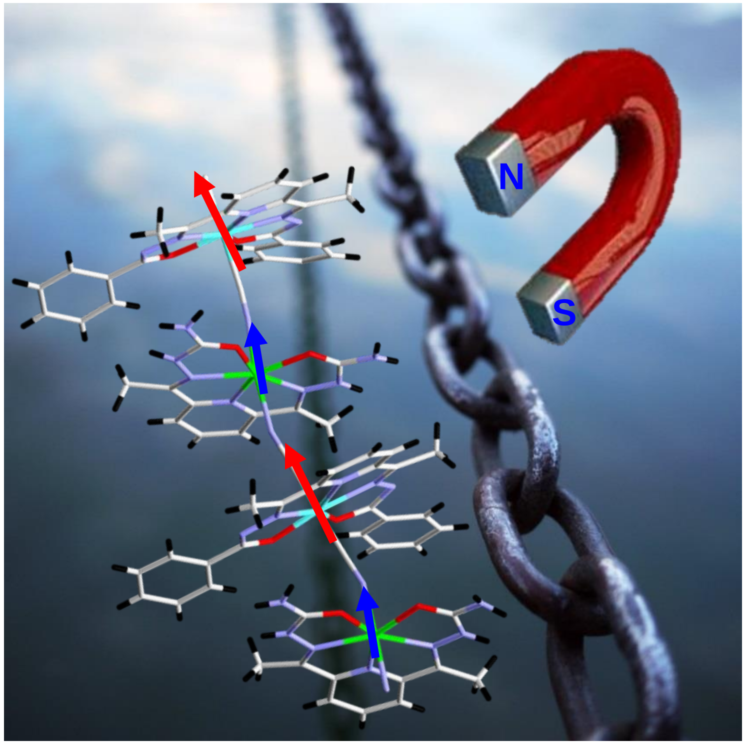
Magnetic anisotropy in heptacoordinated complexes : unique playground for molecular magnetism

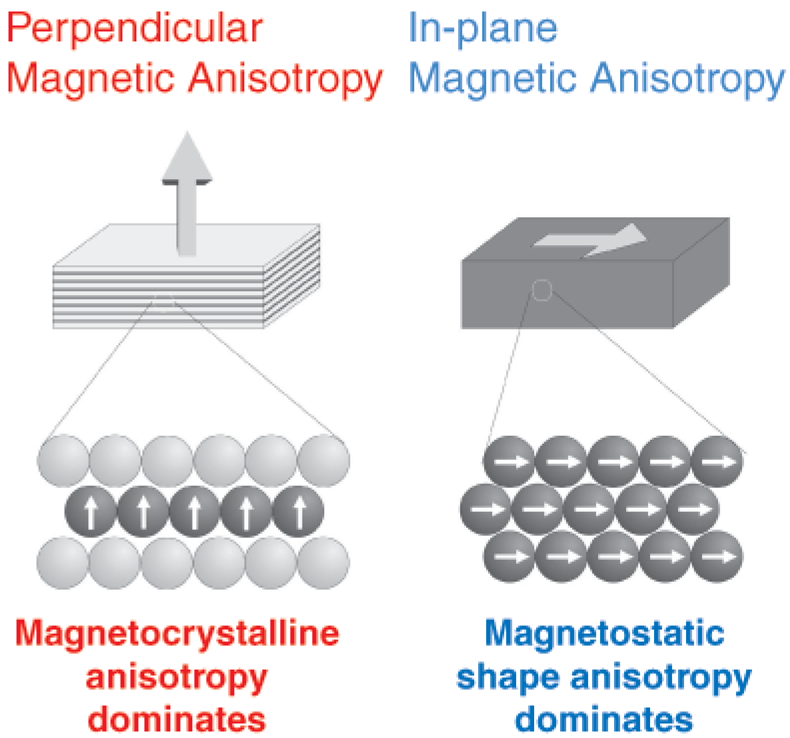


Céline PICHON
LCC-CNRS, Toulouse

Magnetic anisotropy in magnets

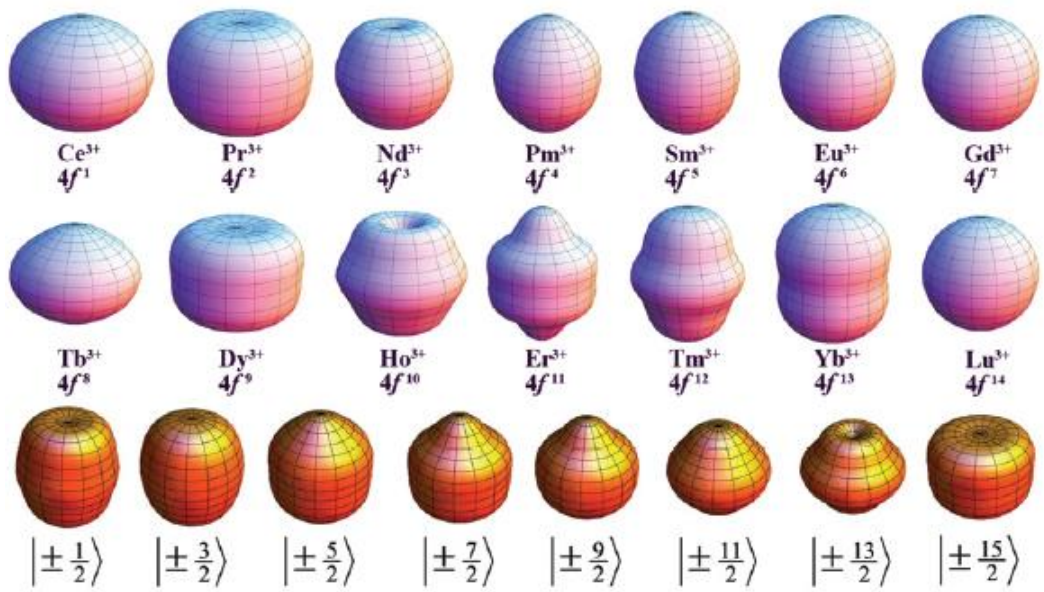
✓ **Necessary in inorganic/bulk magnets and molecule-based ones**

Magnetocrystalline anisotropy linked to local magnetic anisotropy generated by Spin-Orbit Coupling (SOC) and crystalline symmetry



Magnetic anisotropy in molecule-based magnets

- **Case of lanthanide compounds :**



Crystal field parameters matter
Charge effect of point charges (coordinating atoms)

Prolate or oblate type magnetic anisotropy

S.-D. Jiang, S.-X. Qin, *Inorg. Chem. Front.* **2015**, *2*, 613.

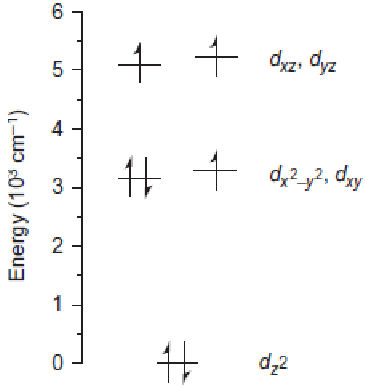
Magnetic anisotropy in molecule-based magnets

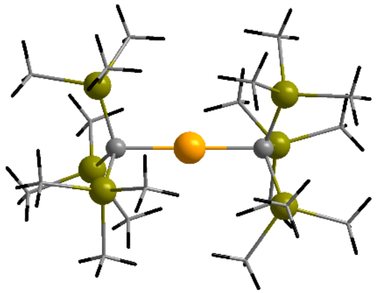
▪ Case of 3d metal-based compounds :

1st order *SOC* generates strong magnetic anisotropy

<u>Requirements:</u> degenerate orbitals => unquenched orbital momentum

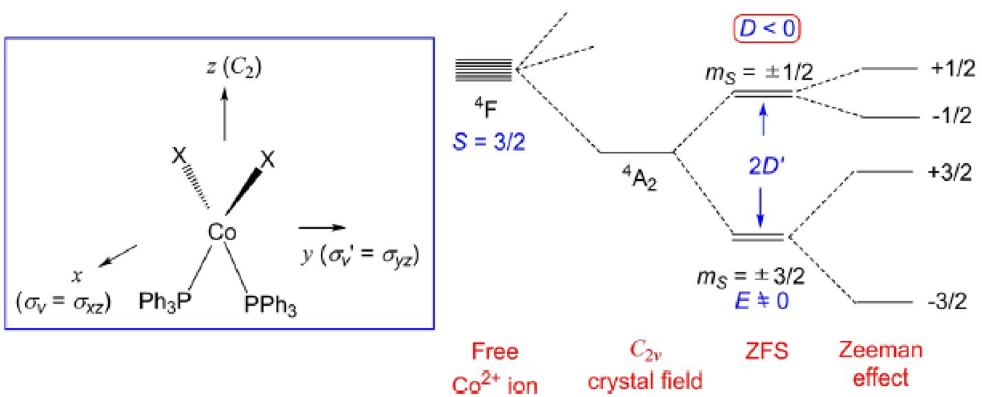
J. M. Zadrozny *et al.*, *Nature Chem.* **2013**, *5*, 577.





$[Fe^I(C(SiMe_3)_3)_2]$

2nd order *SOC* creates Zero-Field Splitting (ZFS) with axial (*D*) and rhombic (*E*) terms



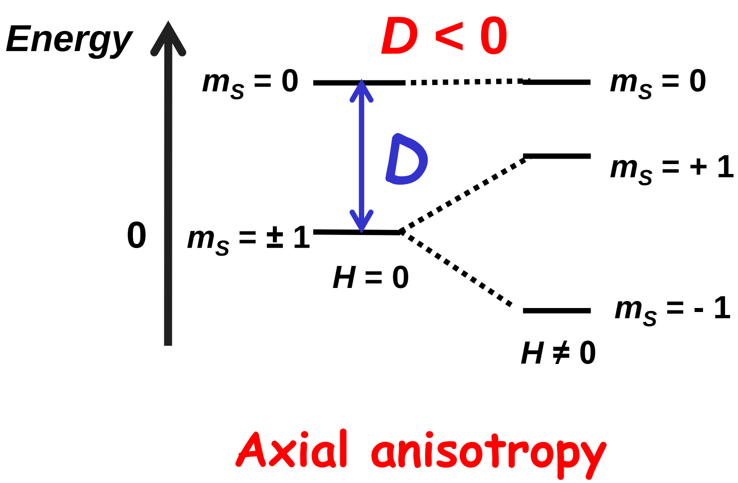
$$\hat{H} = D\hat{S}_z^{\,2} + E(\hat{S}_x^{\,2} - \hat{S}_y^{\,2})$$

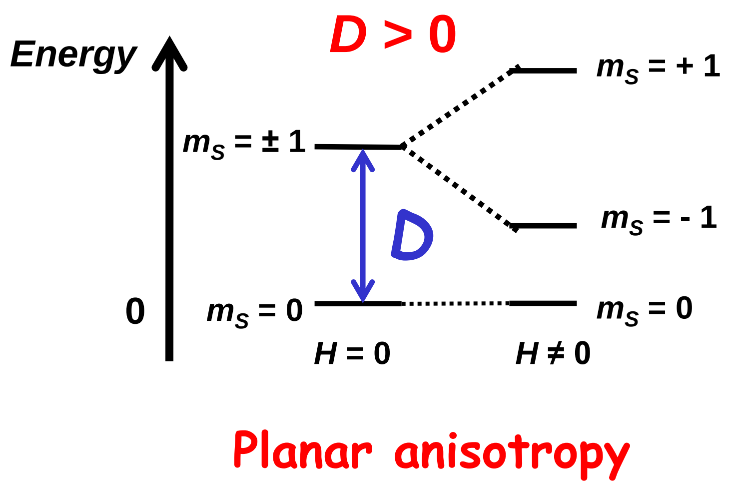
A. N. Bone *et al.*, *Chem. Eur. J.* **2021**, *27*, 11110.

Magnetic anisotropy in 3d complexes

- **Zero-field splitting :**

Example with S = 1 :



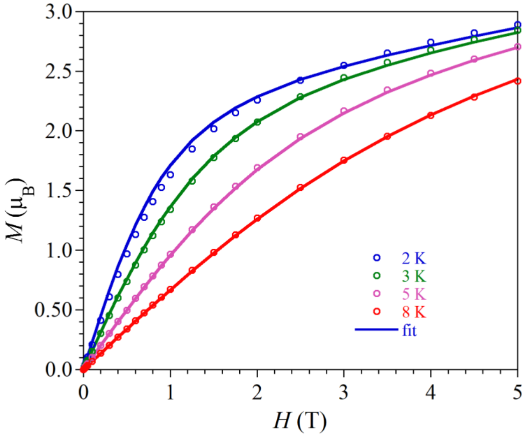


$$\hat{H} = \mu_B B \bullet [g] \bullet \hat{S} + D\hat{S}_z^2$$

$|D| > 3E$ and $E > 0$ by convention (here $E = 0$)

$D < 0$ stabilizes the highest spin value as the ground state

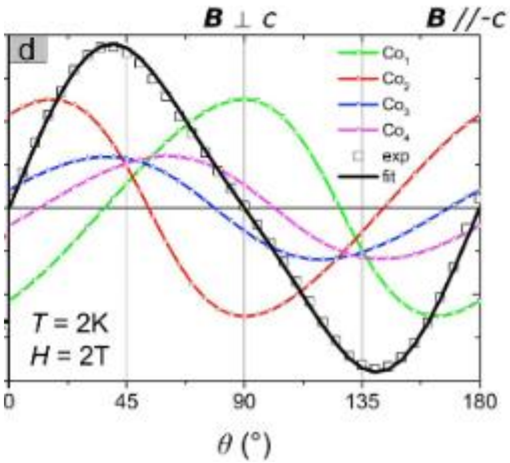
- **Magnetic measurements:**
  - ✓ **Bulk samples**



Routine measurements (bulk)
Mostly adapted to mononuclear complexes

Not sensitive to sign of D ($E/D \approx 1/3$)
Average estimation (best to confirm with other techniques or calculations)

  - ✓ **Single crystal: cantilever Torque magnetometry**



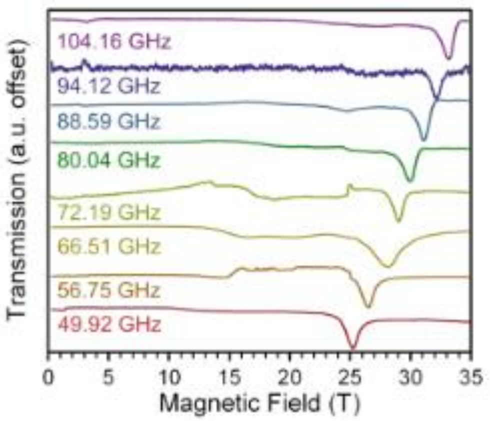
Local anisotropy measured
Orientation *vs.* crystallographic axes

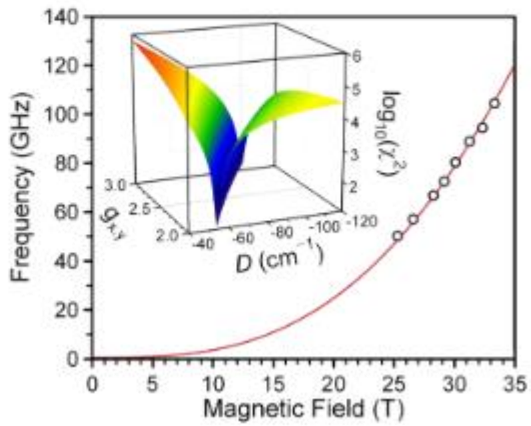
Big crystals needed

B. Cahier *et al.*, *Chem. Eur. J.* **2017**, *23*, 3648.

Methods to evaluate magnetic anisotropy

- **HF-EPR:**



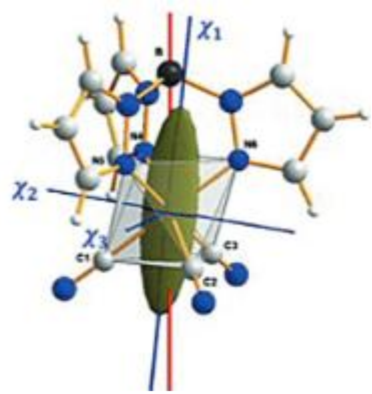


Very precise

Sensitive to some ions
Limited to $D < 80\ cm^{-1}$ (100 GHz)

E. Suturina *et al.*, *Inorg. Chem.* **2017**, *56*, 3102.

- **Polarized neutrons scattering:**



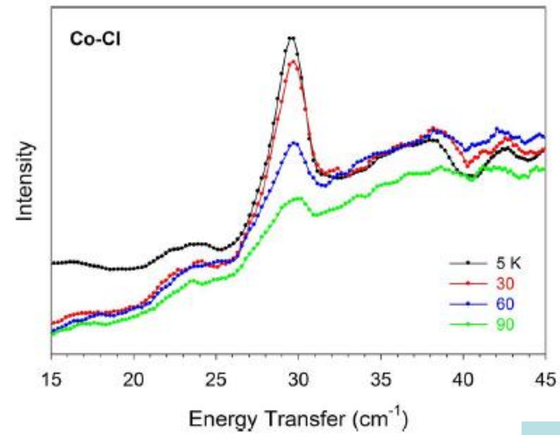
Local anisotropy measured
Orientation *vs.* crystallographic axes

Big crystals needed

D. Luneau, B. Gillon, *Magnetochemistry* **2021**, *7*, 158.

Methods to evaluate magnetic anisotropy

- **Inelastic Neutron Scattering (INS):**

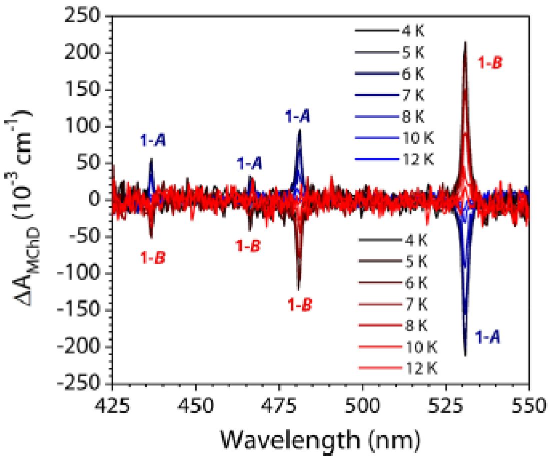


Estimations of *D*

Large amount of samples

A. N. Bone *et al.*, *Chem. Eur. J.* **2021**, *27*, 11110.

- **Magnetic Circular Dichroism:**



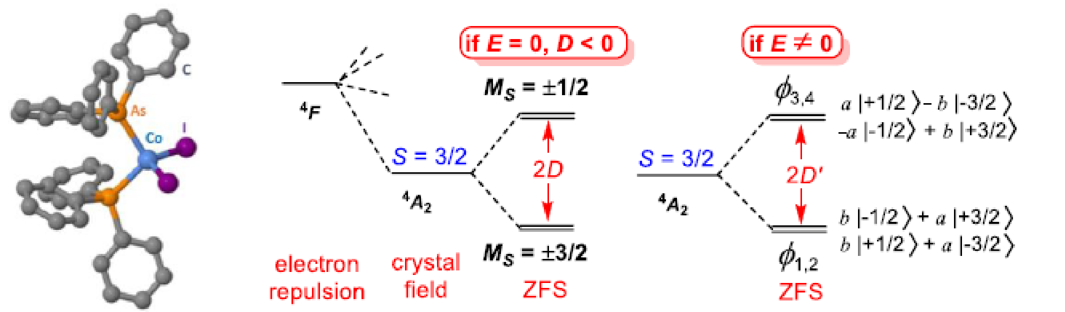
Local anisotropy measured
Orientation vs. crystallographic axes

Big crystals needed
Chiral molecules only

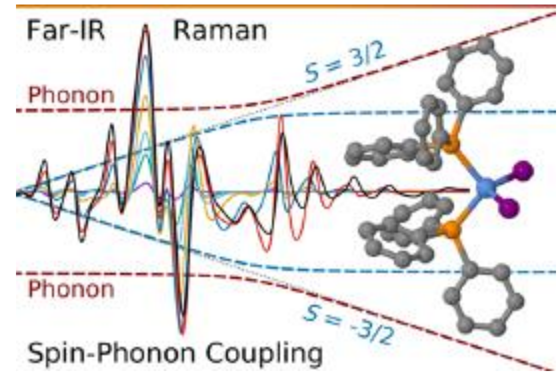
M. Atzori *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 13908.

Methods to evaluate magnetic anisotropy

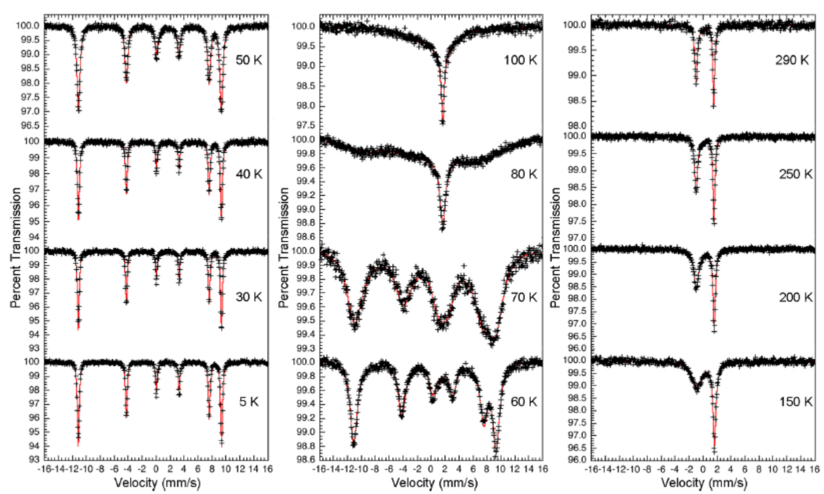
- **Far infrared:**



D. H. Moseley *et al.*, *Inorg. Chem.* **2022**, *61*, 17123.



- **Mössbauer:**



Variable temperature measurements

Metal specific

J. M. Zadrozny *et al.*, *Inorg. Chem.* **2013**, *52*, 13123.

Magnetic anisotropy & SMMs

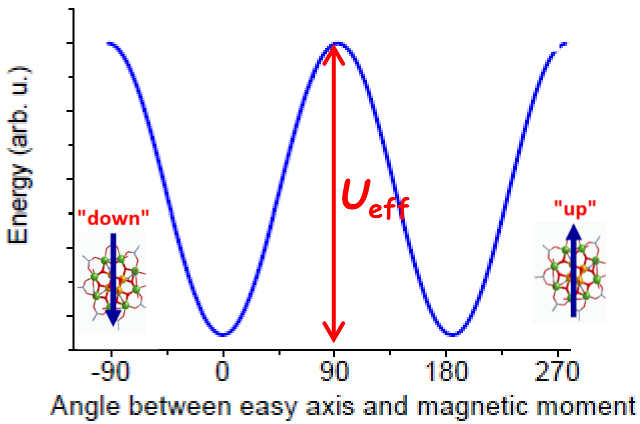
- **Case of SMMs :**

$$U_{eff} = D \cdot S^2$$

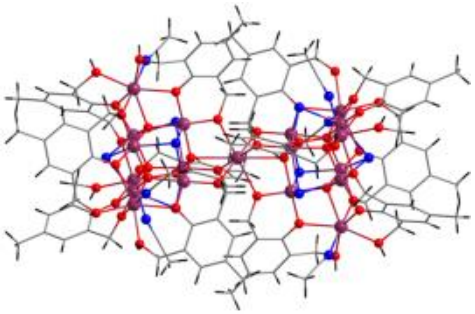
D appears to be the most important parameter as $D \approx cte/S^2$

→ $U_{eff} \approx D$

O. Waldmann, *Inorg. Chem.* **2007**, *45*, 10035.



In polynuclear systems, difficulty to control the alignement of magnetic anisotropy



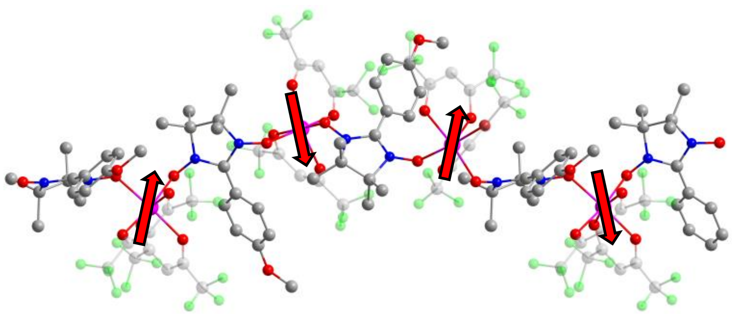
$[Mn^{III}_{12}Mn^{II}_7(\mu_4\text{-}O)_8(\mu_3,\eta_1\text{-}N_3)_8(HL)_{12}(MeCN)_6]^{2+}$
$S = 83/2$

A. M. Ako *et al.*, *Angew. Chem. Int. Ed.* **2006**, *45*, 4926.

Magnetic anisotropy & SMMs/SCMs

- **Case of SCMs :**

$$U_{eff} = D_{AB} \cdot S_{AB}^2 + nJ(S_A \cdot S_B)$$



$[Co^{II}(hfac)_2(NITPhOMe)]$
U_{eff}/k_B = 154 K

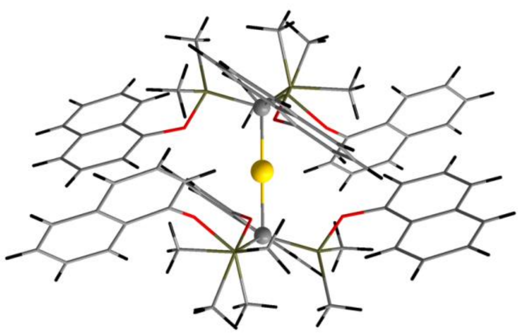
A. Caneschi *et al.*, *Angew. Chem. Int. Ed.* **2001**, *40*, 1760.

Strong interaction (J) through organic radical

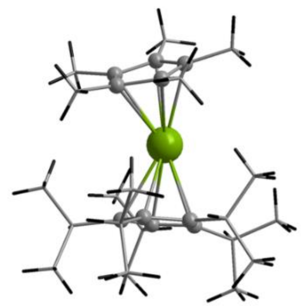
Anisotropy brought by Co^{II} ions
Importance of relative orientation of the anisotropic axes

C. Coulon *et al.*, *Struct. Bond.* **2015**, *164*, 143.

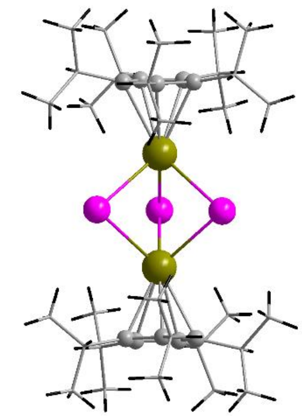
SMMs and SCMs : where are we?



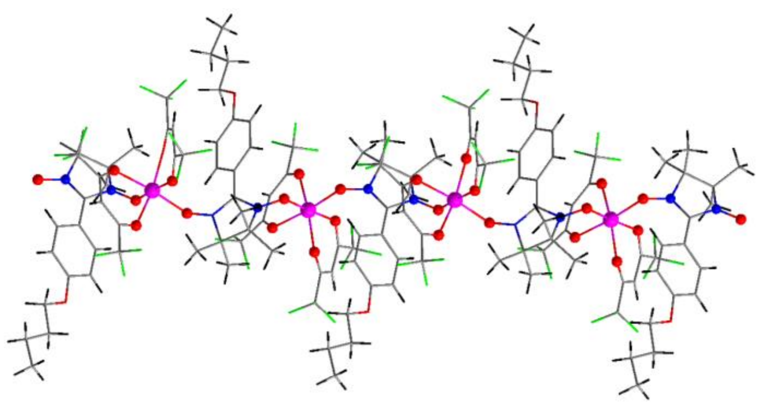
[Co^{II}((C($SiMe_2$ONaph)$_3$)$_2$] (*J* = 9/2)
U_{eff}/k_B = 648 K (SMM)



[(Cp^{iPr5})Dy^{II}(Cp*)]$^+$
U_{eff}/k_B = 2219 K (SMM)



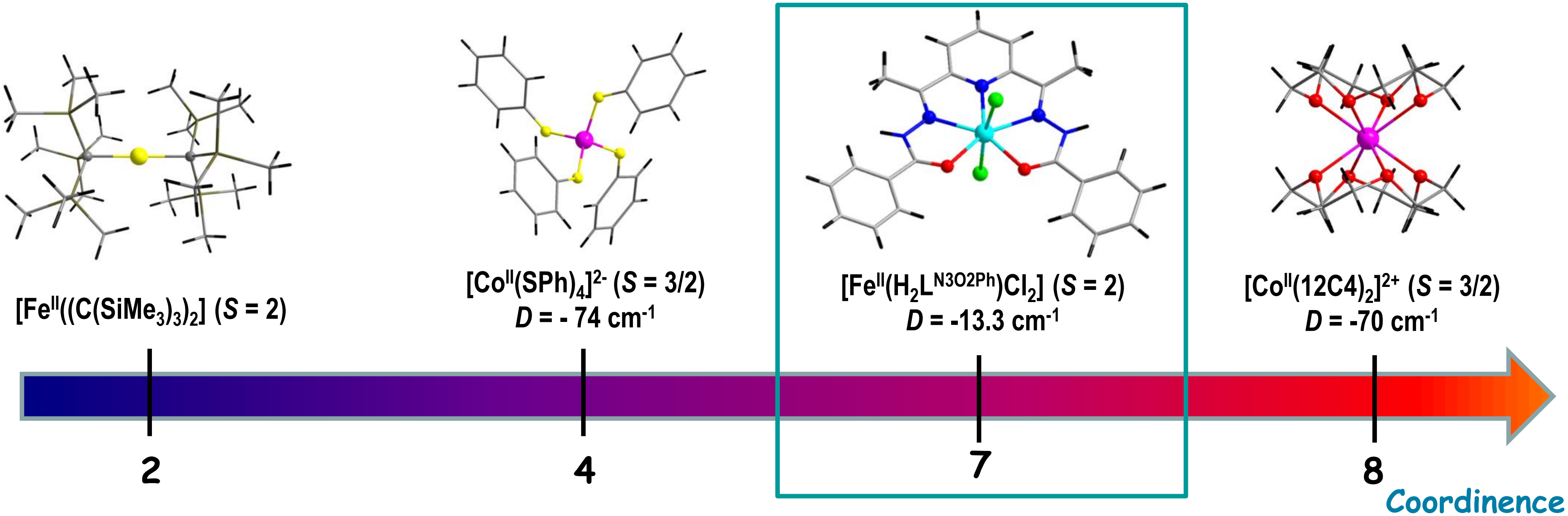
[(Cp^{iPr5})$_2Dy^{II}Dy^{III}I_3$]
U_{eff}/k_B = 2348 K (SMM)



[Co^{II}(hfac)$_2$(NaphNN)]
U_{eff}/k_B = 398 K

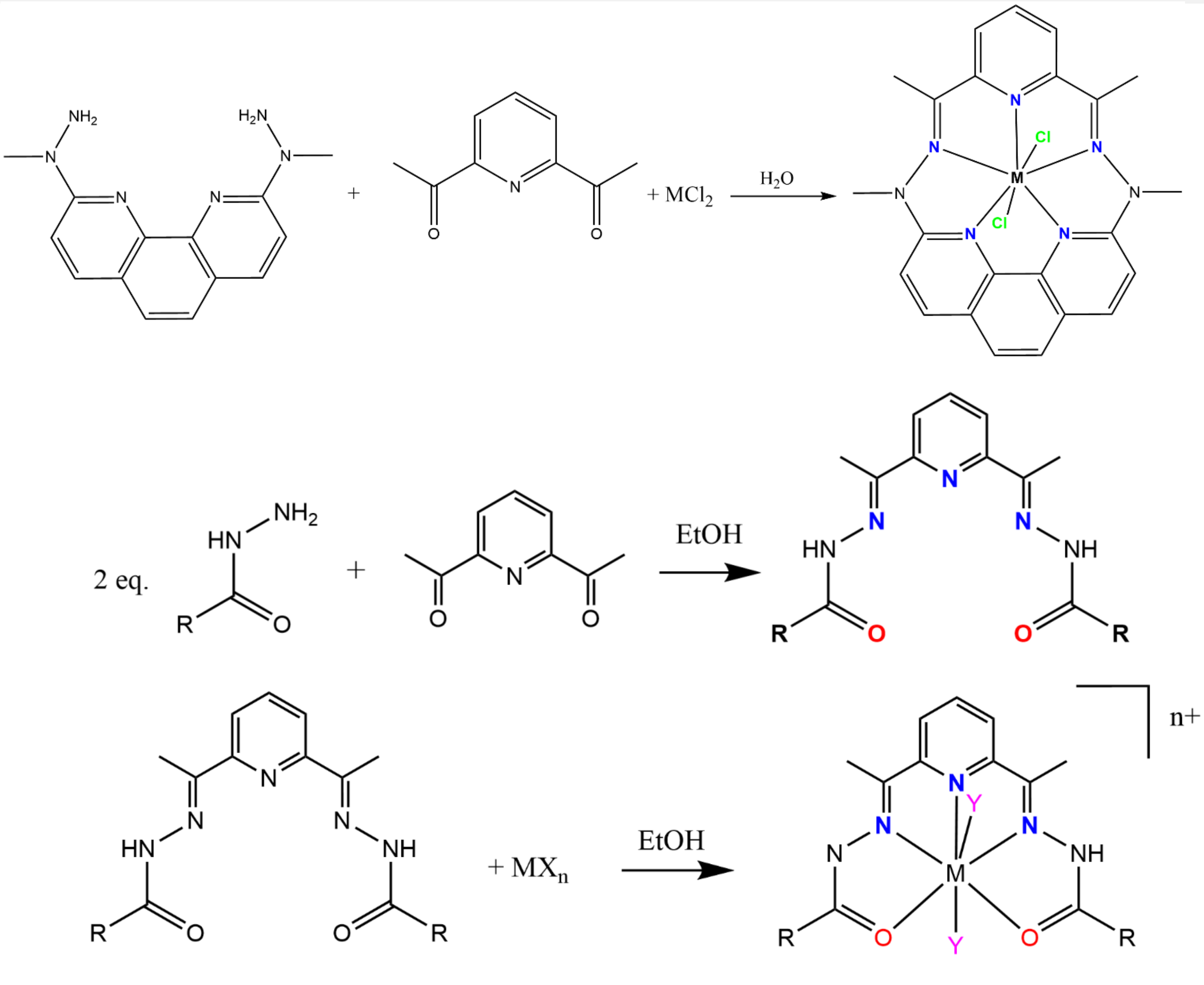
R. A. Allão Cassaro *et al.*, *Inorg. Chem.* **2015**, *54*, 9381; C. A. Gould *et al.*, *Science* **2022**, *375*, 198; V. Vieru *et al.*, *Angew. Chem. Int. Ed.* **2023**, e202303146.

Magnetic anisotropy & SMMs/SCMs



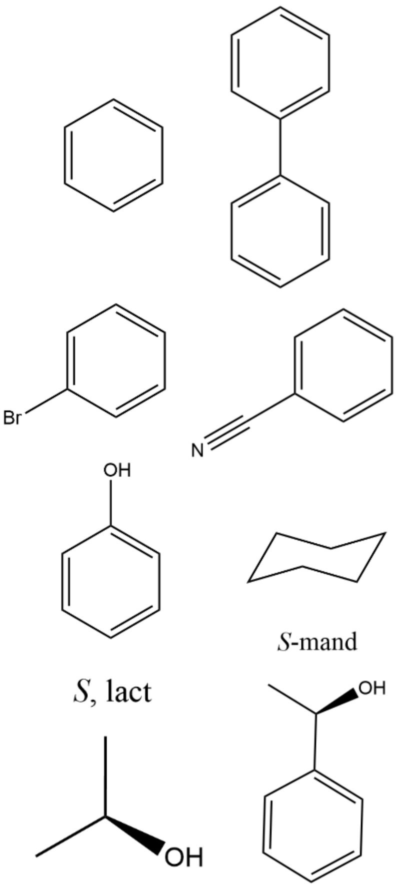
Struct. Bond. **2015**, *164*, 143; *Inorg. Chem.* **2015**, *54*, 9381; *Science* **2018**, *362*, 1378. *Science* **2018**, *362*, 1400.

Syntheses of heptacoordinated complexes



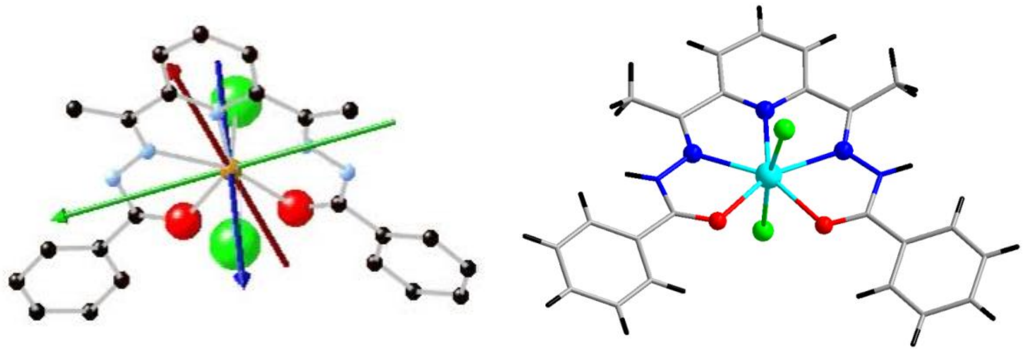
Y = solvant, anions

R = NH_2, NMe_2

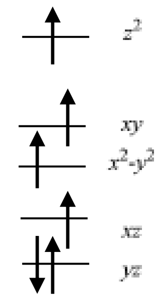


C. W. G. Ansell *et al.*, *J. Chem. Soc., Chem. Commun.* **1982**, 546.
T. J. Giordano *et al.*, *Inorg. Chem.* **1979**, *18*, 2446.

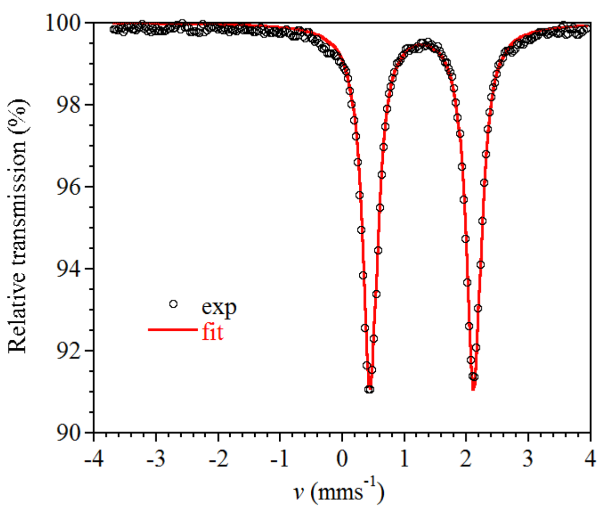
3d mononuclear complexes and unusual coordination



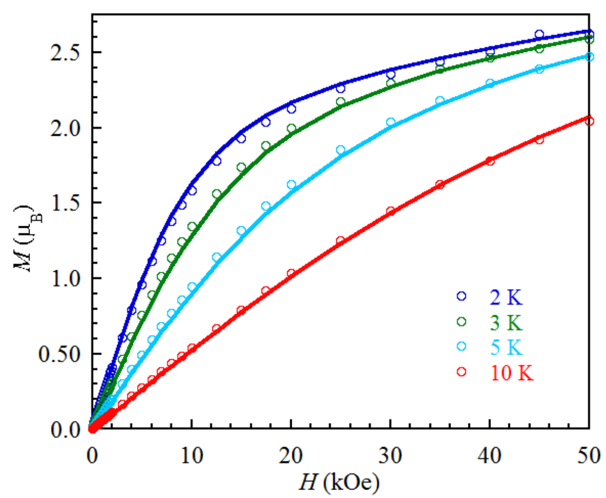
$[Fe^{II}(H_2L^{N3O2Ph})Cl_2]$
$S = 2$



D_{5h}



^{57}Fe Mössbauer

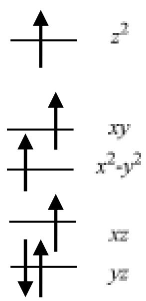


D = -13.3 cm^{-1},
$|E|$ = 0.02 cm^{-1} and g = 2.31

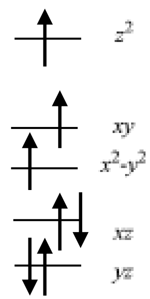
A. K. Bar *et al.*, *Chem. Commun.* **2015**, *51*, 3616;
A. K. Bar *et al.*, *Chem. Eur. J.* **2017**, *23*, 4380.

Interest of heptacoordinated complexes

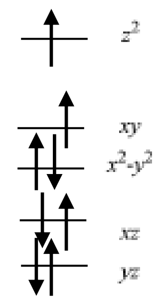
- **Advantages:**
  - ✓ Local magnetic anisotropy for given electronic configuration



Fe^{II} (D < 0)

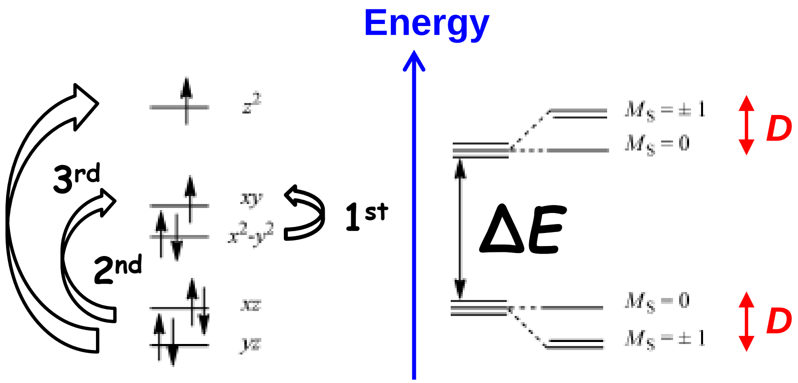


Co^{II} (D > 0)



Ni^{II} (D < 0)

Point group: D_{5h}



Case of Ni^{II} ($3d^8$)

$$\hat{H}_{ZFS} = D \cdot \hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$$

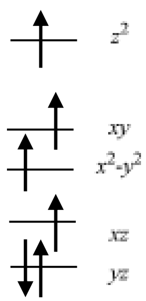
$$D \approx \lambda^2/\Delta E$$

λ = spin-orbit coupling constant,
ΔE = energy splitting between ground and excited states

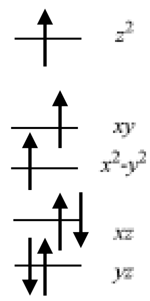
R. Ruamps *et al.*, *Chem. Eur. J.* **2013**, *19*, 950.

Interest of heptacoordinated complexes

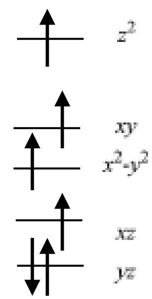
- **Advantages:**
  - ✓ **Local magnetic anisotropy for given electronic configurations**



Fe^{II} (D < 0)

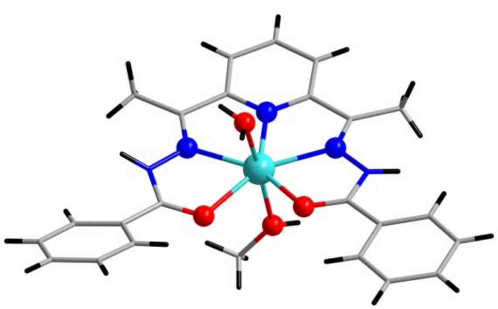


Co^{II} (D > 0)



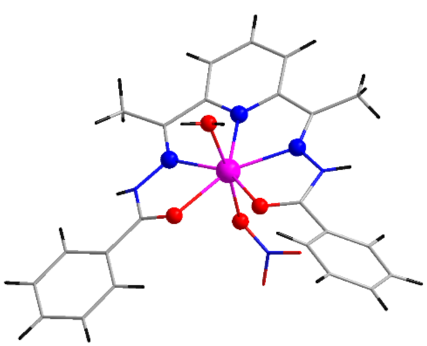
Ni^{II} (D < 0)

Point group: D_{5h}



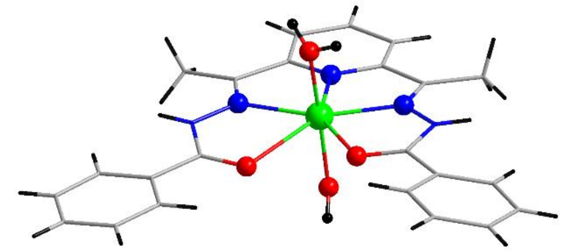
$[Fe^{II}(H_2L^{N3O2Ph})(MeOH)(H_2O)]^{2+}$
(S = 2)

D = -4 cm^{-1}, $|E/D|$ = 0, g = 2.28



$[Co^{II}(H_2L^{N3O2Ph2})(NO_3)(H_2O)]^{+}$
(S = 3/2)

D = +31 cm^{-1}, $|E/D|$ = 0, g = 2.26



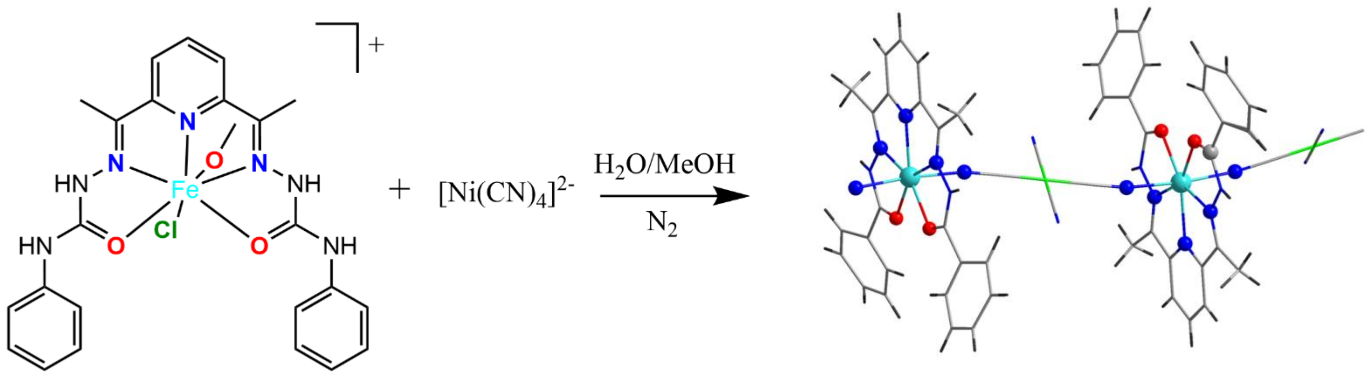
$[Ni^{II}(H_2L^{N3O2Ph2})(H_2O)_2]^{2+}$
(S = 1)

D = -14 cm^{-1}, $|E/D|$ = 0.11, g = 2.23

R. Ruamps *et al.*, *Chem. Eur. J.* **2013**, *19*, 950.

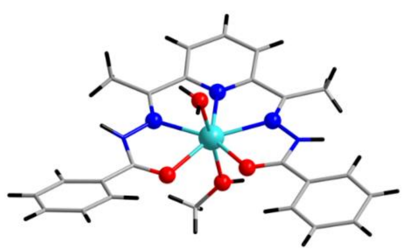
Interest of heptacoordinated complexes

- **Advantages:**
  - ✓ **Modulable and stable geometry: preparation of complexes with different groups in axial positions**

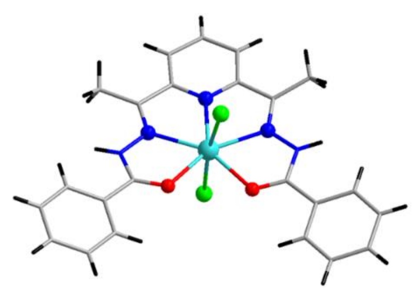


$[Fe^{II}(H_2L^{N3O2Ph})Ni(CN)_4]$

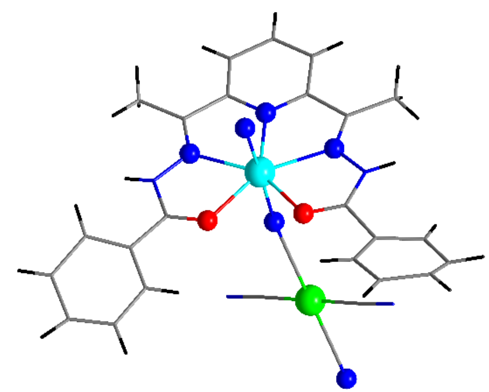
  - ✓ **Modulation of *D* through ligand fields in axial positions**



D = $-4\ cm^{-1}$



D = $-13.3\ cm^{-1}$

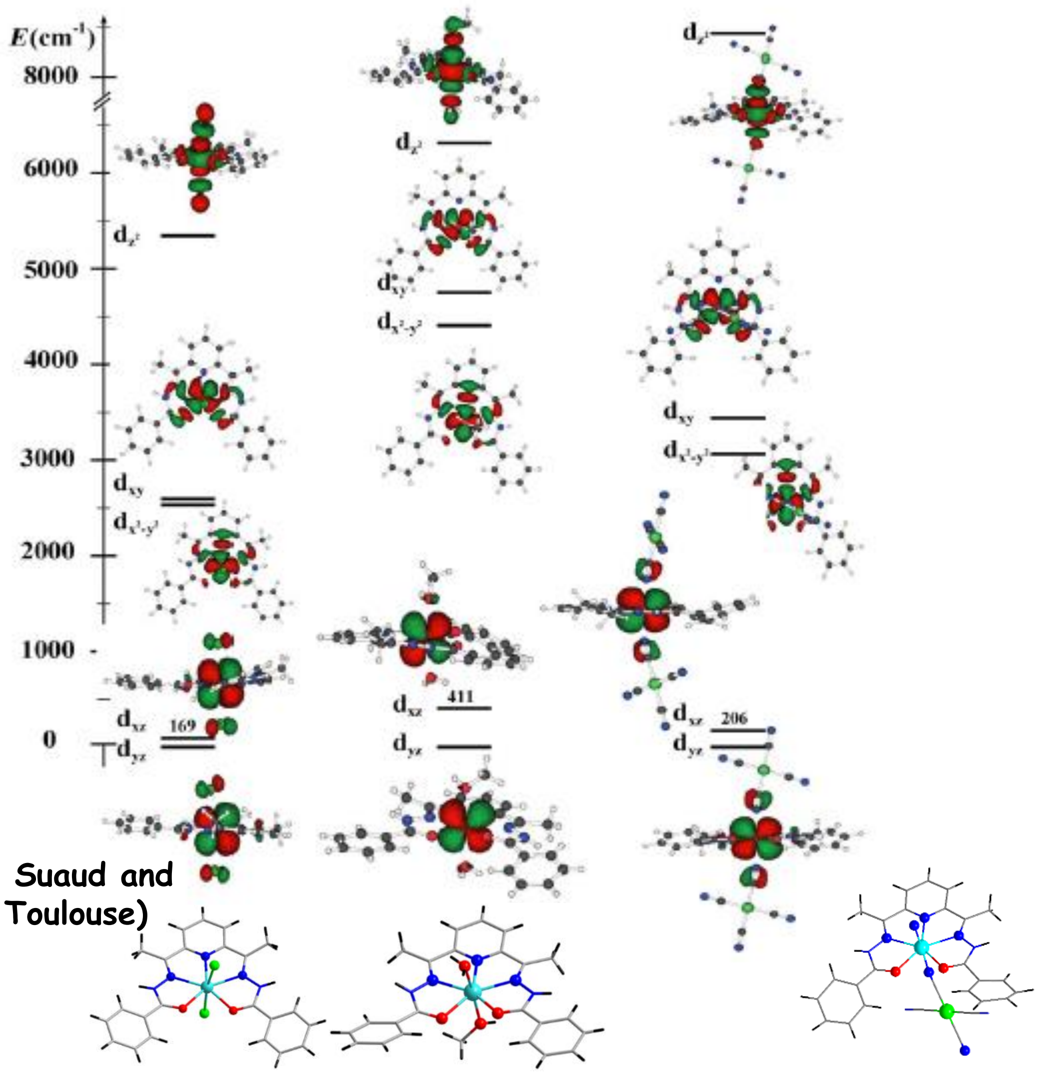


D = $-16\ cm^{-1}$

A. K. Bar *et al.*, *Chem. Commun.* **2015**, *51*, 3616;
A. K. Bar *et al.*, *Chem. Eur. J.* **2017**, *23*, 4380.

Impact of axial ligand field on anisotropy

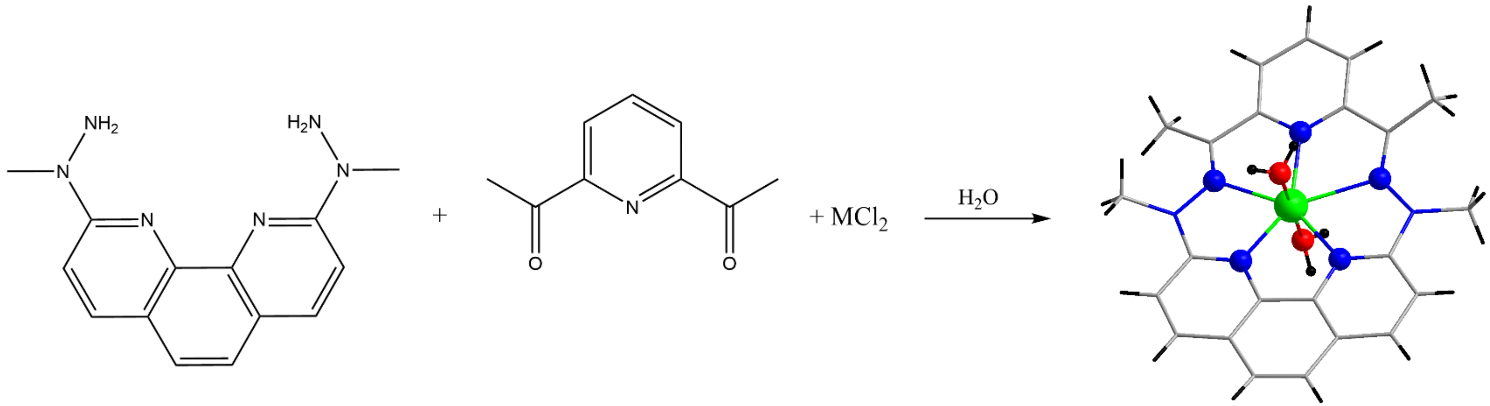
- *Ab-initio* calculations:



Calculations made by Dr. Nicolas Suaud and Prof. Nathalie Guihéry (LCPQ, Toulouse)

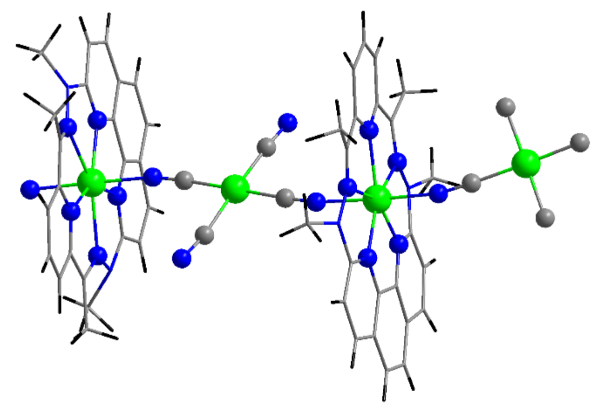
A. K. Bar *et al.*, *Chem. Eur. J.* **2017**, *23*, 4380.

Impact of axial ligand field on anisotropy



$[Ni^{II}(L^{N5phen})(H_2O)_2]^{2+}$
D = -11 cm^{-1}, E = 1.5 cm^{-1}, g = 2.11

More symmetric equatorial plane



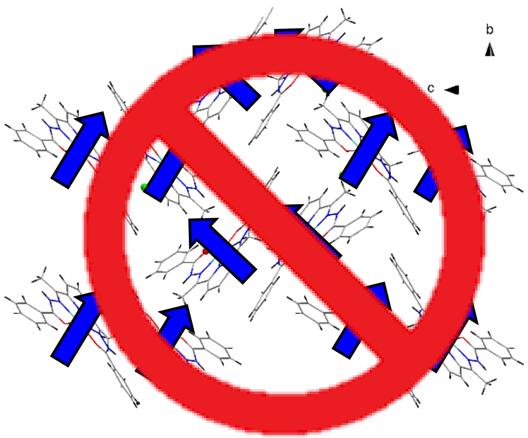
$[Ni^{II}(L^{N5phen})Ni(CN)_4]$
D = -14.4 cm^{-1}, E = 1.9 cm^{-1}, g = 2.13

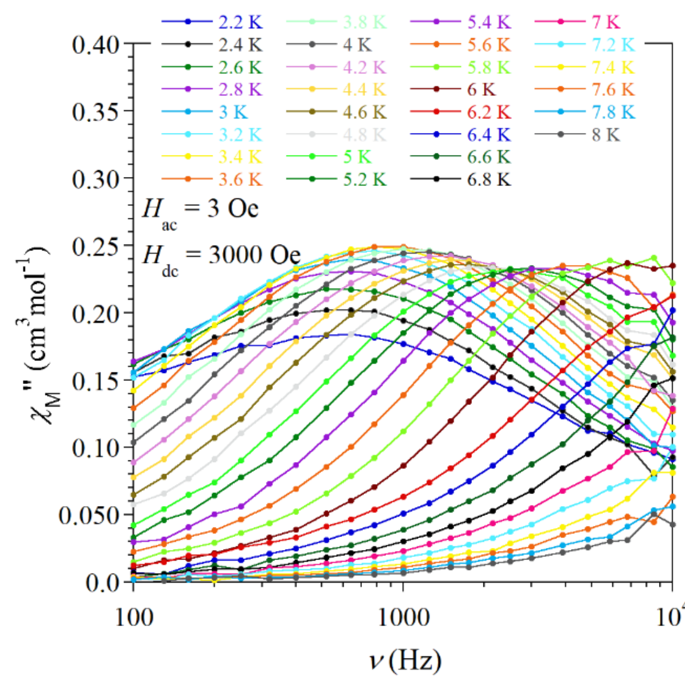
K. Bretosh *et al.*, Inorg. *Chem. Front.* **2020**, *7*, 1503.

Impact of crystal symmetry

- **Others important parameters to control:**

✓ **Mononuclear systems: Syntheses of molecular systems with strong local anisotropy oriented in a single direction in the crystals**



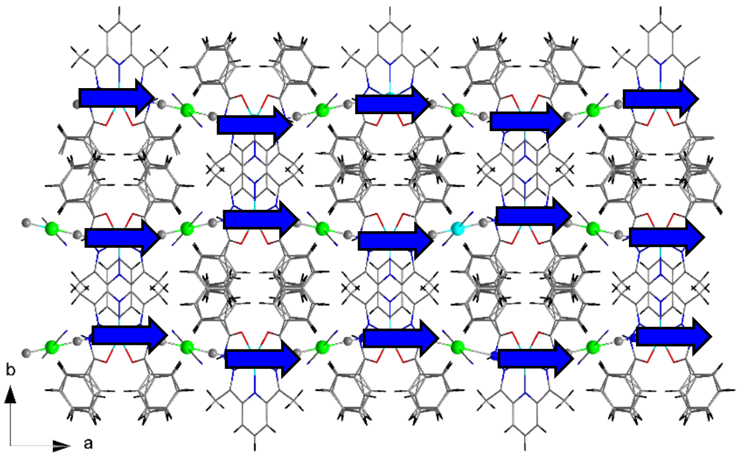


Presence of additional relaxation processes

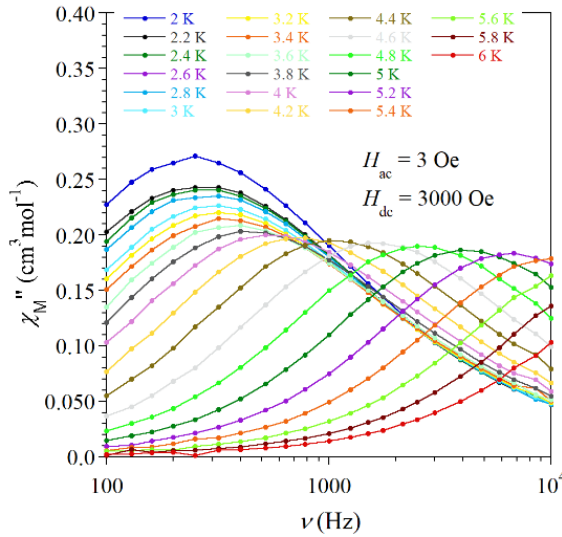
A. K. Bar *et al.*, *Chem. Commun.* **2015**, *51*, 3616.

LCC

Impact of crystal symmetry



Cancellation of tranverse relaxation modes



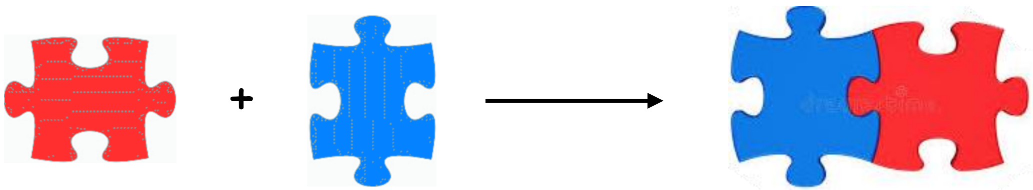
- ✓ **Polynuclear systems: Syntheses of molecular systems with parallel local anisotropy between metal centers and molecules/chains for global anisotropy in the crystals plus strong exchange interactions (for SCMs mostly)**

Difficult to control => chemical control with appropriate ingredients

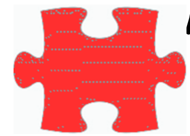
A. K. Bar *et al.*, *Chem. Commun.* **2015**, *51*, 3616.

Synthetic approach

- **Heterometallic SMMs:**

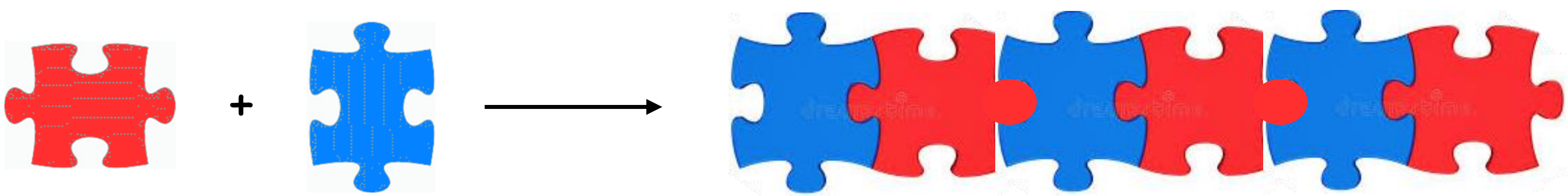


Anisotropic complex

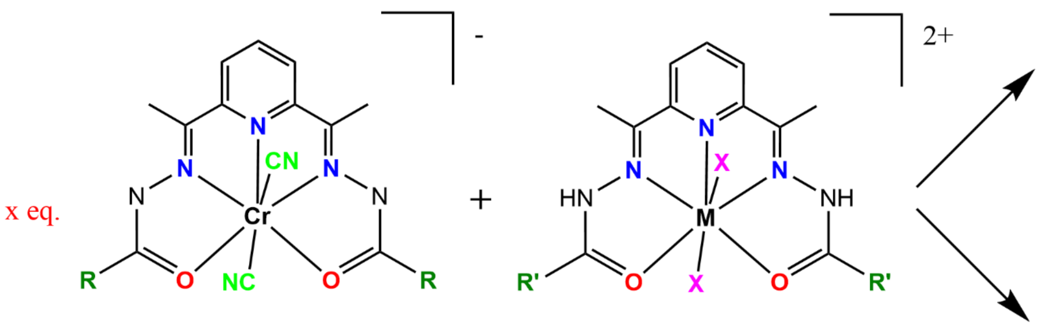


Magnetic linker (isotropic or anisotropic)

- **Heterometallic SCMs:**



- **Building blocks used:**



$[Cr^{III}(L^{N3O2R})(CN)_2]^-$ + $[M^{II}(H_2L^{N3O2R'})X_2]^{2+}$

X = solvant

x = 1

Cationic systems (discrete or 1D)

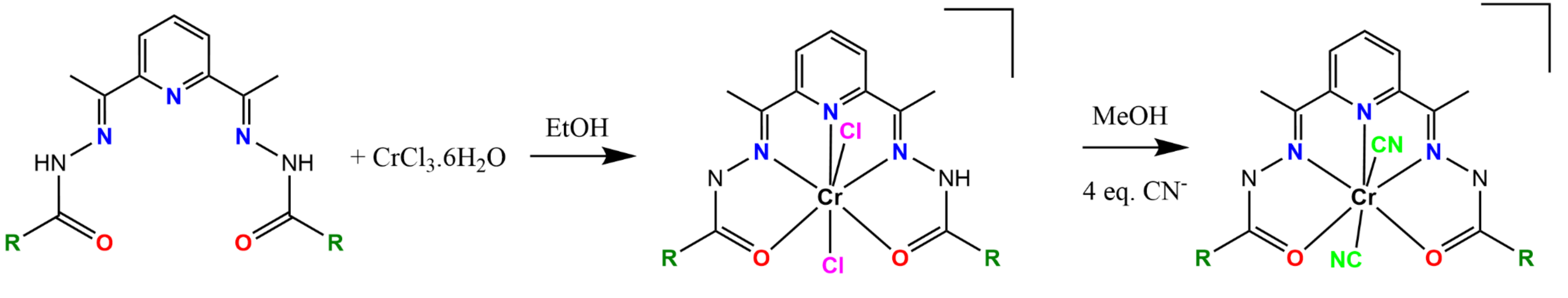
$[Cr^{III}(L^{N3O2R})(CN)_2M^{II}(L^{N3O2R'})]^+$

x = 2

Neutral systems

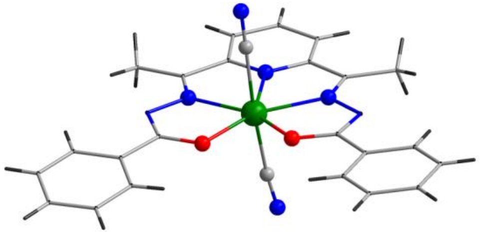
$[\{Cr^{III}(L^{N3O2R})(CN)_2\}_2M^{II}(L^{N3O2R'})]$

Access to heptacoordinated metalloligands



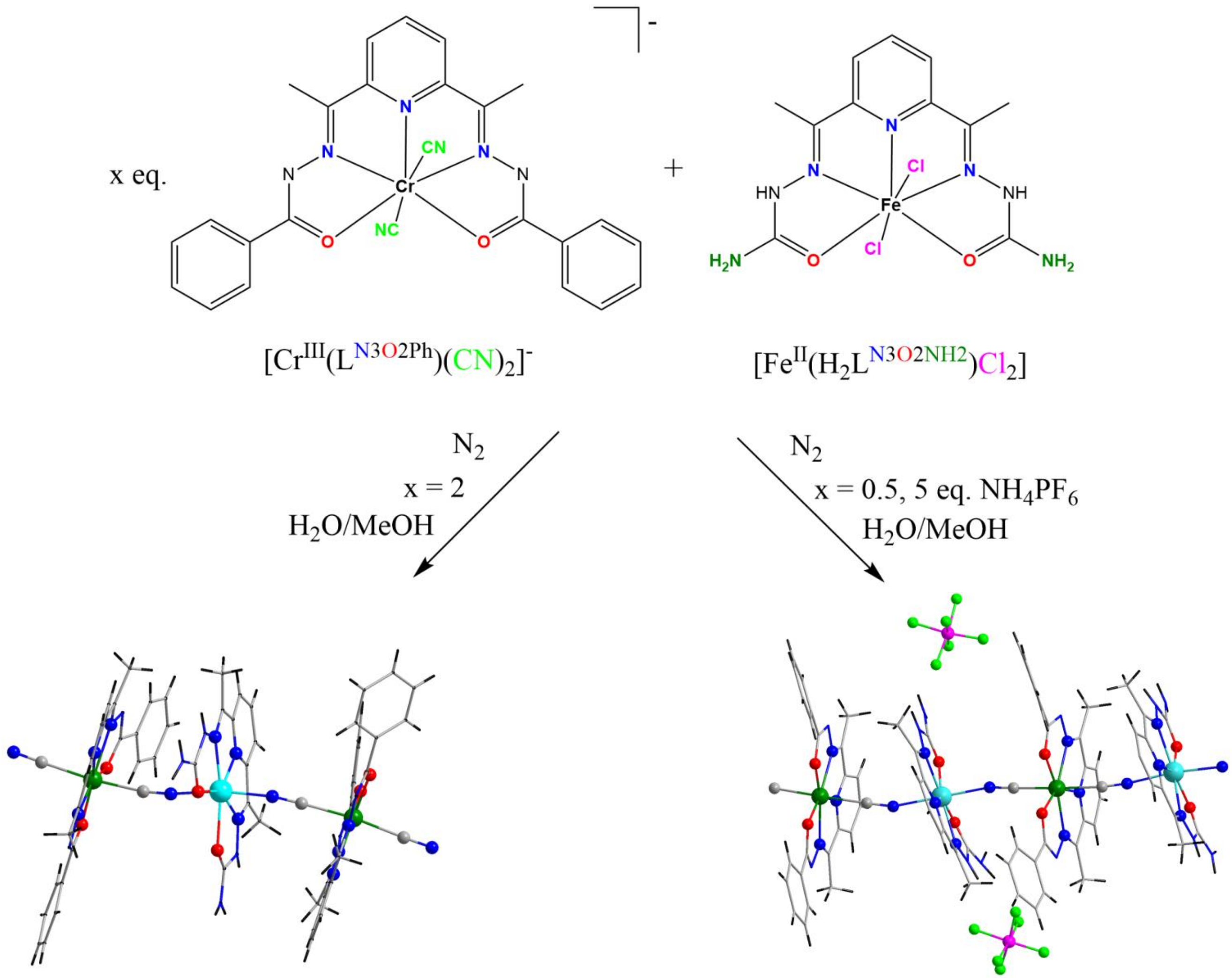
H_2L^{N3O2R} $[Cr^{III}(HL^{N3O2R})Cl_2]$ $[Cr^{III}(L^{N3O2R})(CN)_2]^-$

✓ **Example of structure with R = Ph**



$[Cr(L^{N3O2Ph})(CN)_2]^-$

Effect of stoechiometry

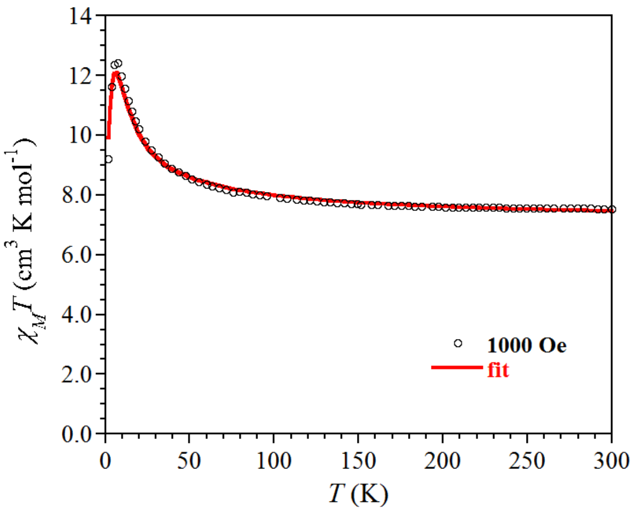


$[\{Cr(L^{N3O2Ph})(CN)_2\}_2Fe(H_2L^{N3O2NH2})]$

$[Cr(L^{N3O2Ph})(CN)_2Fe(H_2L^{N3O2NH2})](PF_6)$

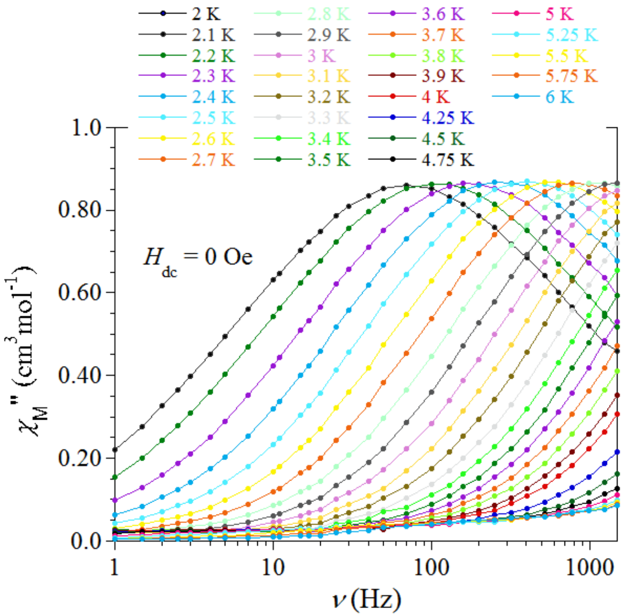
C. Pichon *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 7698.

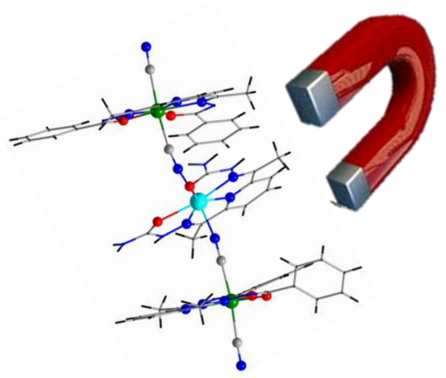
Magnetic properties of the trinuclear



$$\hat{H} = -J(\hat{S}_{Cr1}.\hat{S}_{Fe} + \hat{S}_{Cr2}.\hat{S}_{Fe}) + DS^2_{Fe}$$

J = 2.05 ± 0.01 cm^{-1}, D_{Fe} = -25 ± 0.01 cm^{-1}, zj' = -0.015 ± 0.001 cm^{-1} and g_{Fe} = 2.15 ± 0.03





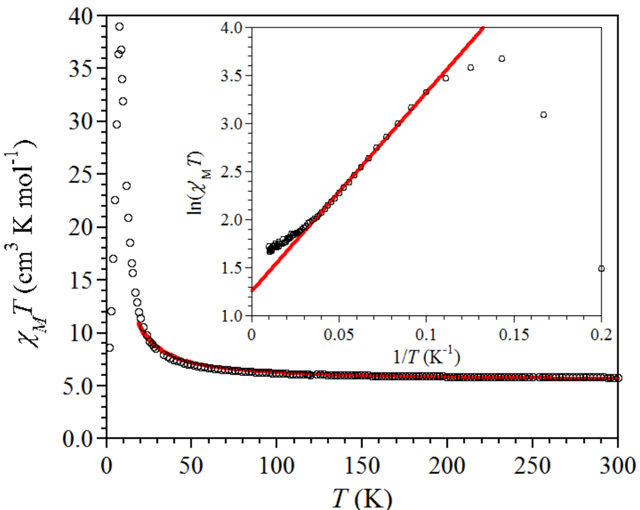
SMM

U_{eff}/k_B = 22 K and τ_0 = 3.8 10^{-8} s

Arrhenius law: $\tau = \tau_0 \exp(-U_{eff}/k_B T)$

C. Pichon *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 7698.

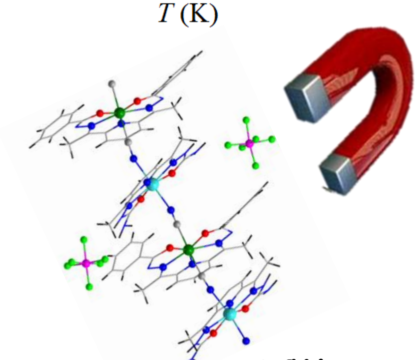
Magnetic properties of the chain

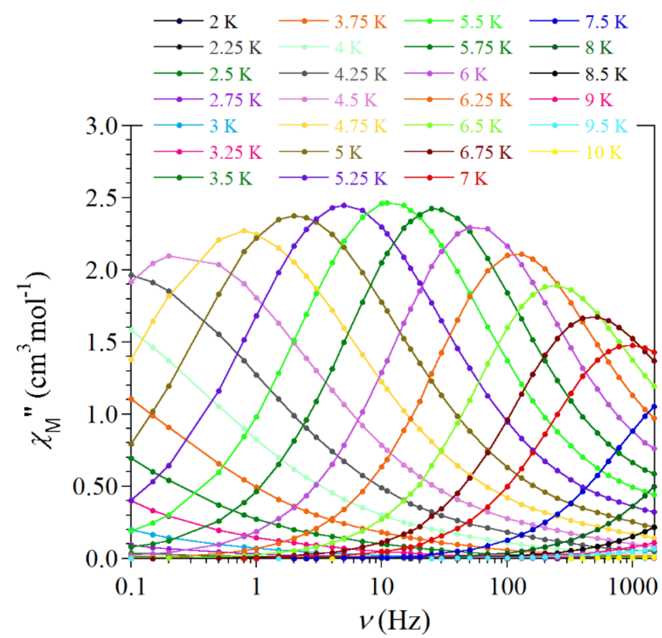


$$\hat{H} = -J \sum_i (\hat{S}_{Cr,i} . \hat{S}_{Fe,i})$$

J = 2.68 ± 0.04 cm^{-1} and g_{Fe} = 2.10 ± 0.04

1D behavior with Δ_ξ = 20.6 K (correlation length) between 10 and 30 K





SCM

$\Delta_{\tau 1}/k_B$ = 113 K and τ_0 = 1.62 10^{-11} s

$\Delta_{\tau 2}/k_B$ = 94 K and τ_0 = 5.7 10^{-10} s

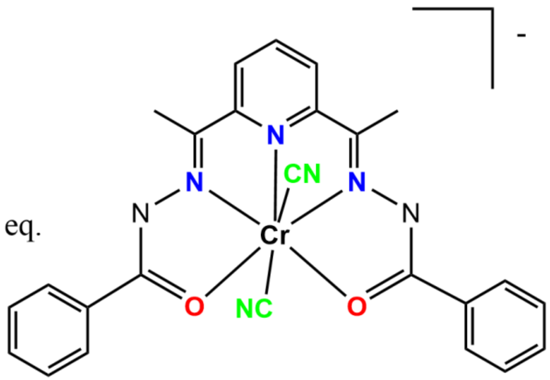
Arrhenius law : $\tau = \tau_0 \exp(-U_{eff}/k_B T)$

Magnetic correlation and spin alignment (local magnetic axes) along the chain boost SCM properties.

C. Pichon *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 7698.

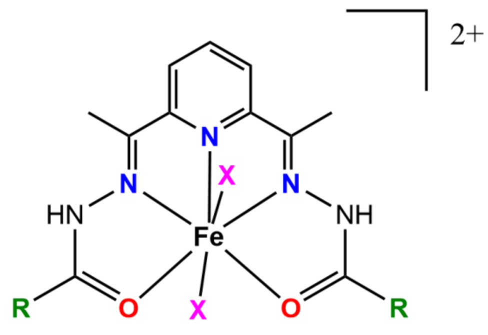
Influence of R groups

2 eq.



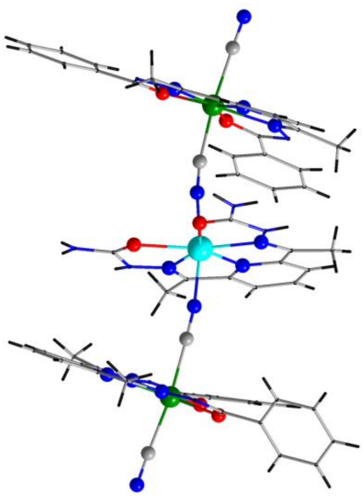
$[Cr^{III}(L^{N3O2Ph})(CN)_2]^-$

+

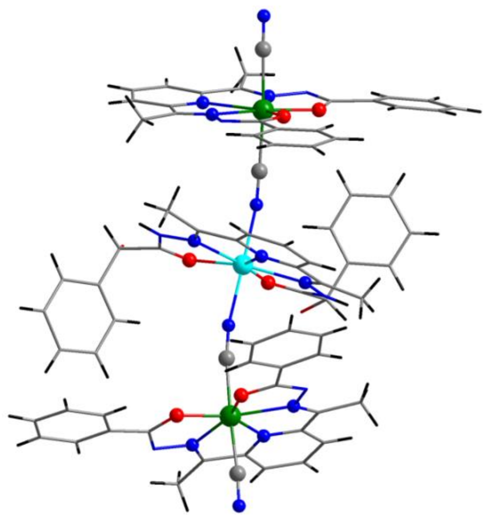


$[Fe^{II}(H_2L^{N3O2R})X_2]^{2+}$

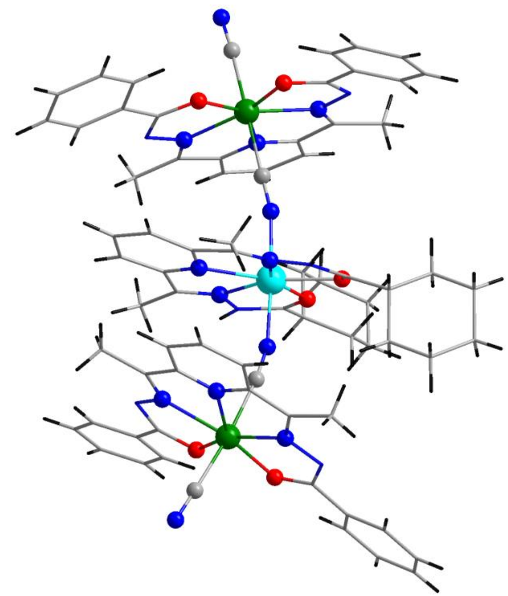
X = solvent



$[\{Cr(L^{N3O2Ph})(CN)_2\}_2Fe(H_2L^{N3O2NH2})]$



$[\{Cr(L^{N3O2Ph})(CN)_2\}_2Fe(H_2L^{N3O2mand})]$

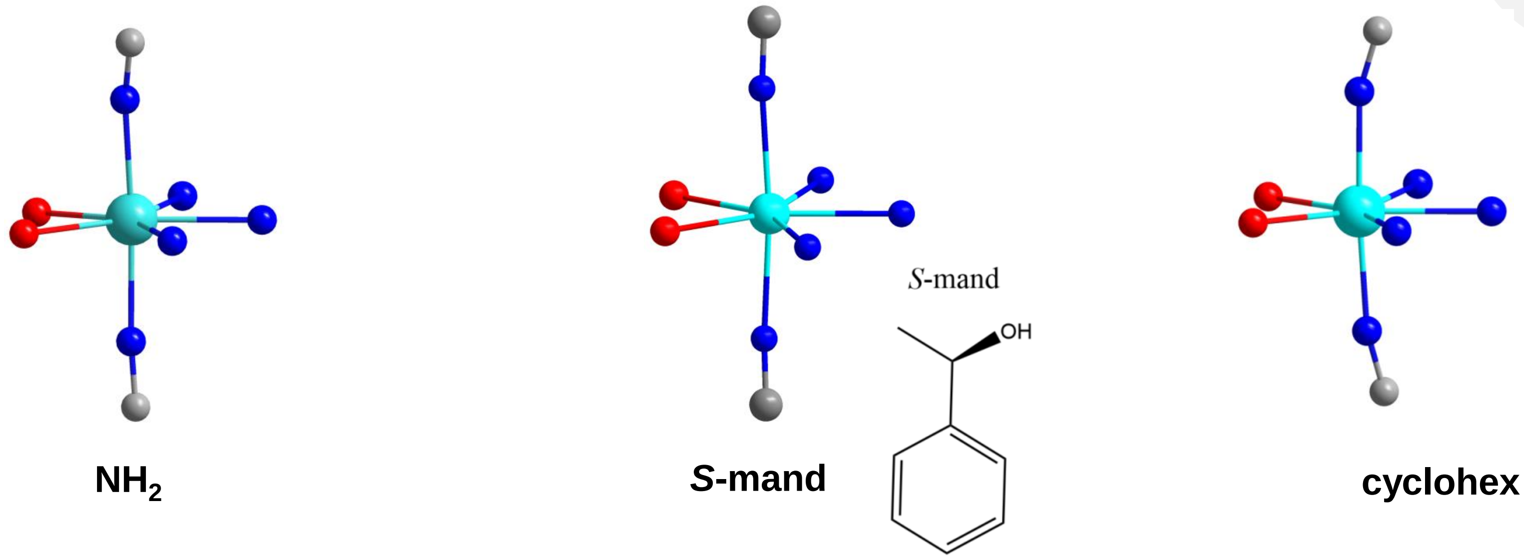


$[\{Cr(L^{N3O2Ph})(CN)_2\}_2Fe(H_2L^{N3O2cyclohex})]$

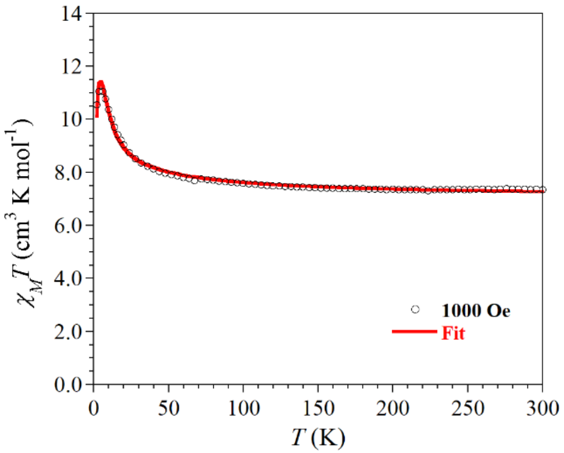
C. Pichon *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 7698.
C. Pichon *et al.*, *Chem. Eur. J.* **2021**, *27*, 15484.

Influence of R groups

- **Maximal distortion around Fe^{II} centers :**



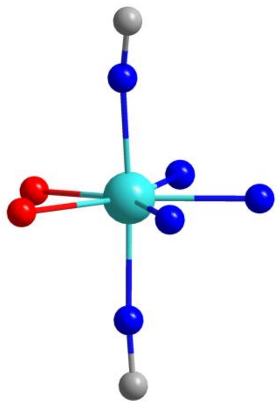
R = NH$_2$ | ***S*-mand** | **cyclohex**

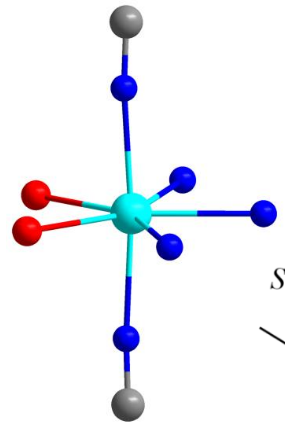


C. Pichon *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 7698.
C. Pichon *et al.*, *Chem. Eur. J.* **2021**, *27*, 15484.

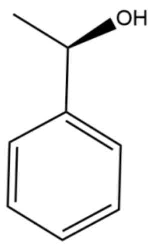
Influence of R groups

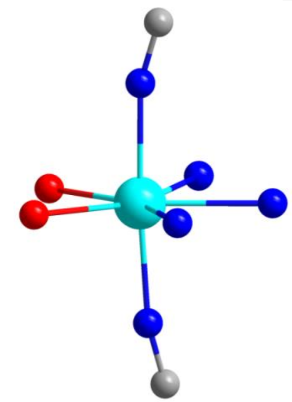
- **Maximal distortion around Fe^{II} centers :**





S-mand





R = **NH_2** **S-mand** **cyclohex**

J = 2.05 ± 0.01 cm^{-1},
D_{Fe} = -25 ± 0.01 cm^{-1},
zj' = -0.015 ± 0.001 cm^{-1}
and g_{Fe} = 2.15 ± 0.03

J = 2.8 ± 0.04 cm^{-1}, D_{Fe} = -20 ± 1 cm^{-1},
zj' = -0.014 ± 0.001 cm^{-1} and g_{Fe} = 2.1 ± 0.01

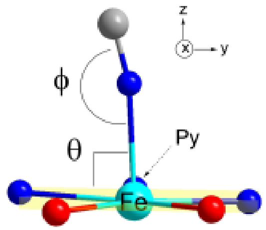
J = 2.12 ± 0.01 cm^{-1},
D_{Fe} = -11 ± 0.07 cm^{-1},
zj' = -0.002 ± 0.001 cm^{-1}
and g_{Fe} = 2.1 ± 0.02

$$\hat{H} = -J(\hat{S}_{Cr1}.\hat{S}_{Fe} + \hat{S}_{Cr2}.\hat{S}_{Fe}) + DS_{Fe}^2$$

C. Pichon *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 7698.
C. Pichon *et al.*, *Chem. Eur. J.* **2021**, *27*, 15484.

Influence of R groups

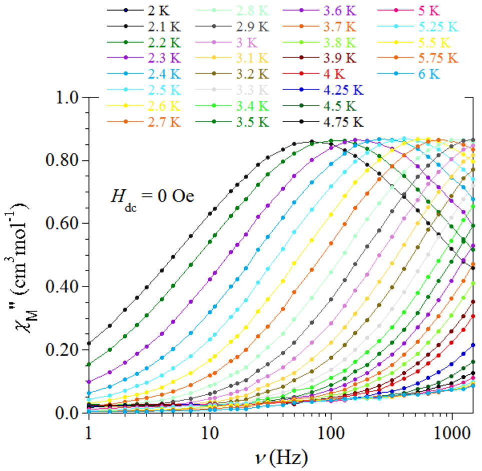
- ***ab-initio* calculations:**

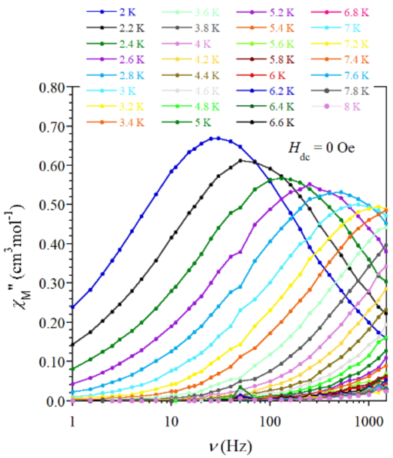


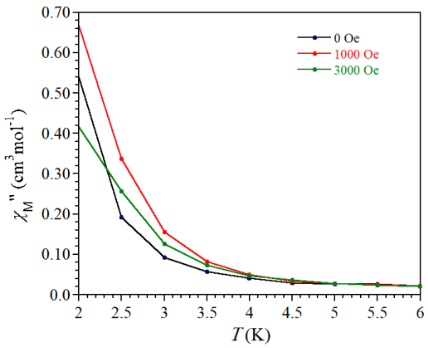
Distortion influences *D* and *J*
CN bending (ϕ angle < 180°) reduces *D*
Perpendicular bending (θ angle < 90°) decreases *J*

Calculations made by Dr. Nicolas Suaud and Prof. Nathalie Guihéry (LCPQ, Toulouse)

- **Impact on the relaxation:**







R = NH_2 — *S*-mand — cyclohex

NH_2: U_{eff}/k_B = 22 K and τ_0 = 3.8 10^{-8} s

S-mand: U_{eff}/k_B = 19 K (35.6 K @ 1000 Oe) and τ_0 = 6.8 10^{-8} s

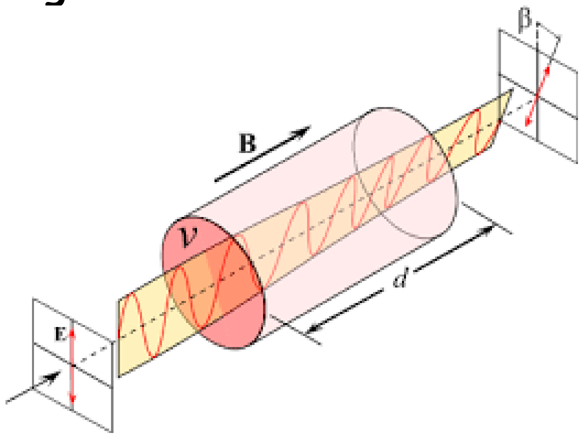
C. Pichon *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 7698.
C. Pichon *et al.*, *Chem. Eur. J.* **2021**, *27*, 15484.

LCC

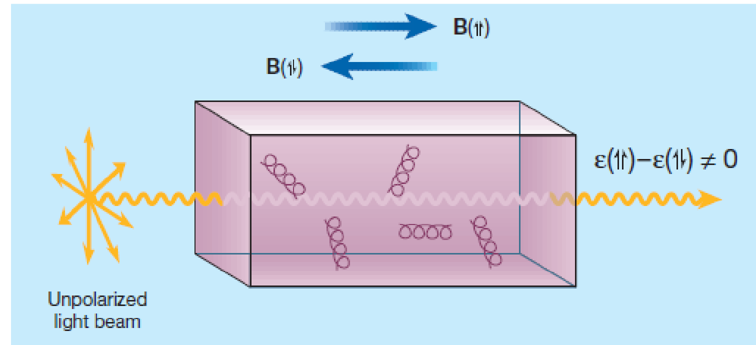
Chirality and heptacoordinated systems

- **Multifunctional materials:**

Synergetic effects between magnetic and optical properties

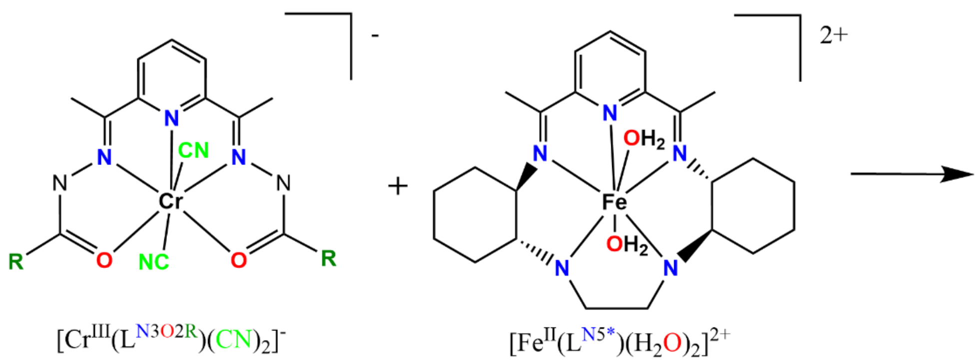


Faraday effect



MagnetoChiral Dichroism effect (MChD)

- **Synthetic approach:**

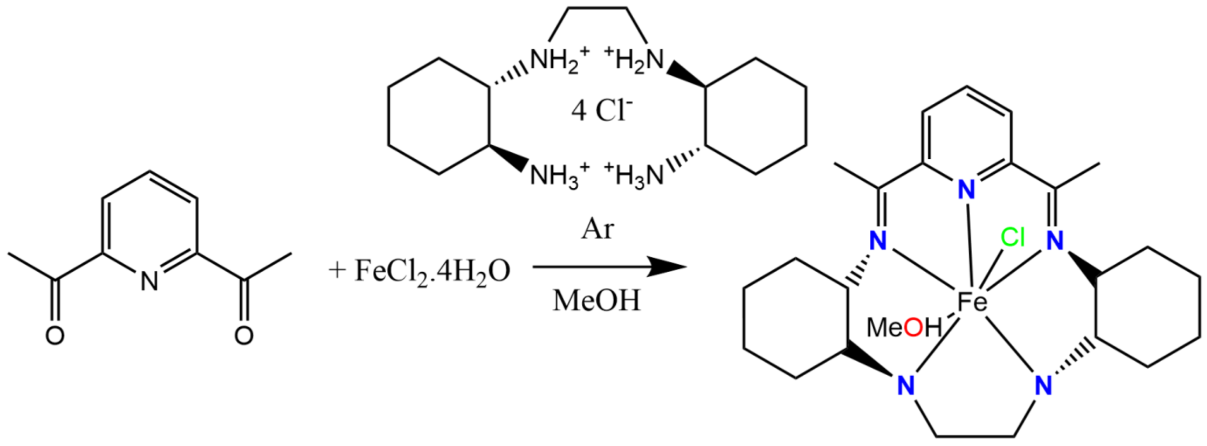


Chiral SMMs/SCMs?

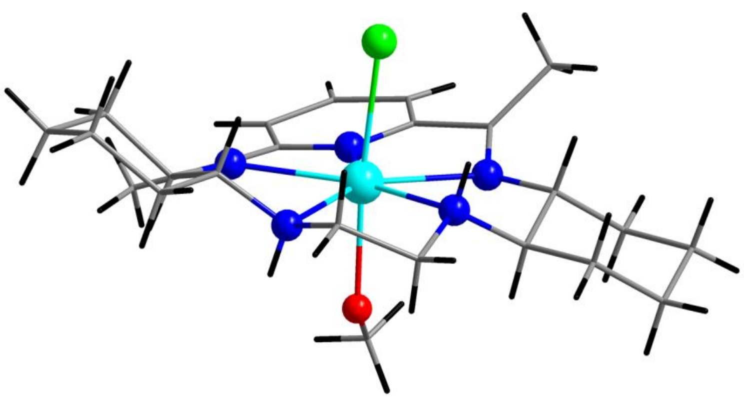
G. L. J. A. Rikken, E. Raupach, *Nature*, **1997**, *390*, 493.
C. Train *et al.*, *Nat. Mat.*, **2008**, *7*, 729.

Chirality and heptacoordinated systems

- **Synthesis of a chiral Fe^{II} complex:**



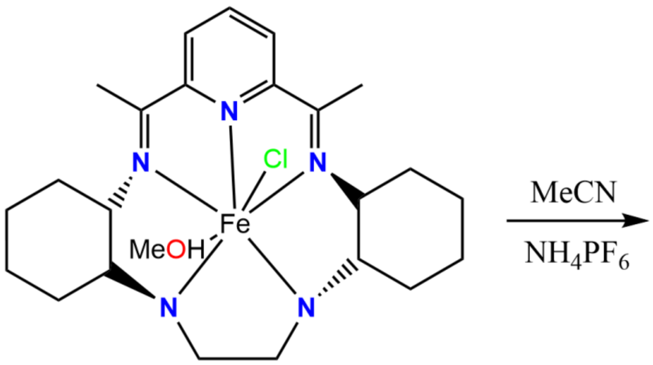
$[Fe^{II}(H_2L^{S,S})(MeOH)Cl]Cl$



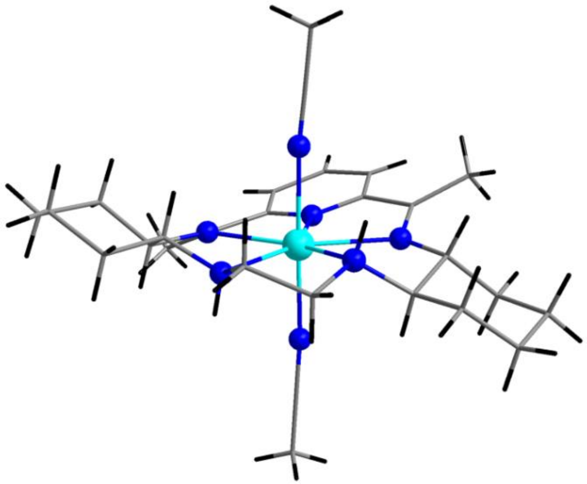
$[Fe(H_2L^{R,R})(MeOH)Cl]^+$

V. Jubault *et al.*, *Cryst. Growth Des.* **2023**, *23*, 1229.

- **Reactivity on axial positions :**



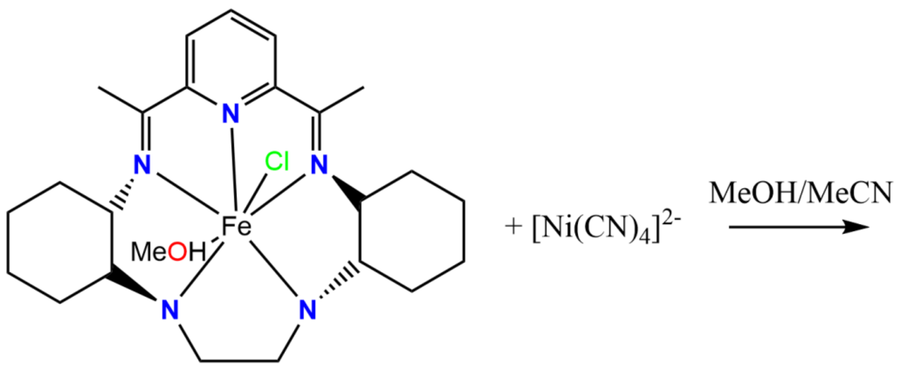
$[Fe^{II}(H_2L^{S,S})(MeOH)Cl]Cl$



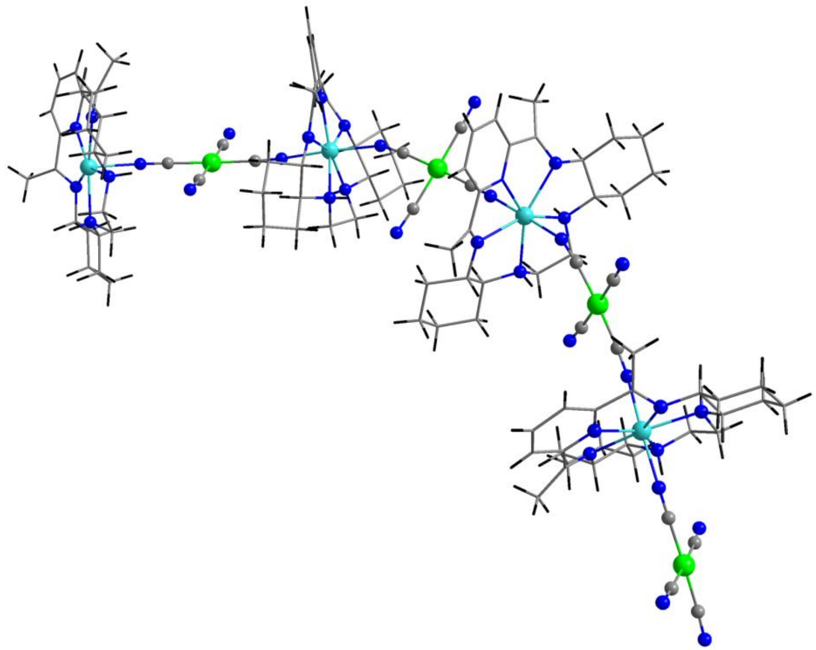
$[Fe(H_2L^{R,R})(MeCN)_2](PF_6)_2$

V. Jubault *et al.*, manuscript in preparation.

- **Reactivity on axial positions :**



$[Fe^{II}(H_2L^{S,S})(MeOH)Cl]Cl$



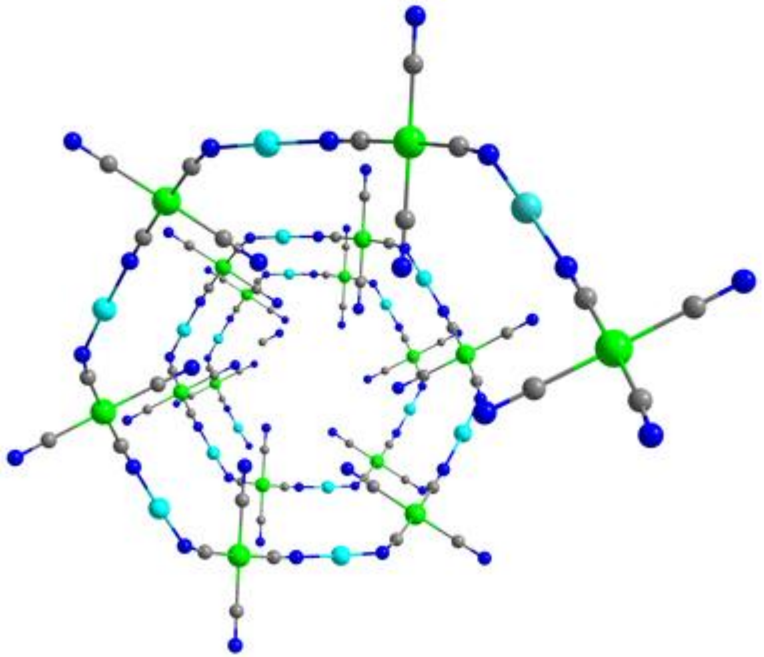
$[Fe(H_2L^{S,S})Ni(CN)_4]$

V. Jubault *et al.*, manuscript in preparation.

Chirality and heptacoordinated systems

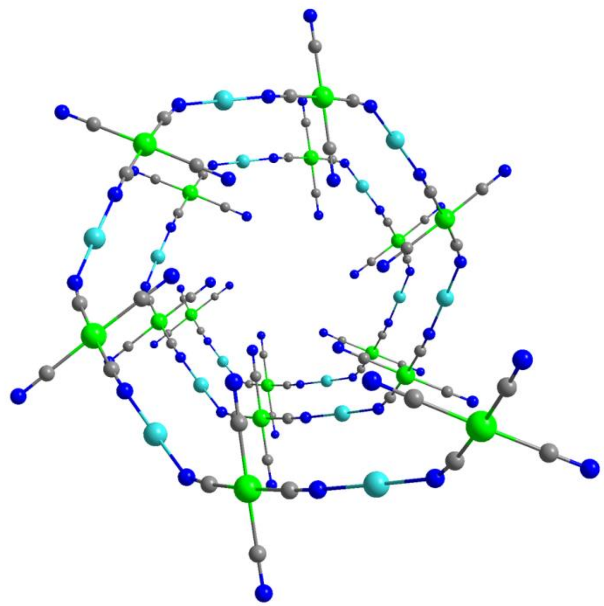
- **Helicoidal supramolecular organization :**

Helicity Λ



$[Fe(H_2L^{R,R})Ni(CN)_4]$

Helicity Δ

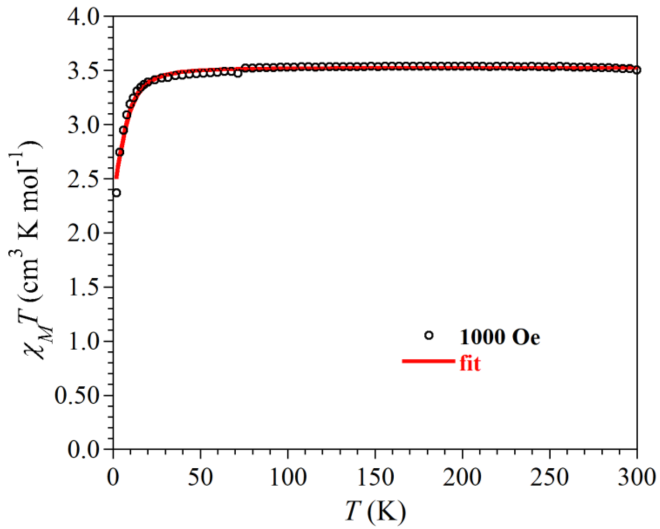


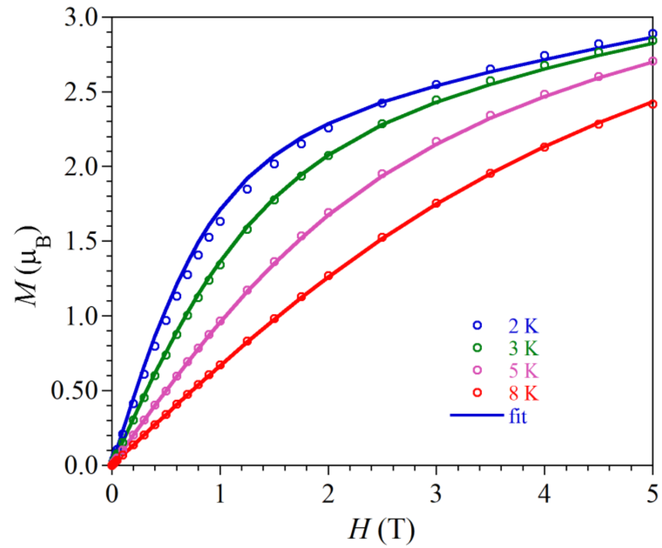
$[Fe(H_2L^{S,S})Ni(CN)_4]$

V. Jubault *et al.*, manuscript in preparation.

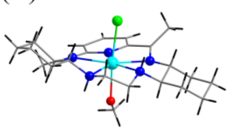
Chirality and heptacoordinated systems

▪ Magnetic anisotropy (SQUID measurements):





Example with the $[Fe(H_2L^{R,R})(MeOH)Cl]Cl$ complex



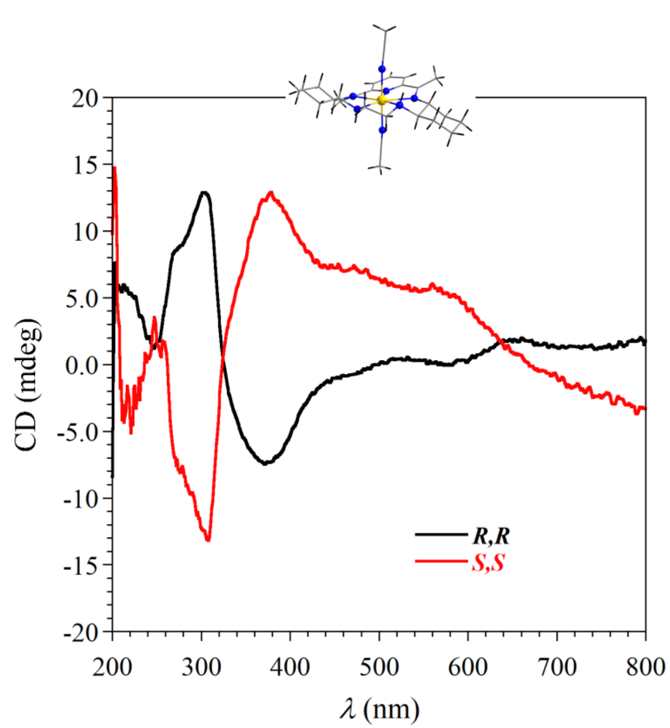
	$[Fe(H_2L^{R,R})(MeOH)Cl]Cl$	$[Fe(H_2L^{S,S})(MeCN)_2](PF_6)_2$	$[Fe(H_2L^{R,R})Ni(CN)_4]$
D **(cm^{-1})**	-5.95 ± 0.12	-7.10 ± 0.37	-10.16 ± 0.3
E **(cm^{-1})**	-	-0.01 ± 0.38	1.59 ± 0.17
g	2.17 ± 0.01	2.17 ± 0.01	2.04 ± 0.01

PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

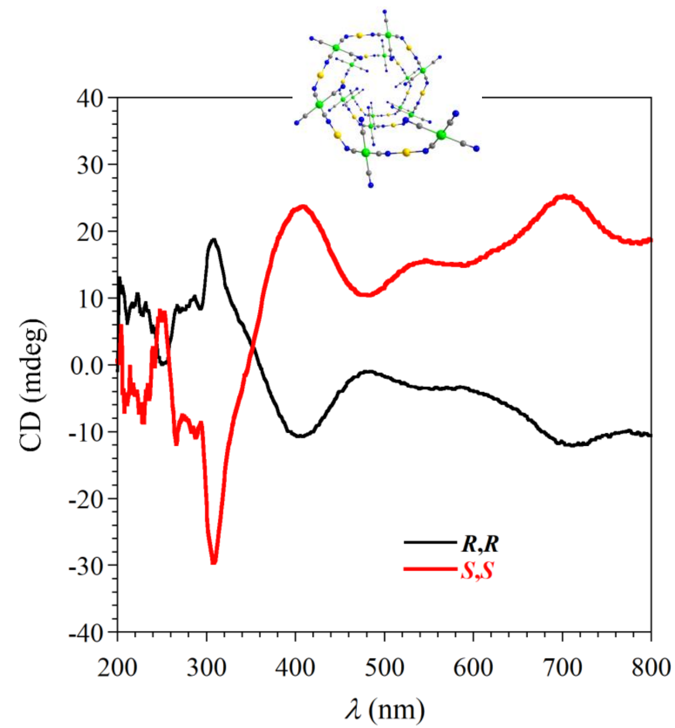
V. Jubault *et al.*, *Cryst. Growth Des.* **2023**, *23*, 1229.
V. Jubault *et al.*, manuscript in preparation.

Chirality and heptacoordinated systems

- **Circular dichroism :**



$[Fe(H_2L^{X,X})(MeCN)_2](PF_6)_2$



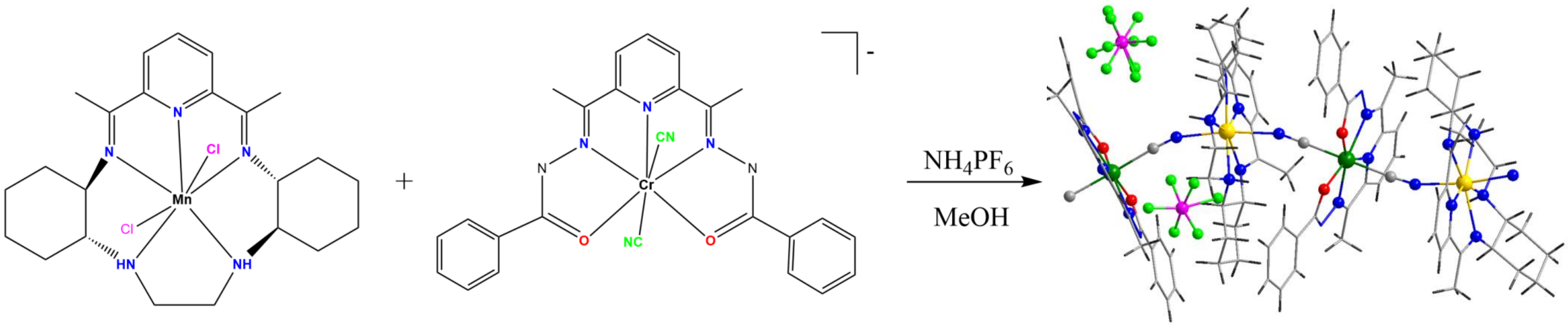
$[Fe(H_2L^{X,X})Ni(CN)_4]$

Enantiomeric purity ✓

Solid state: 1% mass in KBr (pellet)

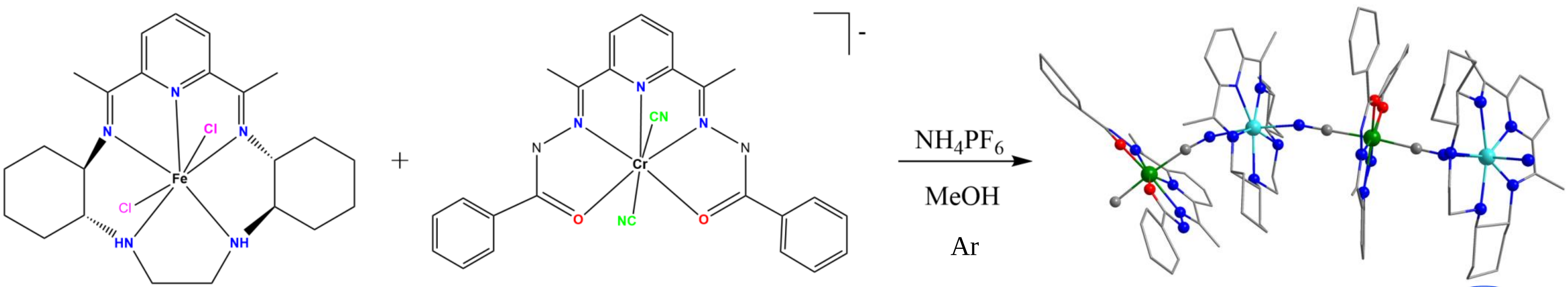
V. Jubault *et al.*, manuscript in preparation.

Chirality and heptacoordinated systems



$[Mn^{II}(L^{N5R,R})Cl_2]$ $[Cr^{III}(L^{N3O2Ph})(CN)_2]^-$

$[Cr(L^{N3O2Ph})(CN)_2Mn(H_2L^{N5R,R})](PF_6)$



$[Fe^{II}(H_2L^{N5R,R})Cl_2]$ $[Cr^{III}(L^{N3O2Ph})(CN)_2]^-$

**$[Cr(L^{N3O2Ph})(CN)_2$
$Fe(H_2L^{N5R,R})]^+$**

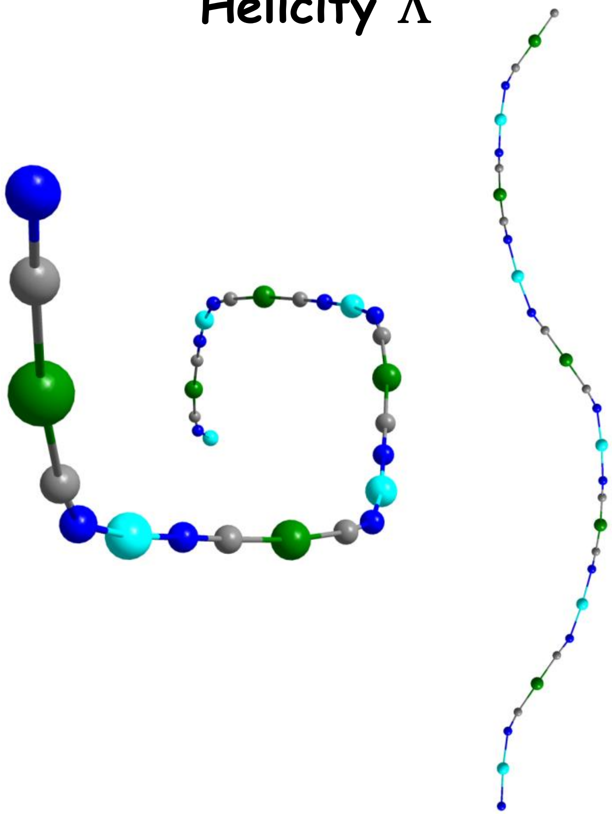
PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

V. Jubault *et al.*, manuscript in preparation.

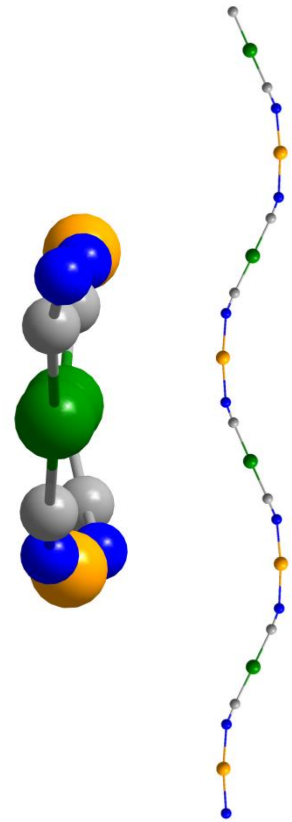
Chirality and heptacoordinated systems

- **Helicoidal supramolecular organization in the CrFe chain:**

Helicity Λ



[Cr(L^{N3O2Ph})$(CN)_2$Fe($H_2L^{N5R,R}$)]$^+$



[Cr(L^{N3O2Ph})$(CN)_2$Mn($H_2L^{N5R,R}$)]$^+$

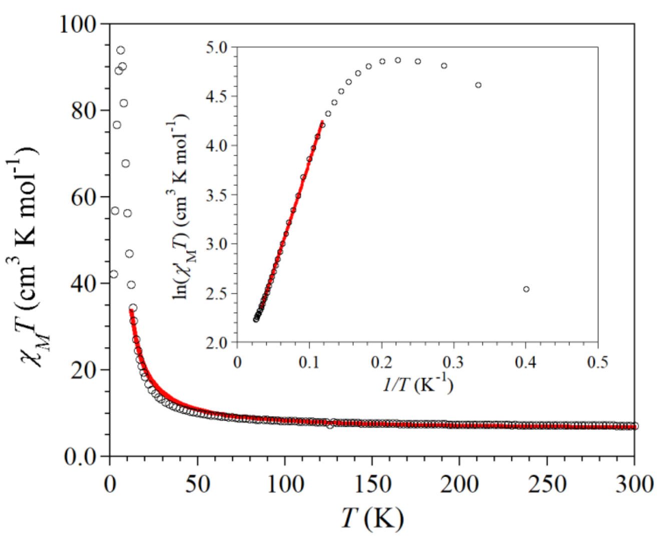
V. Jubault *et al.*, manuscript in preparation.

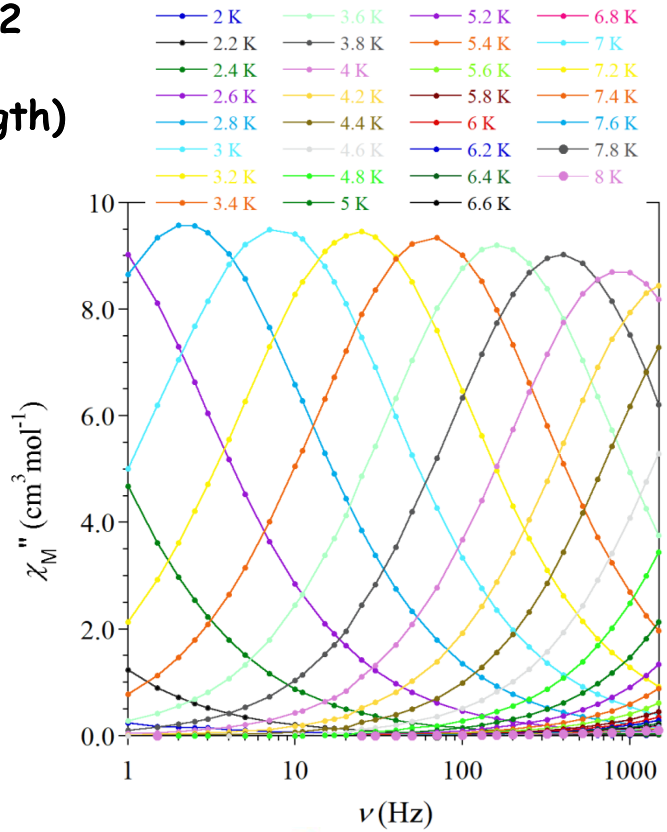
Chirality and magnetism

▪ Magnetic properties of the CrFe chain:

J = 3.82 ± 0.02 cm^{-1} and g_{Fe} = 2.17 ± 0.02

1D behavior with Δ_ξ = 22.3 K (correlation length)





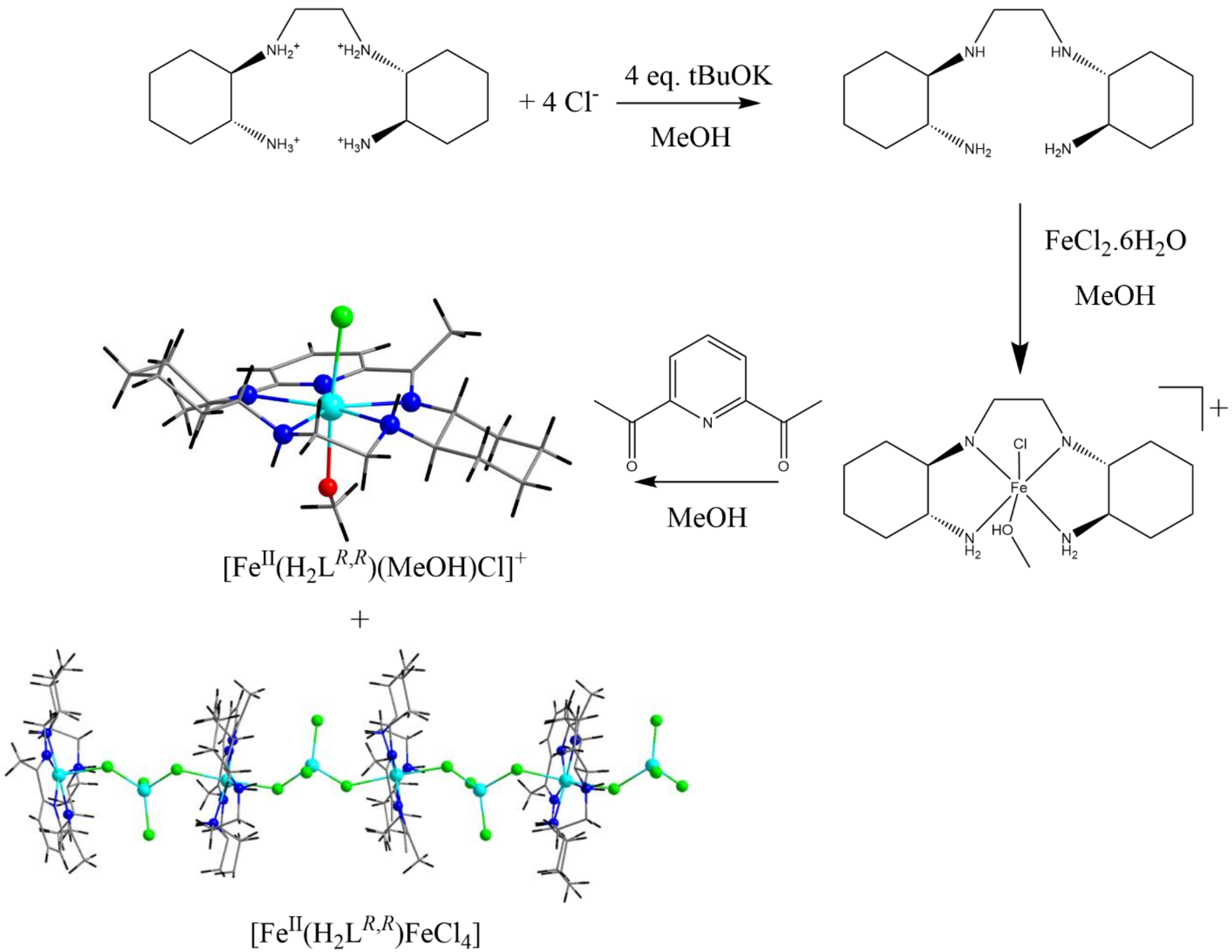
$$\hat{H} = -J\sum_i (\hat{S}_{Cr,i}.\hat{S}_{Fe,i})$$

SCM behavior

U_{eff}/k_B = 55 K and τ_0 = 2.4 10^{-10} s

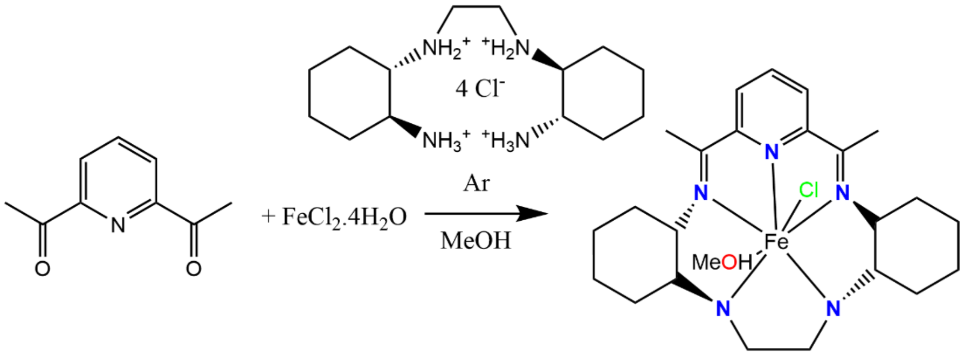
Chirality and magnetism

- **When the addition order matters…**



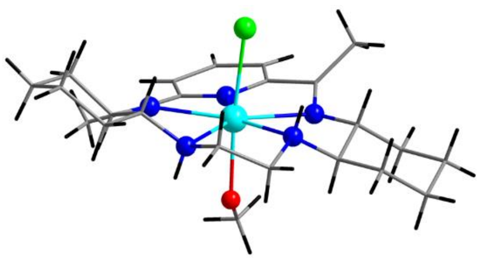
V. Jubault *et al.*, *Cryst. Growth Des.* **2023**, *23*, 1229.

- **When the addition order matters…**



[Fe^{II}(H$_2$L^{S,S})(MeOH)Cl]Cl

84 %



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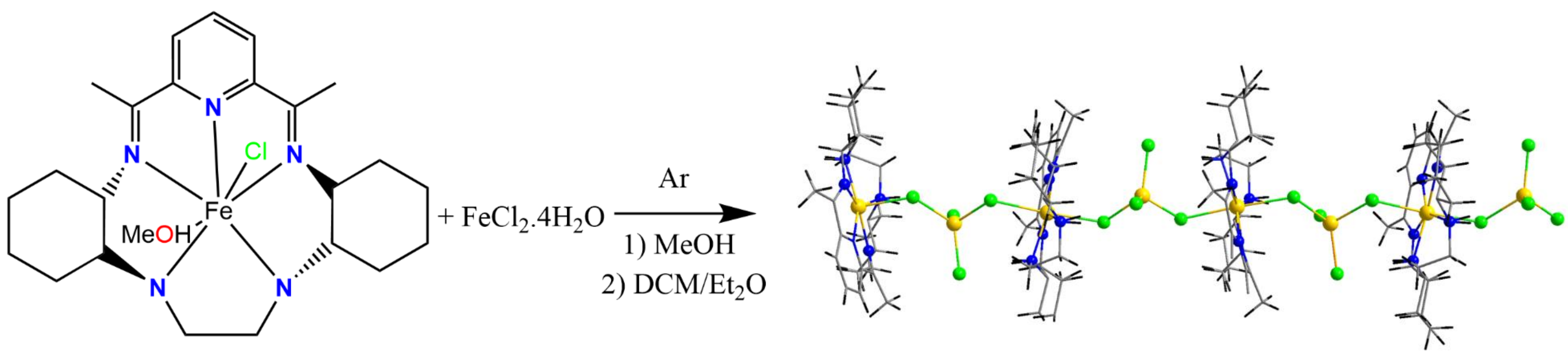
Chirality and magnetism

- **Rational synthesis:**



$[Fe^{II}(H_2L^{S,S})(MeOH)Cl]Cl$

$[Fe^{II}(H_2L^{S,S})FeCl_4]$

77 %

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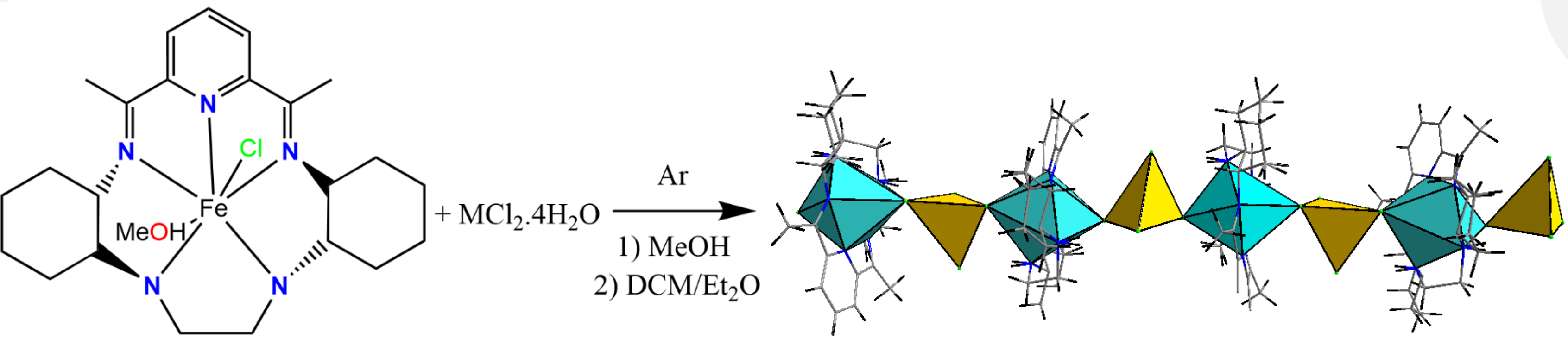
Heterometallic systems with tunable anisotropies



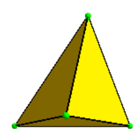
$[Fe^{II}(H_2L^{S,S})(MeOH)Cl]Cl$

$[Fe^{II}(H_2L^{S,S})MCl_4]$
M = Fe, Co and Ni

Nature of MCl_4 units change spin state of M, type of anisotropy and exchange interaction

Based on calculations:

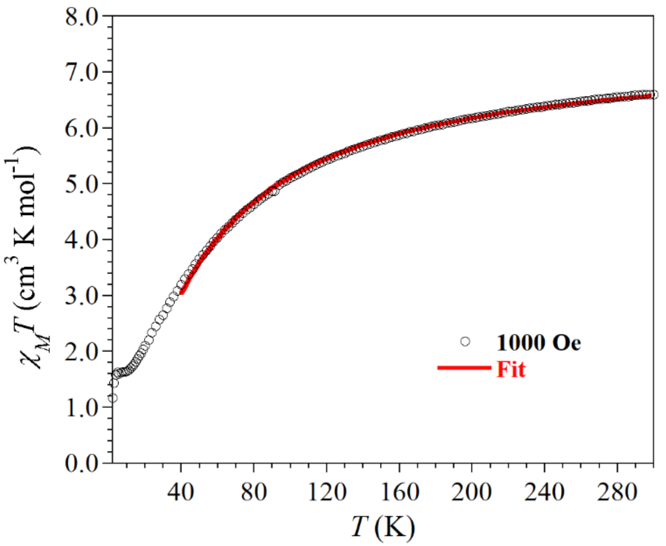
- ✓ **$FeCl_4$: $D = -15\ cm^{-1}$**
- ✓ **$CoCl_4$: $D = +4\ cm^{-1}$**
- ✓ **$NiCl_4$: $D < 0$ and potentially very strong**

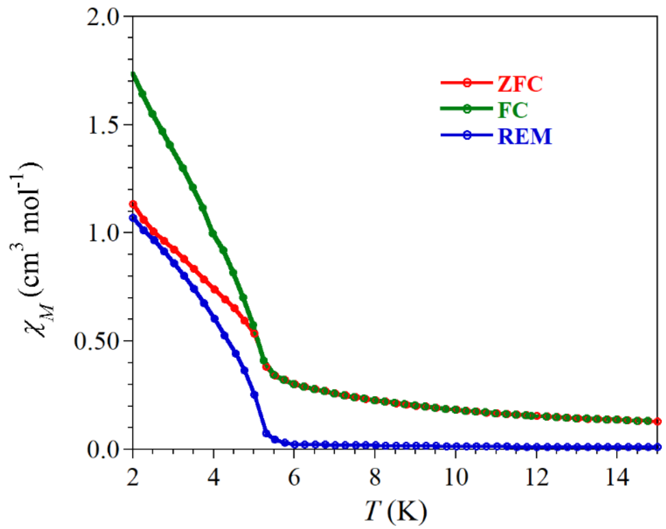


Calculations done in collaboration with Dr. Nicolas Suaud and Prof. Nathalie Guihéry (LCPQ, Toulouse)

Heterometallic systems with tunable anisotropies

- **Magnetic properties:**





J = -6.14 ± 0.05 cm^{-1},
g_{Fe} = 1.911 ± 0.004 and
g_{FeCl4} = 2.17

Canted AF order

$$\hat{H} = -J \sum_{i} (\hat{S}_{Cr,i}.\hat{S}_{Fe,i})$$

PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

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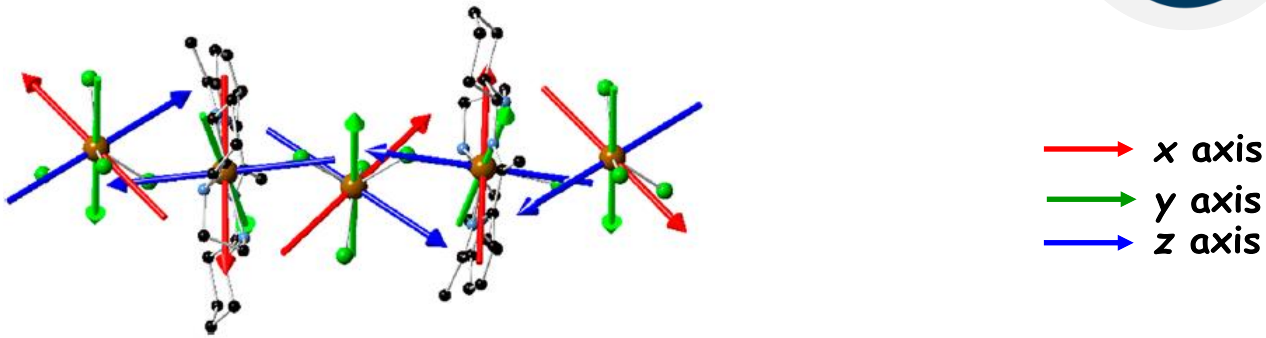
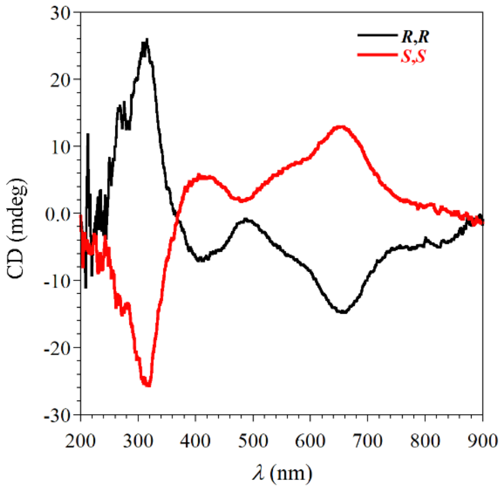
Heterometallic systems with tunable anisotropies

- ***ab-initio* calculations:**



D_{Fe} = -28.6 cm^{-1}, E_{Fe} = 0.3 cm^{-1},
D_{FeCl4} = -15.1 cm^{-1} and E_{FeCl4} = 3.6 cm^{-1}

- **Circular dichroism:**



Enantiopure samples

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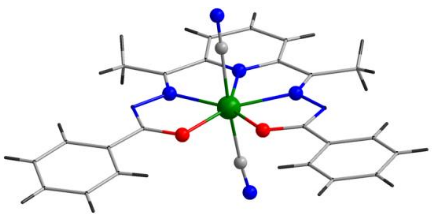
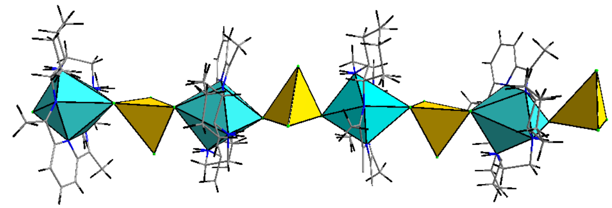
Take home messages

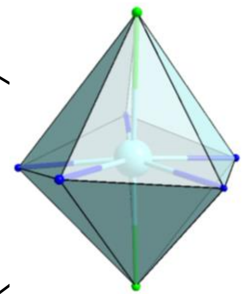
Magnetic anisotropy
(local and relative
orientation)

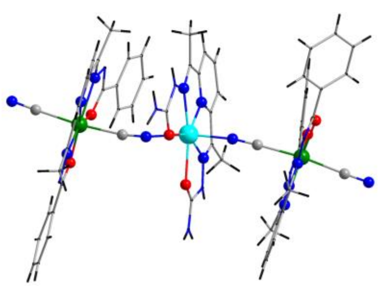


Metalloligands



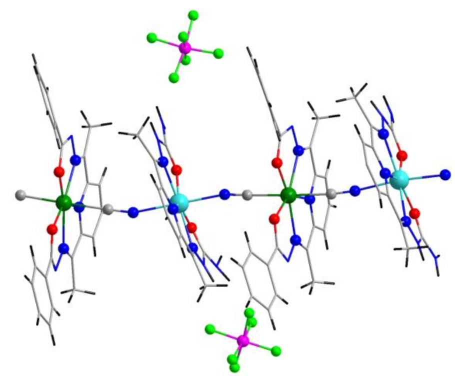
Combination of two
anisotropies





Discrete paramagnets
or SMMs

Valid for others
geometries/coordinences



Chains or SCMs

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Dr. Virginie Béreau (phenantroline and chiral ligands)
Dr. Jean-Pascal Sutter and all team members

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