Высокотемпературные мономолекулярные магниты: современное состояние, проблемы и новые подходы

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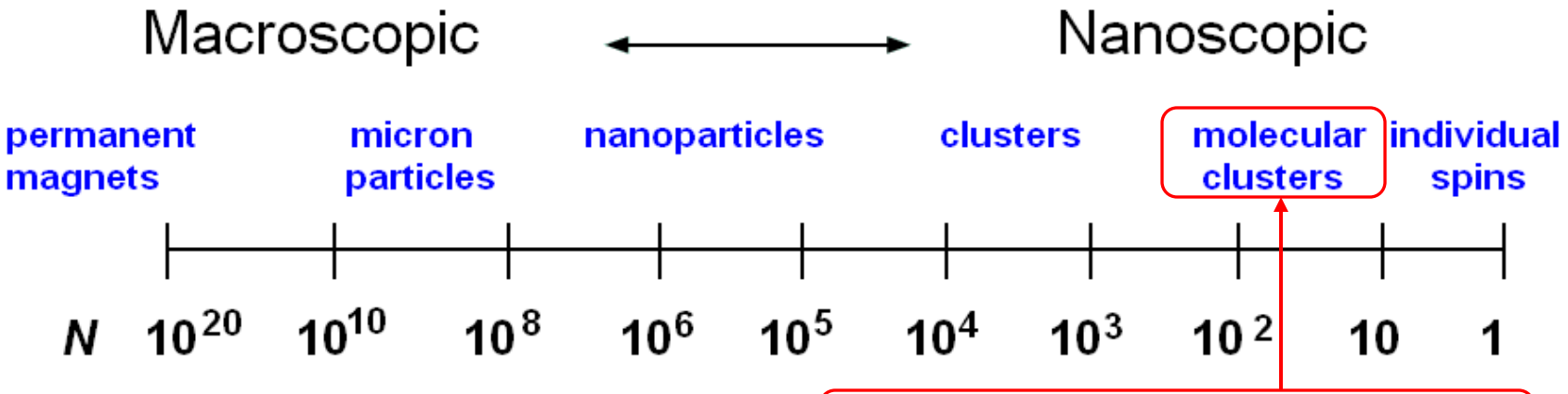
Content:

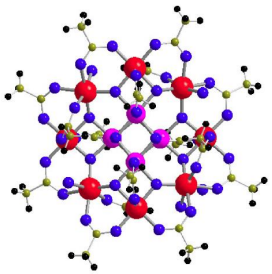
- Single-molecule magnets (SMM): a short overview
- Spin-reversal barrier: the origin and limitations
- The problem of increasing the magnetization blocking temperature of SMM clusters
- New strategy of designing high-temperature SMMs
- Orbitally-degenerate 5*d* complexes as molecular building blocks for high-T SMM
- General principles of designing high-T SMMs
- Conclusion: Problems and perspectives

Nanomagnets and Single-Molecule Magnets

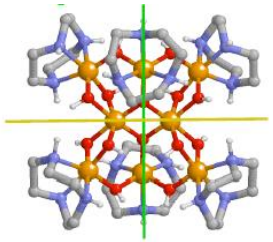


Single-Molecule Magnets: Molecular spin clusters with the magnetic memory effect

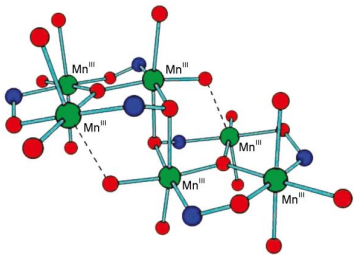
Polynuclear complexes of *d* or *f* metals with organic ligands



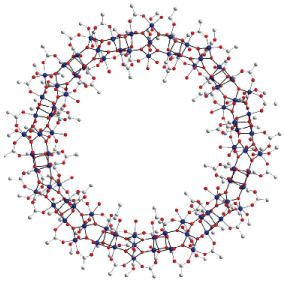
$Mn_{12}Ac$



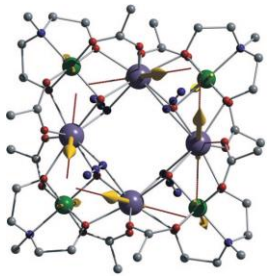
Fe_8



Mn_6



Mn_{84}



Dy_4

Why single-molecule magnets (SMM) are interesting?

Advantages:

- **SMMs are the smallest magnetic nanoparticles (of the molecular-scale size, 1-5 nm)**
- **SMMs are absolutely monodisperse → identical in the size, shape, and magnetic momentum**
- **SMMs are quantum objects → exhibit unique magnetic properties**
- **SMMs are constructed from molecular building blocks → provide a variety of synthetic approaches and flexibility in designing of the molecular structure**
- **SMMs are promising for designing hybrid functional molecular materials combining magnetic, optical, and conducting properties**

Advanced applications for the molecular electronics:

❑ Super high density magnetic memories

Single-molecule magnets are potentially capable to provide information storage density of 10^5 - 10^6 Gb/cm^2 (10^3-10^4 times higher than the current value)

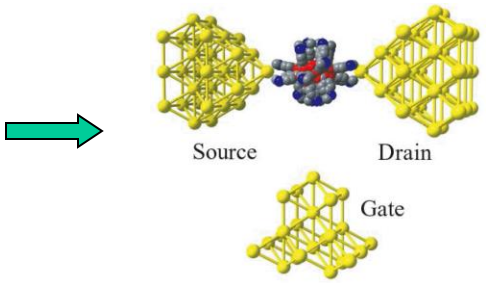
❑ Quantum computers

SMMs are promising qubits and memory elements for quantum computers

M. N. Leuenberger, D. Loss, Quantum computing in molecular magnets, *Nature* **410**, 789-793 (2001)

❑ Molecular spintronics

SMM-based molecular spin transistors



L. Bogani, W.Wernsdorfer, *Nature Mater.* **7**, 179 (2008)

Single-molecule magnet: Molecular spin cluster with a double-well ground-state potential

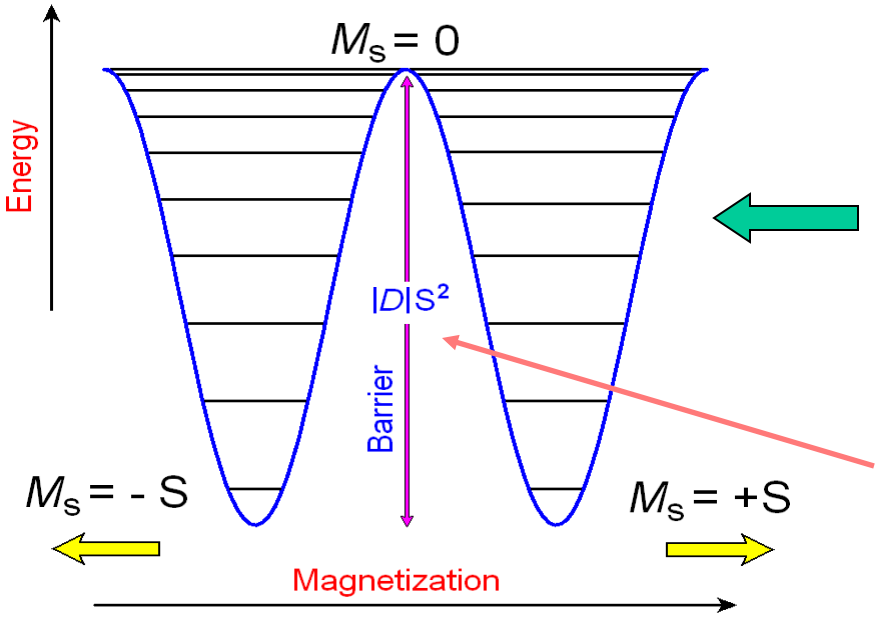
Zero-field splitting of the ground-state spin *S* (the giant-spin splitting model):

$$H = DS_z^2 + E(S_x^2 - S_y^2) + bS_z^4 + c[(S^+)^4 + (S^-)^4] + \ldots$$

high-order spin terms

D – is the axial magnetic anisotropy.

E – is a transverse magnetic anisotropy (in low symmetry)

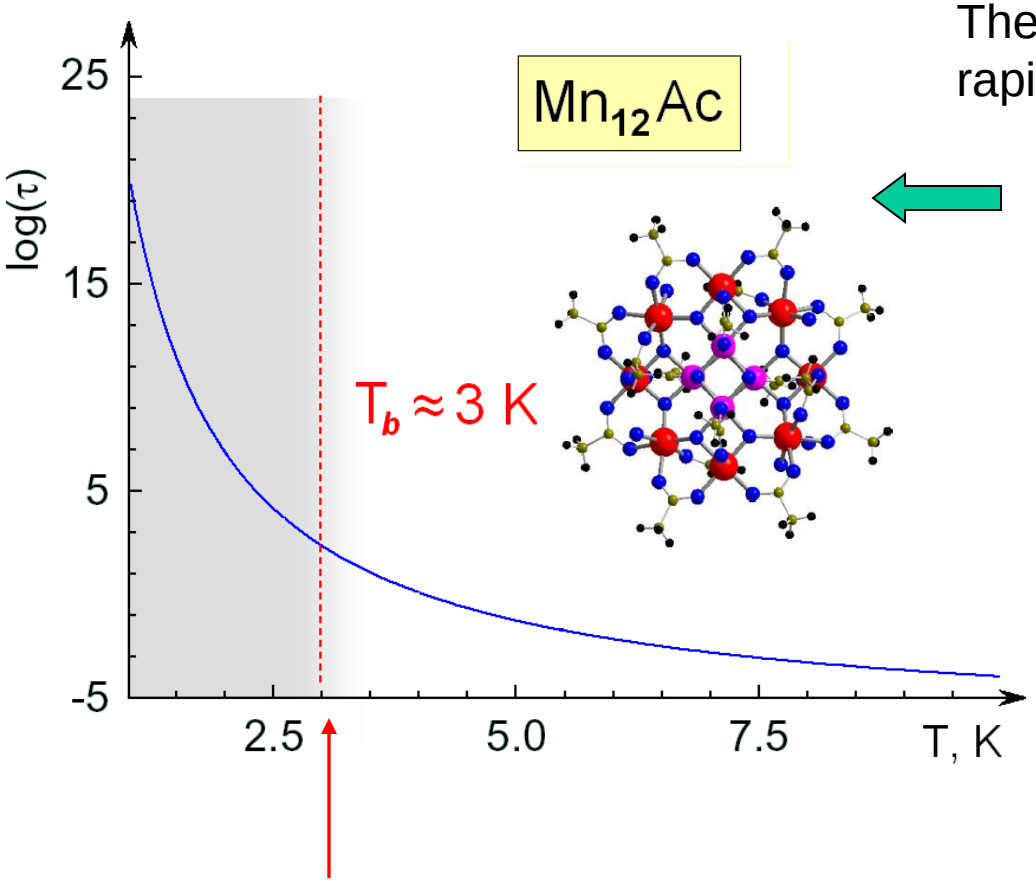


At $D < 0$ a double-well potential DS^2 forms – this is the most important condition for a cluster to be a single-molecule magnet

The spin-reversal barrier $|D|S^2$ blocks transfers between $M_s = +S$ and $M_s = -S$ states and fixes magnetization along the magnetic anisotropy axis z

At low temperature, such a cluster behaves as a molecular size magnet (single-molecule magnet, SMM)

Blocking of magnetization



The relaxation time τ increases very rapidly with lowering temperature

$$\tau = \tau_0 \exp(U_{eff} / kT)$$

For $Mn_{12}Ac$ cluster

$U_{eff} = |D|S^2 \approx 50$ cm^{-1} (70 K)

$T_b \approx 3$ K.

Magnetization is fixed below the critical point T_b - the blocking temperature

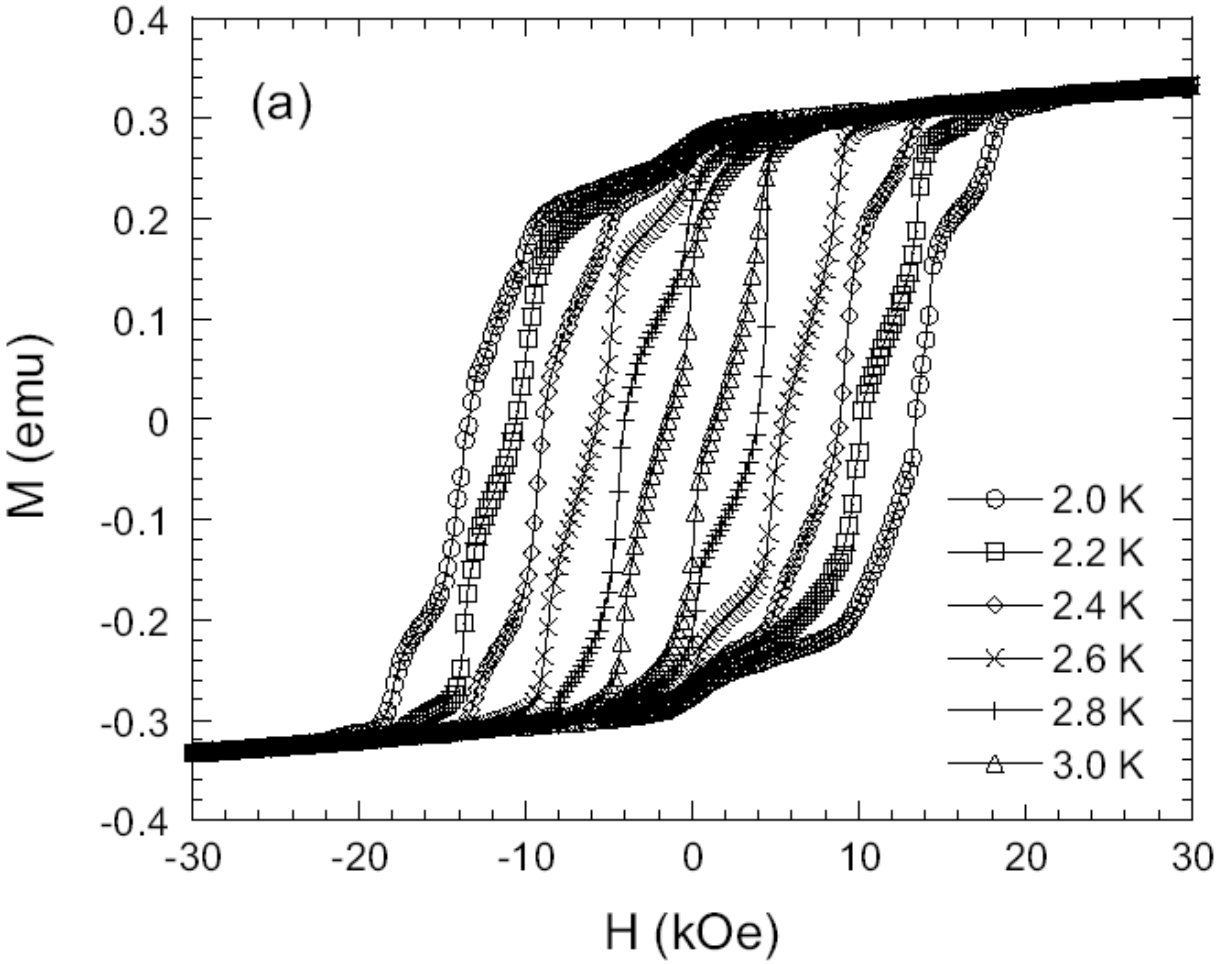
τ ~ 50 years at 1.5 K

τ < 1 sec at 6 K.

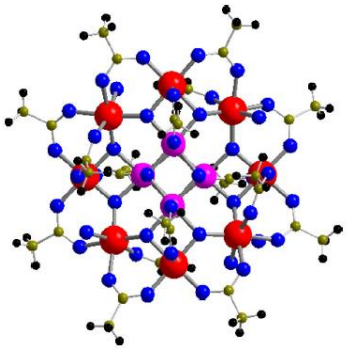
1 eV = 8065 cm^{-1}, 1 cm^{-1} = 1.44 K

Magnetization hysteresis in the single-molecule scale

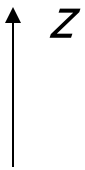
This hysteresis is not related to the long-range magnetic order or with the domain structure – it is just a property of a single molecule !!!



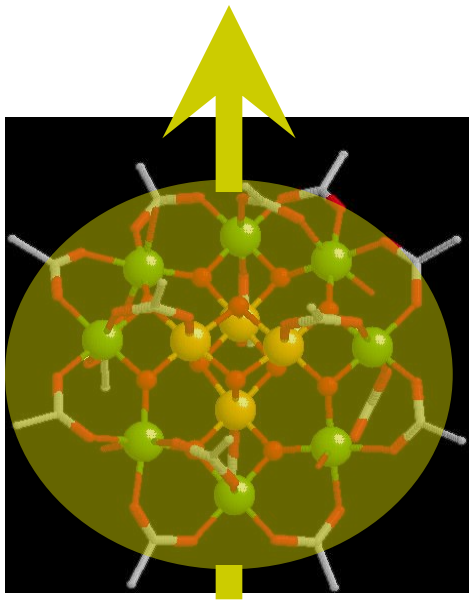
$Mn_{12}Ac$

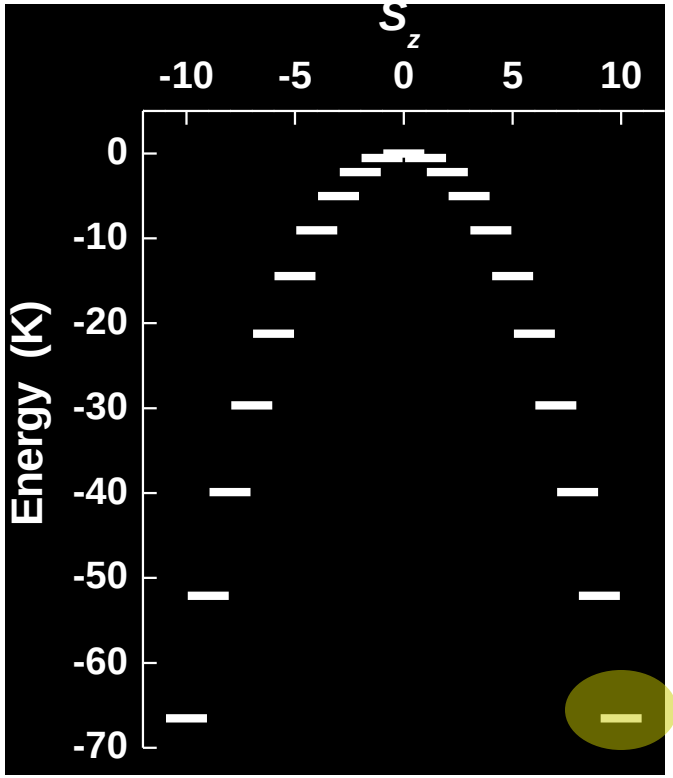


Magnetic anisotropy



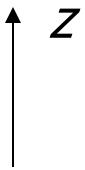
$$\mathcal{H} = -DS_z^2$$





The magnetic moment of the molecule is preferentially aligned along the z – axis.

Magnetic anisotropy



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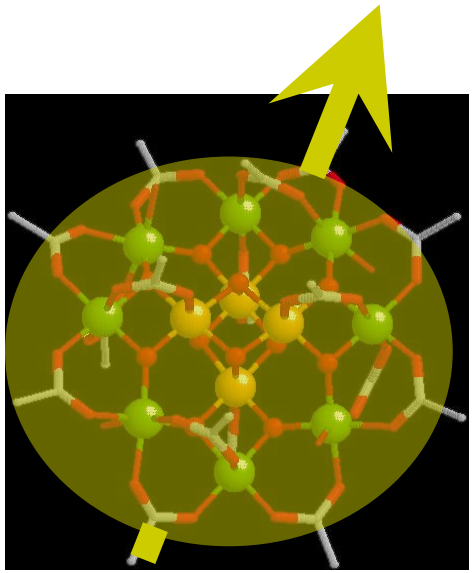

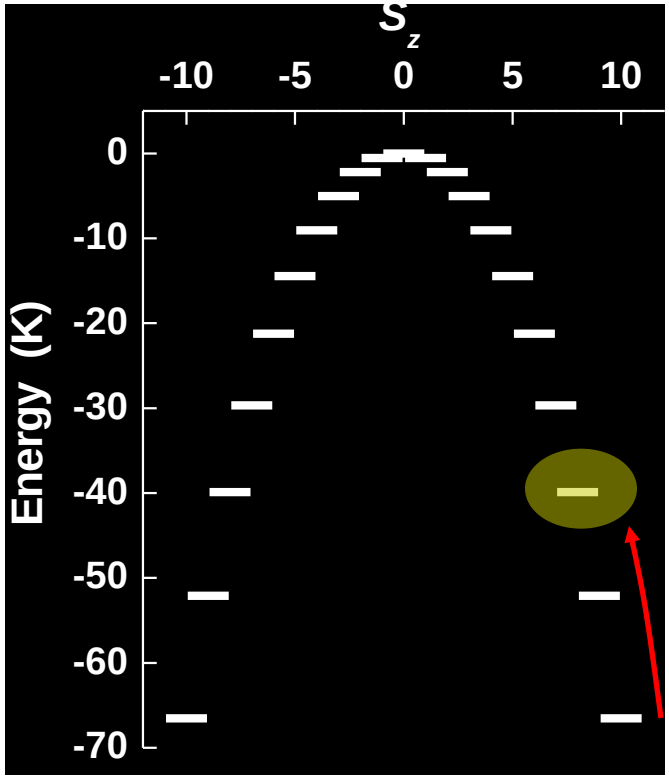

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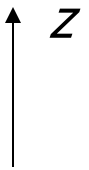

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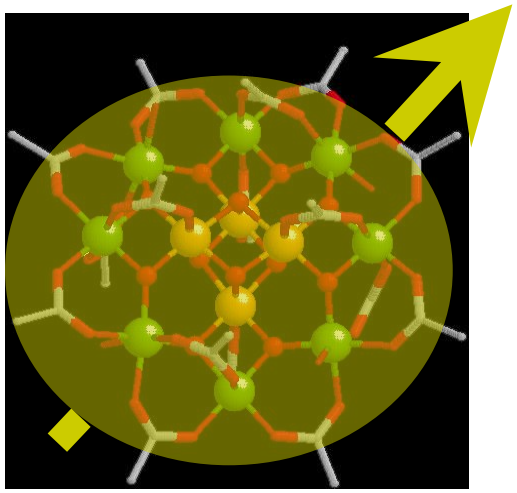

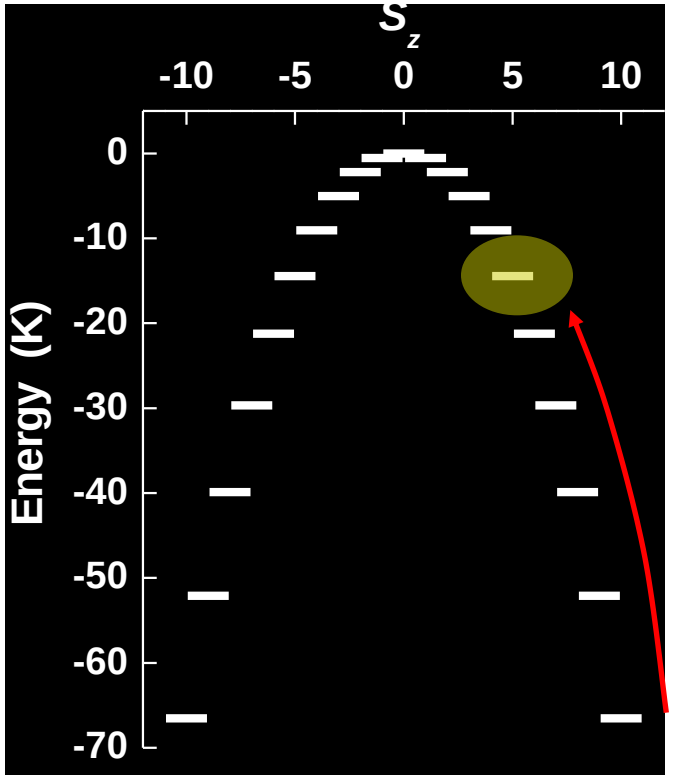

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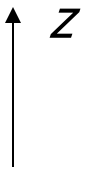

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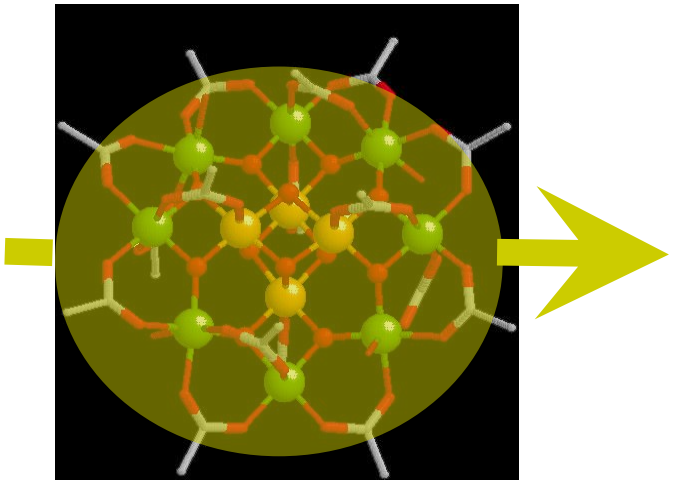

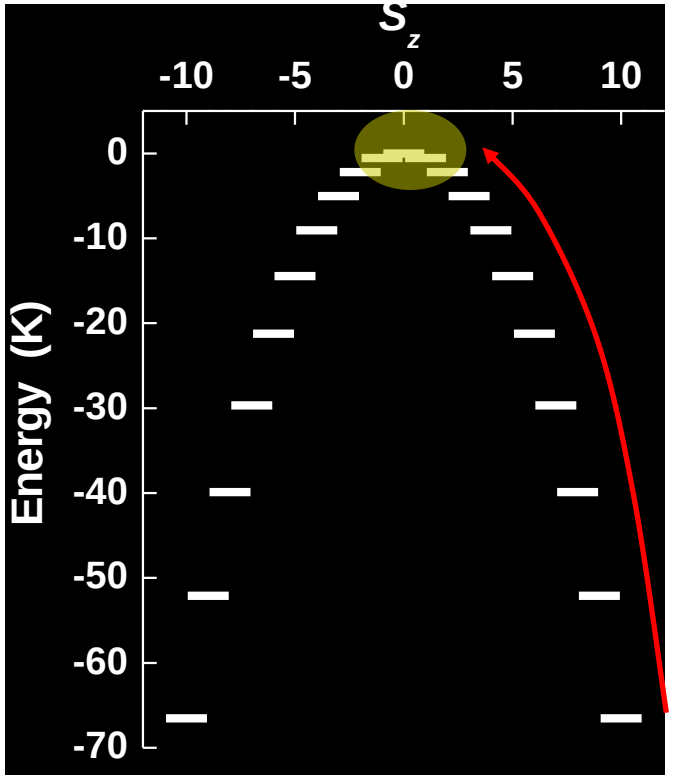

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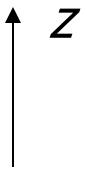
Magnetic anisotropy



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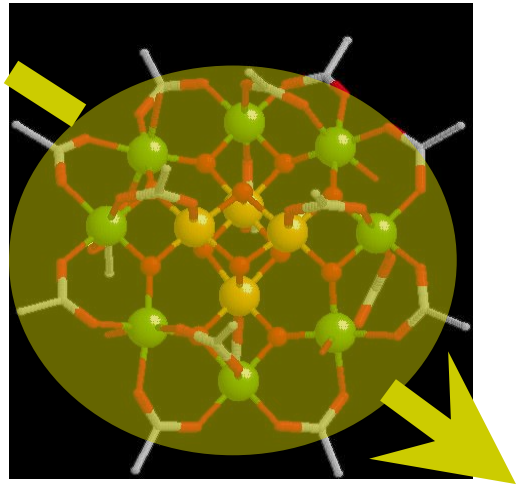

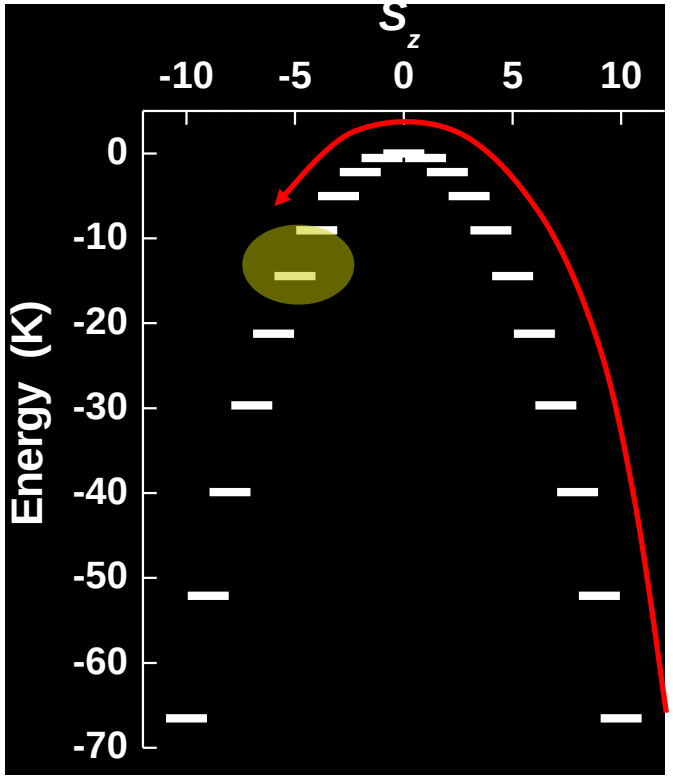

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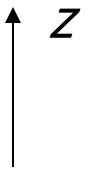

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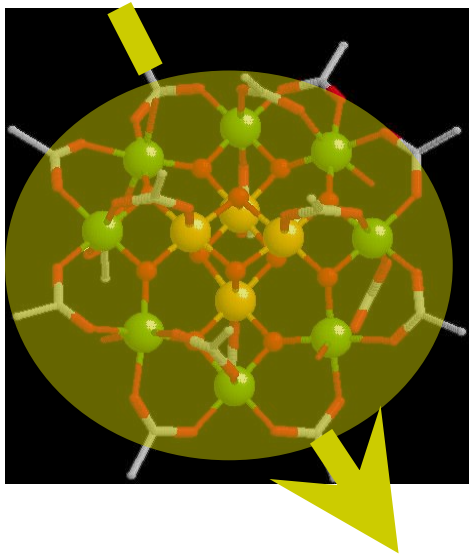

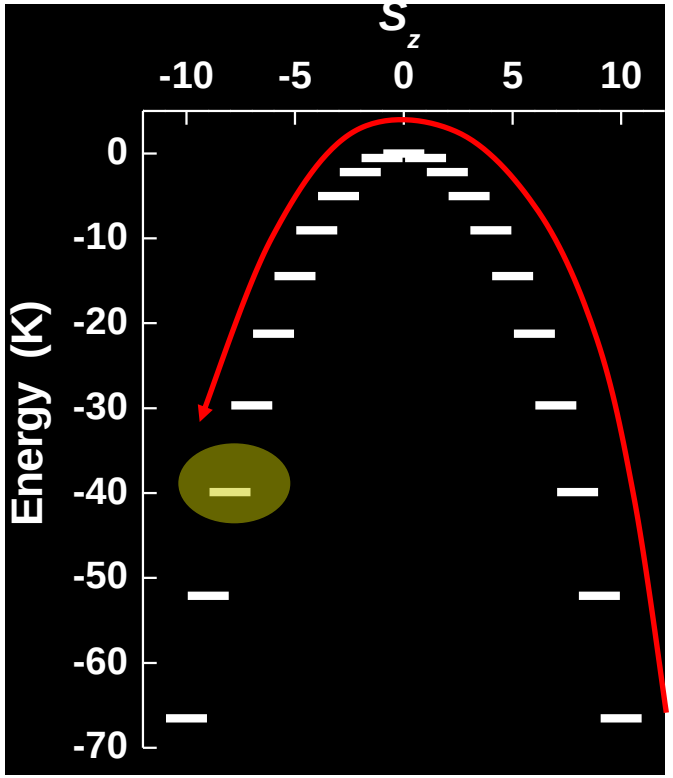

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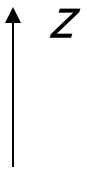
Magnetic anisotropy



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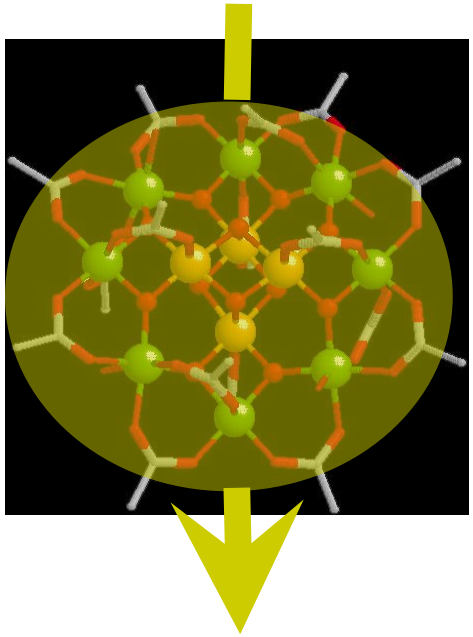
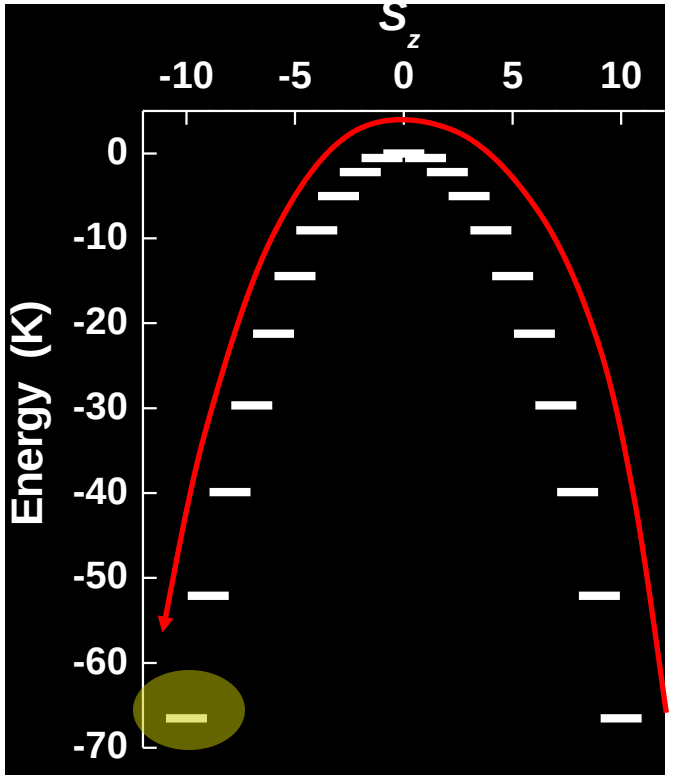
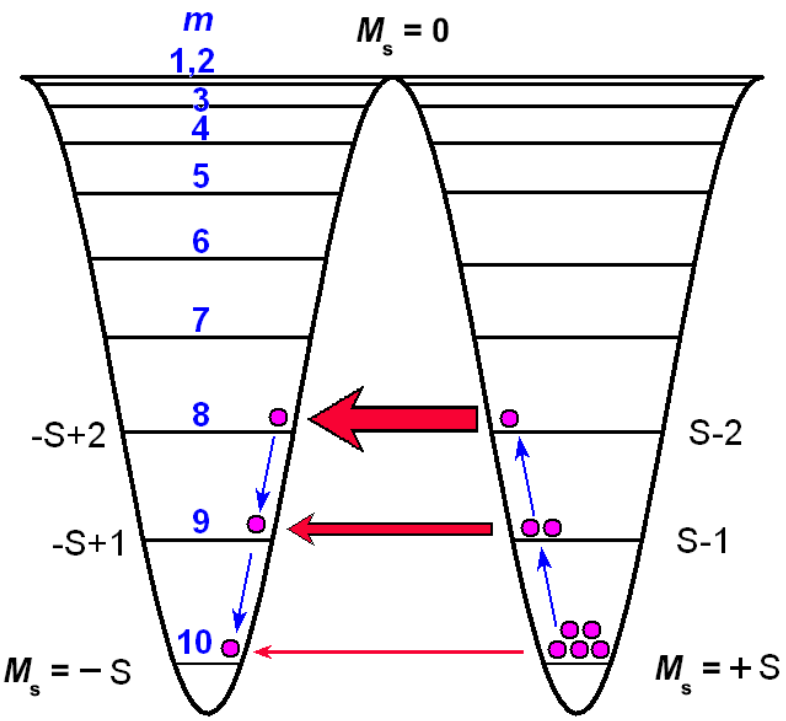




It takes an energy of $|D|S^2$ to reverse the spin.

Thermally-assisted tunneling of magnetization

The rate of through-barrier quantum tunneling between the $+M_s$ and $-M_s$ states rapidly increases for excited spin states

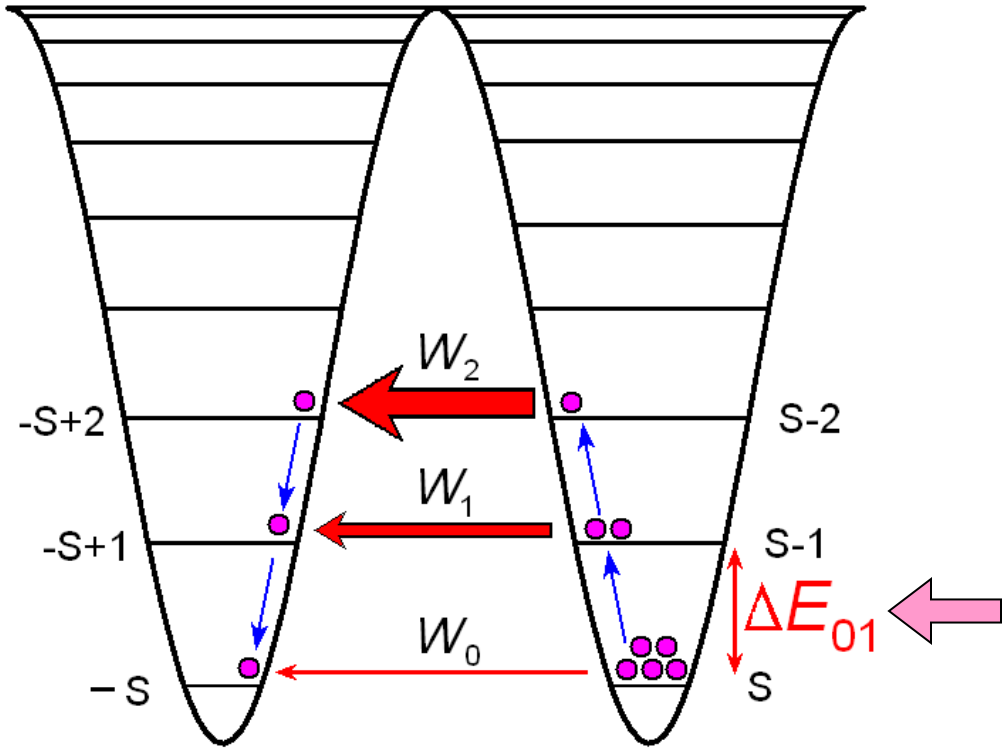


Spin state m	Tunneling frequency $\Delta_{m,-m}$ (Hz)
1	3.2×10^{8}
2	1.1×10^{5}
3	3.5×10^{0}
4	2.3×10^{-5}
5	4.7×10^{-11}
6	3.7×10^{-17}
7	1.2×10^{-23}
8	1.7×10^{-30}
9	1.1×10^{-37}
10	2.11×10^{-45}

Fast relaxation of magnetization is due thermal population of low-lying spin levels

The rate of tunneling increases by a factor of ~10^8 (!!!) for the first excited spin state $m = 9$

The blocking temperature is generally much smaller than the spin-reversal barrier



$kT_b << |D|S^2$

For $Mn_{12}Ac$ cluster:

$U_{eff} = |D|S^2 \approx 50\ cm^{-1}$ (70 K)

$T_b \approx 3$ K.

In fact, T_b is mainly measured by the energy gap ΔE_{01} between the ground spin state and first excited spin state

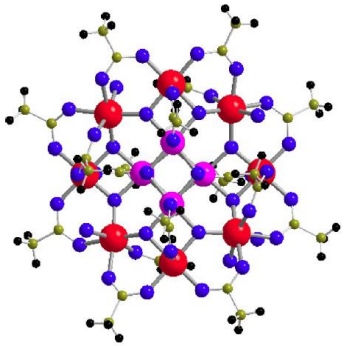
In $Mn_{12}Ac$:

$\Delta E_{01} = 9\ cm^{-1}$ (13 K), $T_b \approx 3$ K.

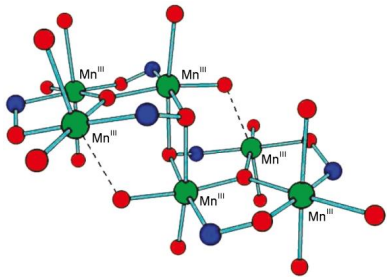
$\Delta E_{01}/kT_b \sim 5\text{-}10$

The central problem: Increasing the blocking temperature T_b

Many hundreds of various SMM clusters were isolated and characterized (2013)
The blocking temperature is still very low, $T_b < 5$ K



$Mn_{12}Ac$
U_{eff} = 65 K
T_b = 3 K
1993



Mn_6
U_{eff} = 89 K
T_b = 4.5 K
2007

How to increase the barrier $U_{eff} = |D|S^2$?

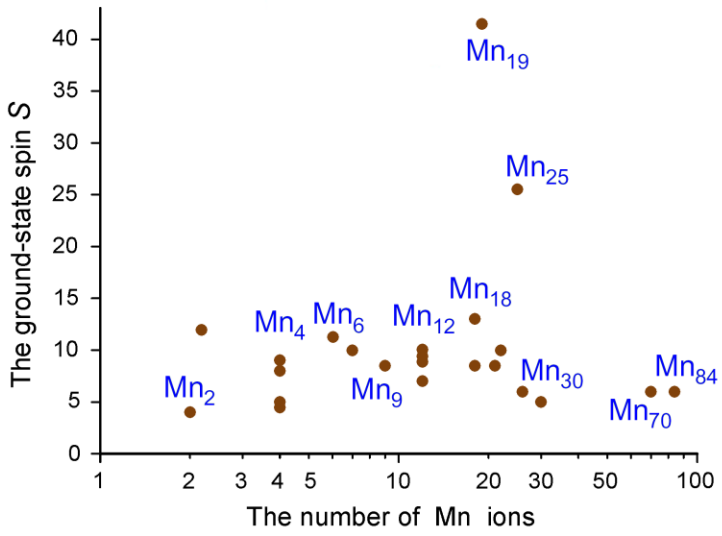
- To increase *S*
- To increase the size of SMM cluster

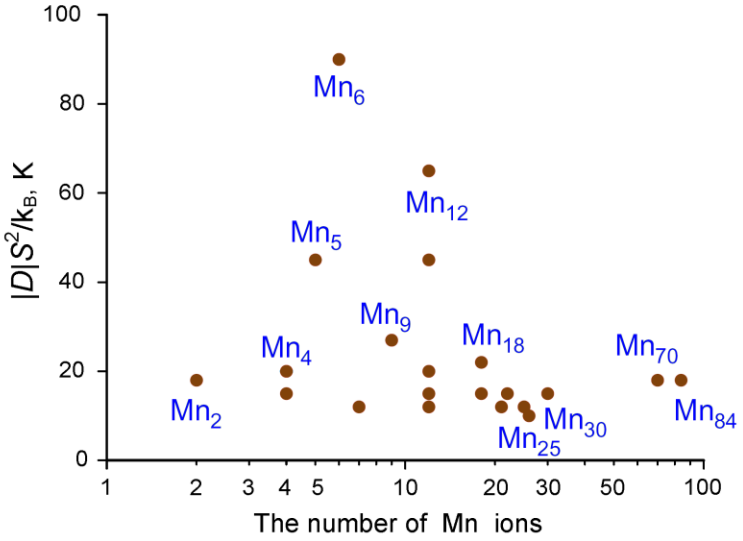
To increase magnetic anisotropy *D*

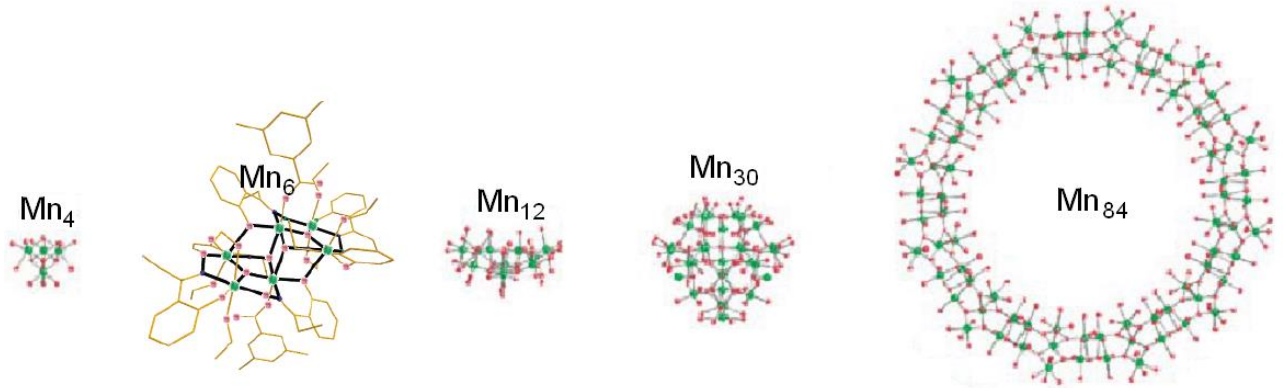
In fact, the barrier $\boldsymbol{U_{eff} = |D|S^2}$ is largely independent on ***S*** and nuclearity : $\boldsymbol{D \sim S^{-2}}$
O. Waldmann, *Inorg. Chem.* **46**, 10350 (2007)

Increasing magnetic anisotropy *D*
is the only way to enhance U_{eff} and T_b !!!

Large size and spin does not necessarily mean large U_{eff} and T_b !







U_{eff}/k_B →	20 K	86 K	65 K	15 K	18 K
T_b →	1.2 K	4.5	3 K	1.2 K	1.5 K

No correlation between the size/spin of the cluster and its SMM characteristics

Very slow progress in increasing the blocking temperature of SMM clusters: It has taken about 15 years to increase T_b from 3K to 4.5 K !!!

Sources of the molecular magnetic anisotropy

Spin Hamiltonian of a SMM cluster:

$$H = \sum_{ij} J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j + \sum_i \boldsymbol{S}_i \boldsymbol{D}_i \boldsymbol{S}_i + \sum_{ij} \boldsymbol{S}_i \boldsymbol{G}_{ij} \boldsymbol{S}_j + \sum_{ij} \boldsymbol{A}_{ij} [\boldsymbol{S}_i \times \boldsymbol{S}_j]$$

Isotropic exchange interaction: forms the spin energy spectrum of a SMM, but does not contribute to the magnetic anisotropy

Single-center magnetic anisotropy: zero-field splitting (ZFS) on separate magnetic centers

Two-center magnetic anisotropy: anisotropic spin coupling between magnetic centers

No contribution to the magnetic anisotropy

Contributions from individual magnetic centers

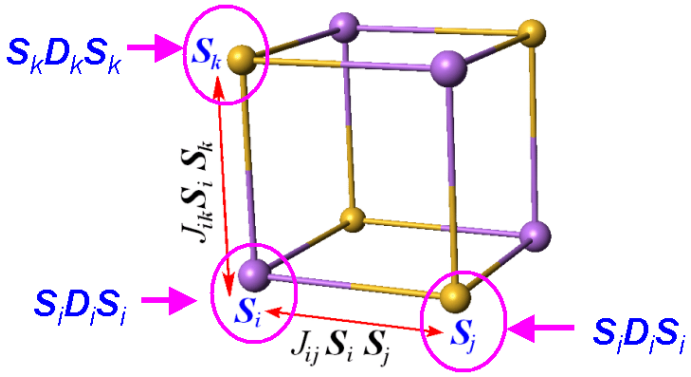
Contributions from exchange-coupled pairs

Alternative approach for designing SMMs

$$H = \sum_{ij} J_{ij} \boldsymbol{S}_i \boldsymbol{S}_j + \sum_i \boldsymbol{S}_i \boldsymbol{D}_i \boldsymbol{S}_i + \sum_{ij} \boldsymbol{S}_i \boldsymbol{G}_{ij} \boldsymbol{S}_j + \sum_{ij} \boldsymbol{A}_{ij} [\boldsymbol{S}_i \times \boldsymbol{S}_j]$$

Conventional approach:

Isotropic exchange interaction + one-center contributions to the molecular magnetic anisotropy: zero-field splitting $S_iD_iS_i$ on separate magnetic centers



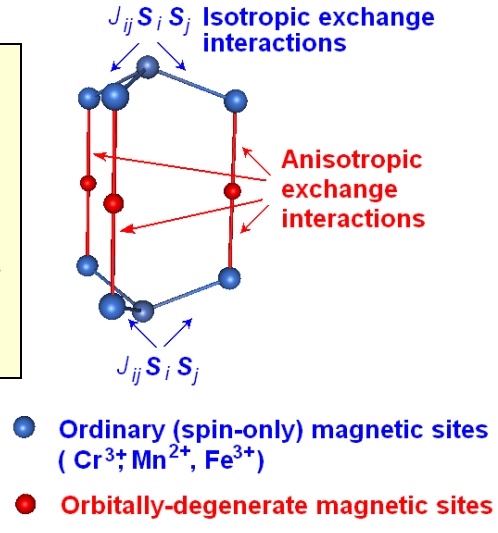
New approach:

Two-center contributions to the molecular magnetic anisotropy: anisotropic exchange interactions

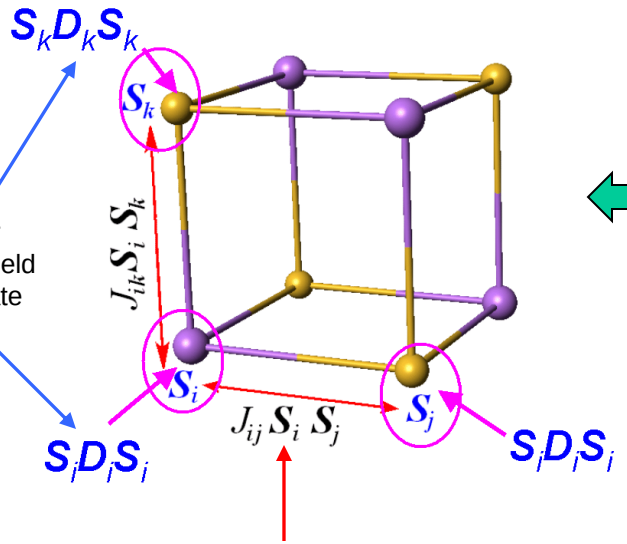
General idea: **The use of strong exchange anisotropy of orbitally-degenerate magnetic sites for designing high-temperature SMM clusters**

V.S. Mironov, L.F. Chibotaru, A. Ceulemans, *J. Amer. Chem. Soc.* **125**, 9750-9760 (2003).

V.S. Mironov, *Dokl. Akad. Nauk* **397**, 155 (2004)



Single-center contributions to the barrier U_{eff}: General limitations



The spin-reversal barrier $U_{eff} = |D|S^2$ is due zero-field splitting $S_iD_iS_i$ on separate magnetic centers (i)

Exchange interactions are isotropic $J_{ij}S_iS_i$

The spin Hamiltonian of the SMM cluster

$$H = \sum_{ij} J_{ij}\boldsymbol{S}_i\boldsymbol{S}_j + \sum_i \boldsymbol{S}_i\boldsymbol{D}_i\boldsymbol{S}_i$$

The maximal value of the barrier U_{eff} is estimated by

$$U_{eff} = |D|S^2 < \sum_i \boldsymbol{S}_i\boldsymbol{D}_i\boldsymbol{S}_i$$

Small ZFS energy $S_iD_iS_j$ makes problematic considerable increase of the magnetic anisotropy D in spin clusters with ordinary (spin-only) magnetic ions

For 3*d* ions ZFS energy is generally limited by $S_iD_iS_i$ < 15 cm^{-1}

Cr^{3+} : $S_iD_iS_i$ ~ 0.1 - 1 cm^{-1}

Mn^{2+},Fe^{3+} : $S_iD_iS_i$ ~ 0.01 – 0.5 cm^{-1}

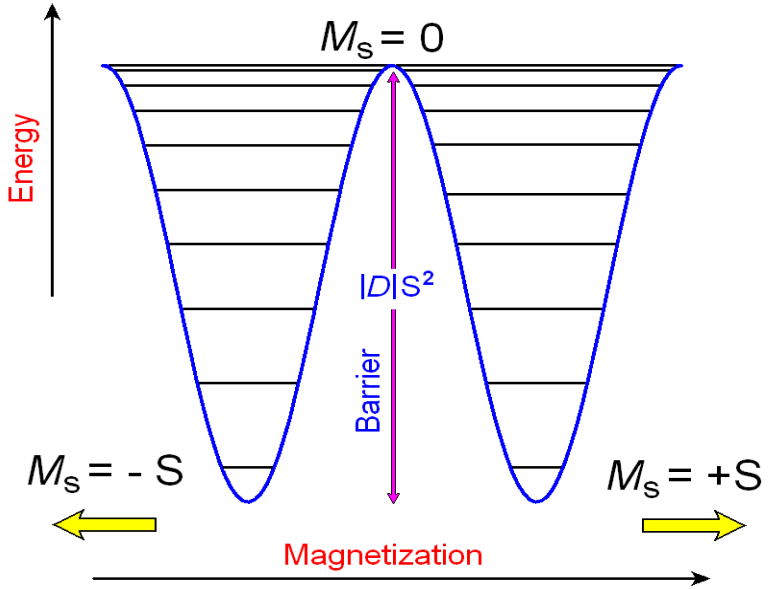
Mn^{3+} : $S_iD_iS_i$ ~ 10-15 cm^{-1}

Ni^{2+}: $S_iD_iS_i$ ~ 1 – 10 cm^{-1}

To obtain $|D|S^2$ ~1000 cm^{-1} (T_b ~ 50-70 K), the spin cluster should involve many hundreds or thousands of magnetic ions:

$$|D|S^2 << \sum_i \boldsymbol{S}_i \boldsymbol{D}_i \boldsymbol{S}_i$$

$|\boldsymbol{D}|\boldsymbol{S}^2$ ~ 1000 cm^{-1} , $\boldsymbol{S}_i\boldsymbol{D}_i\boldsymbol{S}_i$ < 15 cm^{-1} , N >> 100

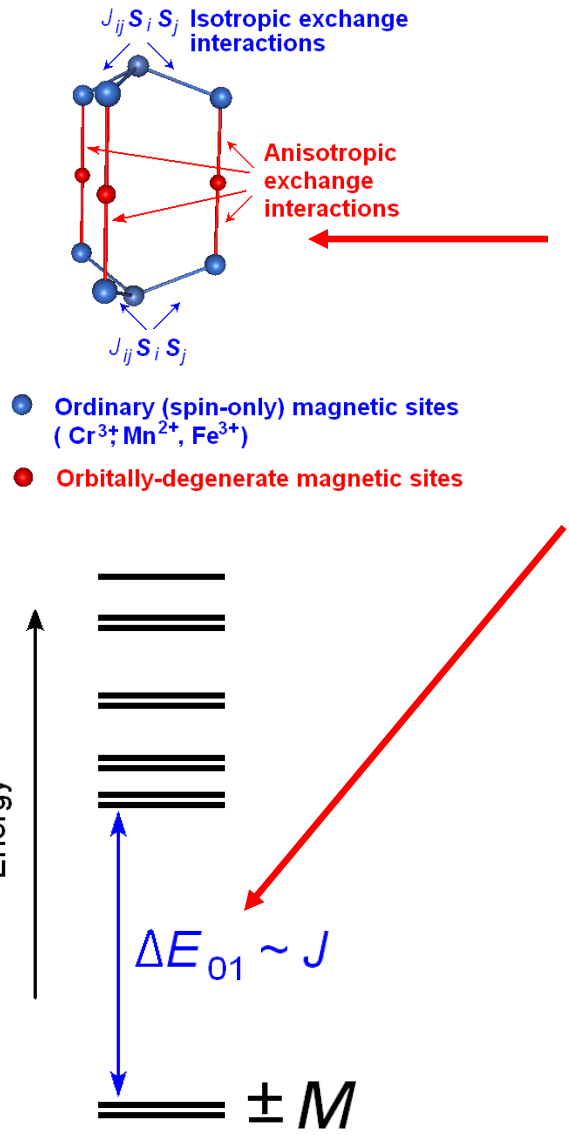


General conclusion:

In medium-size spin clusters (N < 50) with ordinary (spin-only) 3*d* ions (such as Fe^{3+}, Mn^{2+}, Ni^{2+}) the spin-reversal barrier $|D|S^2$ is probably limited to 100-200 cm^{-1} (T_b < 10-15 K)

Single-center ZFS contributions of 3*d* ions are incapable to provide high barrier U_{eff} and blocking temperature T_b !

Alternative approach: Molecular spin clusters based on magnetic centers with unquenched orbital momentum as potential high-T SMMs



General features and conditions:

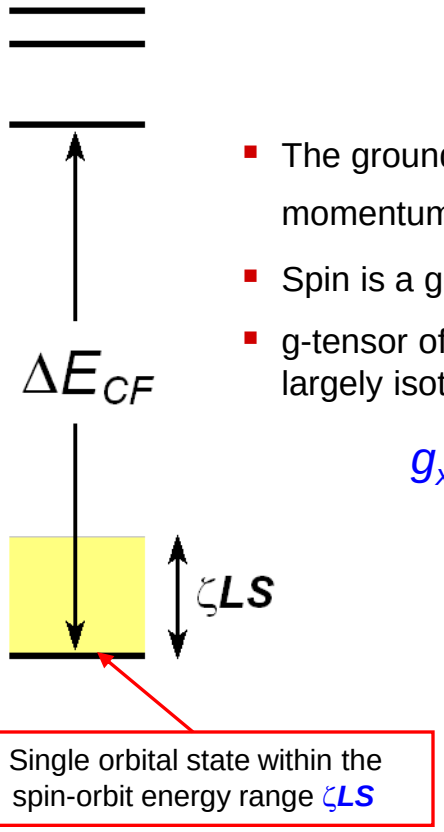
- Small or medium-size molecular spin cluster (N < 30-50) containing magnetic centers with unquenched orbital momentum ($L \neq 0$) that create anisotropic exchange linkages;
- The ground spin level is doubly degenerate ($\pm M$) and is separated by *a large energy gap* ΔE_{01} from the first excited spin level. Large gap ΔE_{01} prevents thermal population of excited spin levels with fast tunneling of magnetization;
- The energy spin spectrum differs considerably from the usual DS^2 double-well pattern.
- The blocking temperature T_b is controlled by the energy gap ΔE_{01}

$$\Delta E_{01}/kT_b \sim 5\text{-}10$$

ΔE_{01} ~ 100 cm^{-1} or more ⇒ T_b > 10 K

Magnetic centers with unquenched orbital momentum: the difference from spin-only magnetic centers

Spin-only magnetic centers, $L = 0$

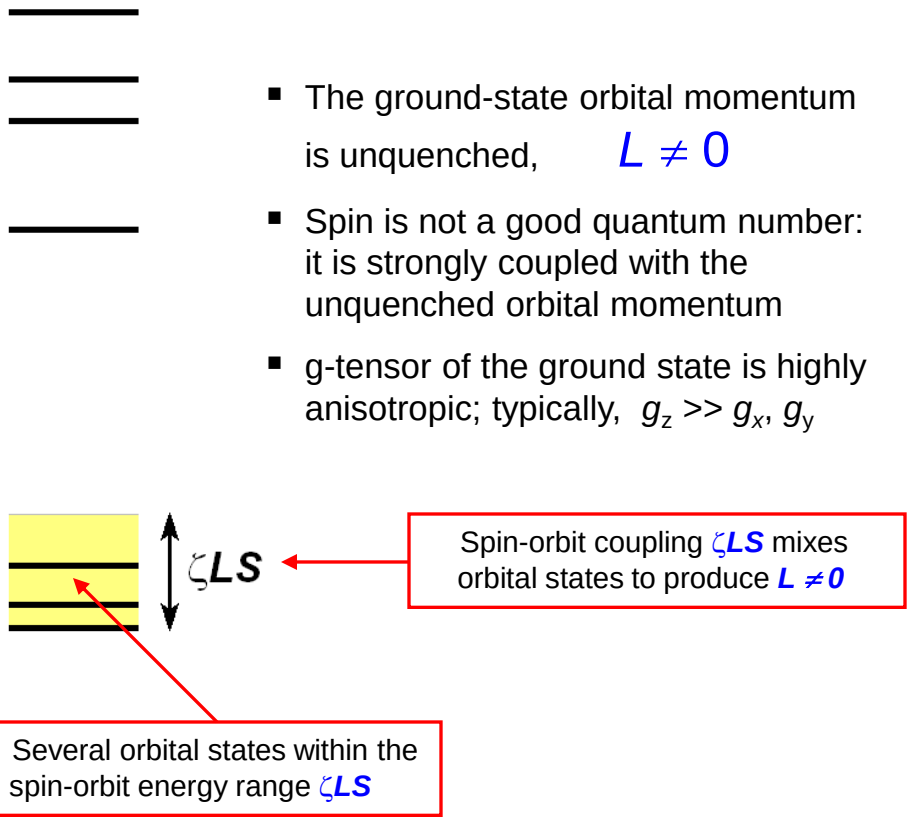


- The ground-state orbital momentum is quenched, $L = 0$
- Spin is a good quantum number
- g-tensor of the ground state is largely isotropic

$g_x, g_y, g_z \sim 2$

Examples: Cr^{3+}, Mn^{2+}, Fe^{3+} (high-spin), Ni^{2+}, Mo^{3+} (high-spin)

Magnetic centers with unquenched orbital momentum, $L \neq 0$



- The ground-state orbital momentum is unquenched, $L \neq 0$
- Spin is not a good quantum number: it is strongly coupled with the unquenched orbital momentum
- g-tensor of the ground state is highly anisotropic; typically, $g_z >> g_x, g_y$

Examples: Rare-earth ions R^{3+} (except Gd^{3+}), Co^{2+}(high-spin), $Fe(CN)_6^{3-}$, $Re(CN)_7^{3-}$

Spin-only magnetic centers: dominant isotropic spin coupling

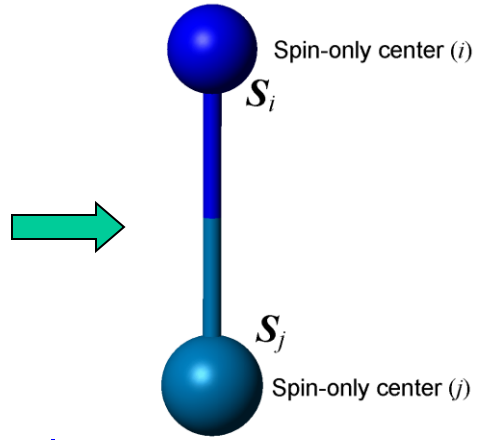
- Most of transition-metal ions - Cr^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+}
- All stable organic radicals

$$H_{ij} = J\boldsymbol{S}_i\boldsymbol{S}_j + \boldsymbol{S}_i\boldsymbol{G}_{ij}\boldsymbol{S}_j + \boldsymbol{A}_{ij}[\boldsymbol{S}_i \times \boldsymbol{S}_j]$$

Isotropic exchange

Symmetric (pseudo-dipolar) part of the anisotropic exchange interaction

Antisymmetric part of the anisotropic exchange: Dzyaloshinsky-Moria term



Isotropic exchange interaction dominates: $|J| >> |\boldsymbol{A}|, |\boldsymbol{G}|$

Anisotropic terms are small. For *d* metal ions anisotropic exchange parameters are estimated by the $\zeta/\Delta E_{CF}$ ratio

$\boldsymbol{S}_i\boldsymbol{G}_{ij}\boldsymbol{S}_j \rightarrow |\boldsymbol{G}/\boldsymbol{J}| \sim (\zeta/\Delta E_{CF})^2$

$\boldsymbol{A}_{ij}[\boldsymbol{S}_i \times \boldsymbol{S}_j] \rightarrow |\boldsymbol{A}/\boldsymbol{J}| \sim \zeta/\Delta E_{CF}$

ζ - spin-orbit coupling constant

ΔE_{CF} – crystal-field splitting energy

$\zeta/\Delta E_{CF} \sim 0.01 - 0.1$

Anisotropic terms of the spin coupling of spin-only 3*d* metal ions weakly contribute to the molecular magnetic anisotropy

Anisotropic spin coupling of magnetic centers with unquenched orbital momentum

Examples:

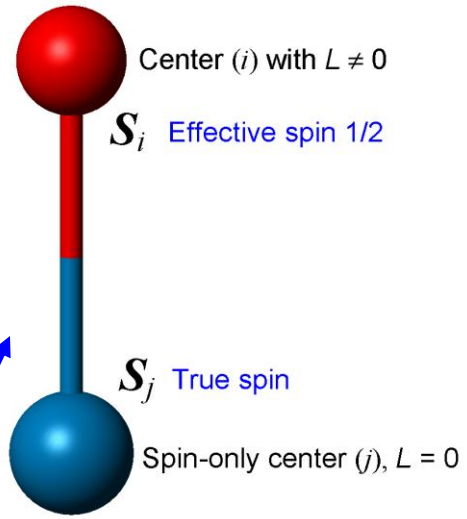
- *f* ions - lanthanides and actinides - Ce^{3+}, Nd^{3+}, Tb^{3+}, Dy^{3+}, Yb^{3+}, U^{4+}
- Orbitally degenerate *d* ions and complexes – Co^{2+}, $[Mo^{III}(CN)_7]^{4-}$, $[Fe(CN)_6]^{3-}$

Exchange interactions are strongly anisotropic

$$H_{ij} = JS_iS_j + S_iG_{ij}S_j + A_{ij}[S_i \times S_j]$$

Isotropic and anisotropic exchange interactions are generally comparable in magnitude !!!

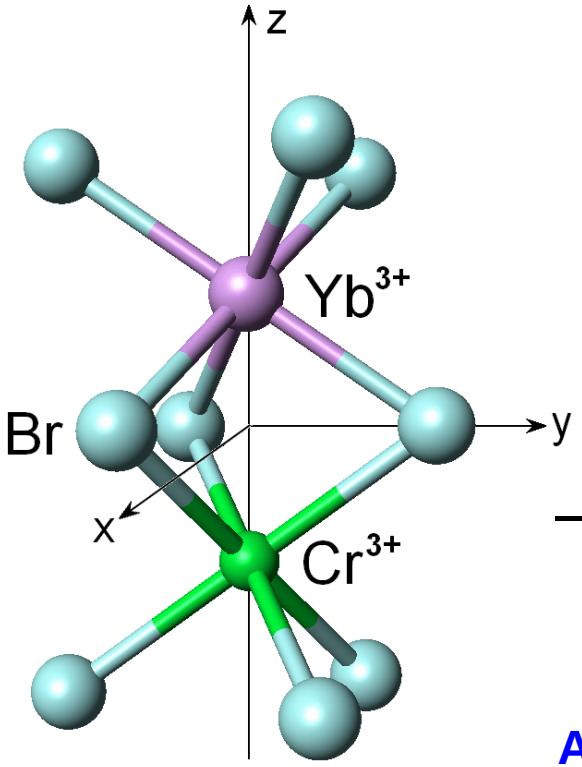
$$|J| \sim |G| \sim |A|$$



The resulting magnetic moment is strongly coupled with the molecular axis of the exchange-coupled pair **(*i*, *j*)**

Strong contribution of anisotropic spin coupling to the molecular magnetic anisotropy

Highly anisotropic 4*f*-3*d* exchange interaction in a mixed dimer $YbCrBr_9^{3-}$



The $YbCrBr_9^{3-}$ dimer

$Yb^{3+} \Rightarrow 4f^{13}$,S_{Yb}=1/2 **$Cr^{3+} \Rightarrow 3d^3$, S_{Cr}=3/2**

Orbitally degenerate **Spin only**

Exchange parameters J_z and J_{xy} have opposite signs!

$$-J_z S^z_{Yb} S^z_{Cr} - J_{xy}\left(S^x_{Yb} S^x_{Cr} + S^y_{Yb} S^y_{Cr}\right)$$

J_z = - 5.16 cm^{-1} **Antiferromagnetic**

J_{xy} = + 4.19 cm^{-1} **Ferromagnetic**

Exchange anisotropy is so strong that the overall sign of the Yb^{3+} - Cr^{3+} spin coupling is uncertain !

Experiment: M. A. Aebersold et al, *Phys. Rev. B* **48**, 12723 (1993).

Theory : V.S. Mironov, L.F. Chibotaru, A. Ceulemans, *Phys. Rev. B* **67**, 014424 (2003).

How to select proper orbitally-degenerate magnetic centers for designing SMM? A criterion

The efficiency of orbitally-degenerate magnetic centers for designing high-T SMM clusters can be measured by the *Jr* factor :

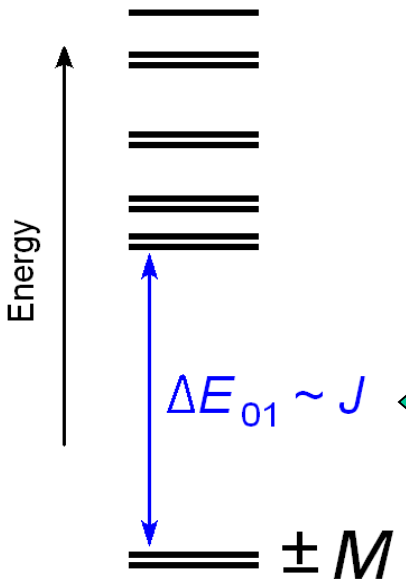
Jr

where ***J*** is the absolute exchange parameter and **0 < *r* < 1** is a dimensionless factor describing the degree of the exchange anisotropy, i.e.

$$H = J_0 \boldsymbol{S}_i \boldsymbol{S}_j + \boldsymbol{S}_i \boldsymbol{G} \boldsymbol{S}_j + \boldsymbol{A}[\boldsymbol{S}_i \times \boldsymbol{S}_j]$$

$$J = \left[|J_0|^2 + |\boldsymbol{G}|^2 + |\boldsymbol{A}|^2 \right]^{1/2}$$

$$r = \left[\frac{|\boldsymbol{G}|^2 + |\boldsymbol{A}|^2}{|J_0|^2 + |\boldsymbol{G}|^2 + |\boldsymbol{A}|^2} \right]^{1/2}$$



The ***Jr*** factor measures the contribution to the molecular magnetic anisotropy and estimates maximal energy gap ΔE_{01} in a molecular spin cluster

For the axial symmetry:

$$H = -J\left((1-r)\boldsymbol{S}_1\boldsymbol{S}_2 + rS_1^zS_2^z\right)$$

$r = 0 \rightarrow$ Heisenberg

$r = 1 \rightarrow$ Ising

Jr factor for various orbitally-degenerate magnetic building blocks: a comparison

Rare-earth ions (4f): Yb^{3+}, Dy^{3+}, Ce^{3+}, Er^{3+}, Tb^{3+} $\Rightarrow$ *Jr* < 10 cm^{-1}

- high exchange anisotropy (r ~ 1), but weak exchange interactions (J <10 cm^{-1})

Generally, 4f ions are poor candidates for designing high-T SMM

Orbitally-degenerate 3*d* ions and complexes: Co^{2+}, Cr^{2+}, V^{3+}, $[Fe^{III}(CN)_6]^{3-}$ $\Rightarrow$ *Jr* ~ 10-50 cm^{-1}

- weak exchange anisotropy (r ~ 0.1- 0.5), rather strong exchange interactions (J ~10-100 cm^{-1})

These systems are more suitable than 4f ions, but their potentialities are rather limited

Orbitally-degenerate 4*d* and 5*d* complexes: $\Rightarrow$ *Jr* > 100 cm^{-1}

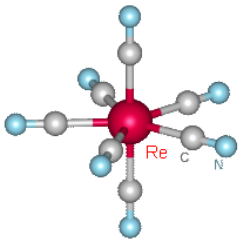
- high exchange anisotropy (r ~ 1), strong exchange interactions

(J ~100 -300 cm^{-1} and more)

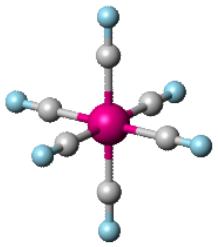
These systems are the best candidates for designing high-T SMM !!!

Orbitally degenerate 5*d* complexes are especially promising

Examples: $[Re^{IV}(CN)_7]^{3-}$ and $[Os^{III}(CN)_6]^{3-}$ cyanocomplexes



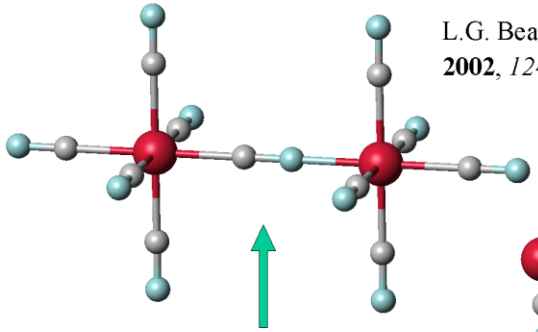
$[Re^{IV}(CN)_7]^{3-}$



$[Os^{III}(CN)_6]^{3-}$

4*d* and 5*d* magnetic centers provide strong exchange interactions, $J > 100\ cm^{-1}$

$Mo^{III}_2(CN)^{5-}_{11}$



L.G. Beauvais *et al J. Am. Chem. Soc.* **2002**, *124*, 2110

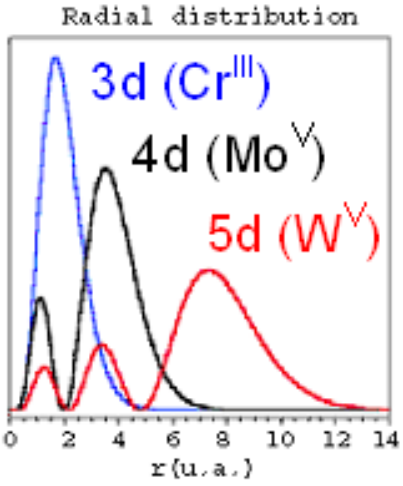
$Mo^{III}(4d^3)$, $S = 3/2$

C

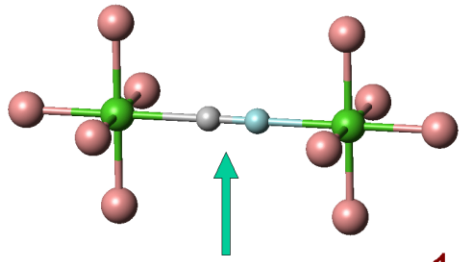
N

$J = -226\ cm^{-1}$

General reason: **4*d* and 5*d* magnetic orbitals are more diffuse than 3*d* orbitals. They overlap much better with the valence orbitals of bridging groups thus providing much higher exchange parameters for a similar molecular geometry**



$[(NH_3)_5Cr^{III}CN\,Cr^{III}(NH_3)_5]^{5+}$



J. Glerup *et al Acta Chem. Scand.* **1991**, *45*, 444.

$Cr^{III}(3d^3)$, $S = 3/2$

NH_3

C

N

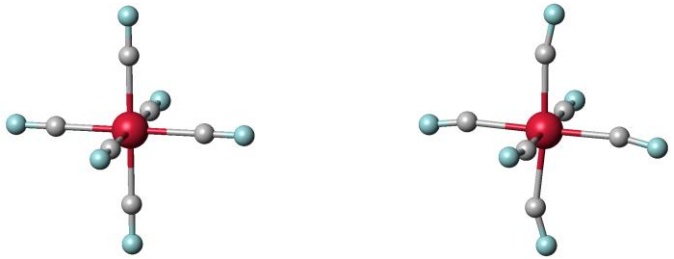
$J = -32\ cm^{-1}$

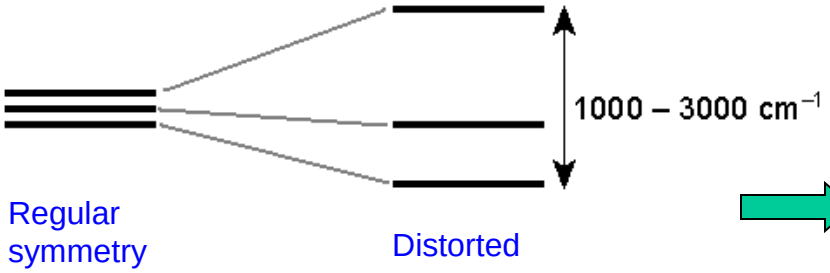
Strong spin-orbit coupling is highly preferable

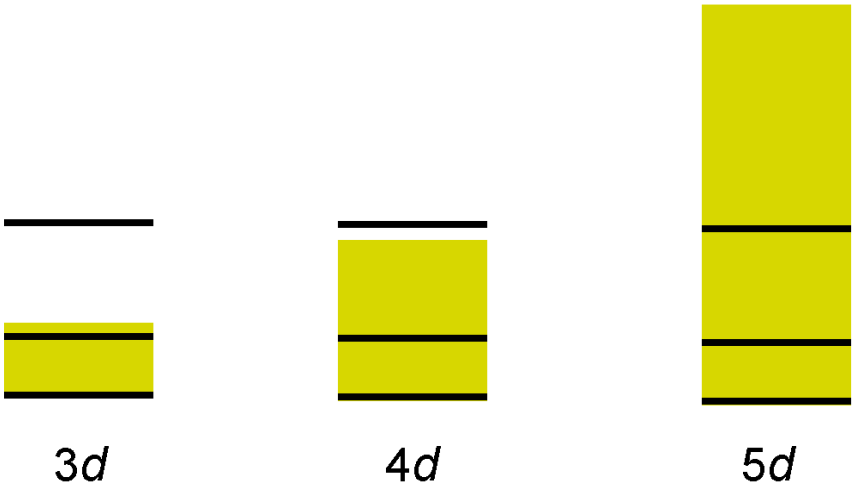
Low-symmetry distortions tend to quench orbital momentum → **negative influence**

Strong spin-orbit coupling favors for unquenched orbital momentum → **positive influence**

3*d*: $\zeta_{3d} \sim$ 100-500 cm^{-1}, **4*d*:** $\zeta_{4d} \sim$ 1000 cm^{-1}, and **5*d*:** $\zeta_{5d} \sim$ 2000-3000 cm^{-1}







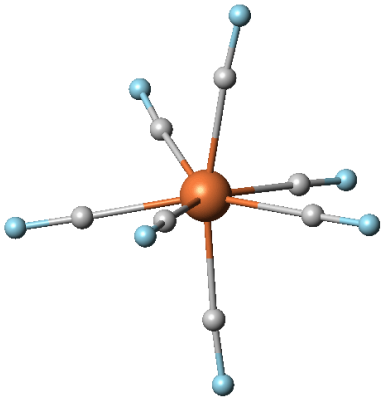
In real molecular clusters orbitally-degenerate complexes are often distorted. Distortions lift the orbital degeneracy of ground level. The orbital splitting is typically 1000 – 3000 cm^{-1}

Relation between the orbital splitting energy and the spin-orbit splitting energy (yellow) in 3*d*, 4*d*, and 5*d* complexes:

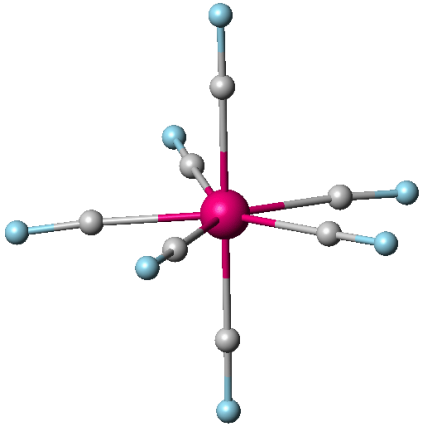
Spin-orbit splitting must be larger than the orbital splitting !

In 3*d* orbitally-degenerate complexes distortions quench the orbital momentum, while in 5*d* complexes the orbital momentum remains unquenched. In 4*d* complexes the situation is intermediate

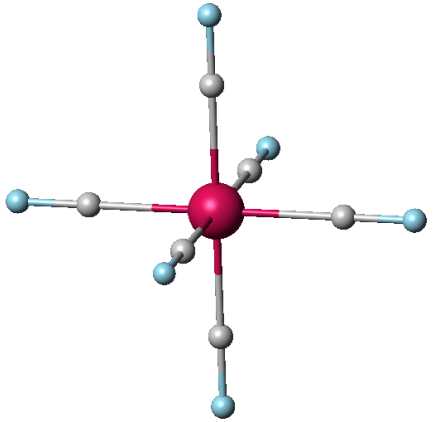
Orbitally-degenerate 4*d* and 5*d* cyanocomplexes : molecular building blocks with high magnetic anisotropy (large ***Jr*** factor)



$Mo^{III}(CN)_7^{4-}$



$Re^{IV}(CN)_7^{3-}$



$Os^{III}(CN)_6^{3-}$

Advantages:

- **High exchange parameters *J* with attached high-spin 3d ions (Cr^{3+}, Mn^{2+}),**
- **Strong exchange anisotropy for apical M-CN linkages (Ising-like, *r* ~ 1)**

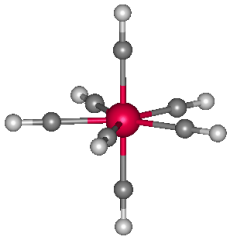
Jr ~ 100 cm^{-1}

Disadvantages:

- **Too large number of coordination positions is unfavorable for obtaining clusters; very often 3D or 2D polymer structures are formed;**
- **Weak exchange anisotropy for the equatorial M-CN linkages in $Mo^{III}(CN)_7^{4-}$ and $Re^{IV}(CN)_7^{3-}$;**
- **$Mo^{III}(CN)_7^{4-}$ is strongly distorted – this reduces the magnetic anisotropy (small *r* parameter);**
- **$Re^{IV}(CN)_7^{3-}$ and $Os^{III}(CN)_6^{3-}$ are oxidizers; they are incompatible with many high-spin 3*d* ions (V^{2+}, V^{3+}, Cr^{2+}, Fe^{2+}) providing high exchange parameters *J*.**

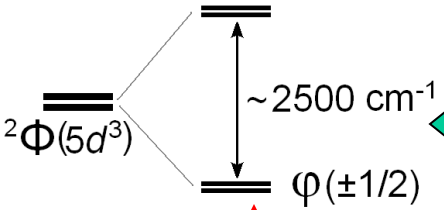
Orbitally degenerate $[Re^{IV}(CN)_7]^{3-}$ pentagonal-bipyramidal heptacyano complex: the electronic structure and magnetic properties

$[Re^{IV}(CN)_7]^{3-}$ is an almost regular pentagonal bipyramid



$[Re(CN)_7]^{3-}$

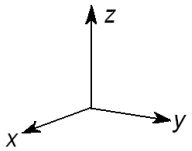
$5d^3 \quad S = 1/2$

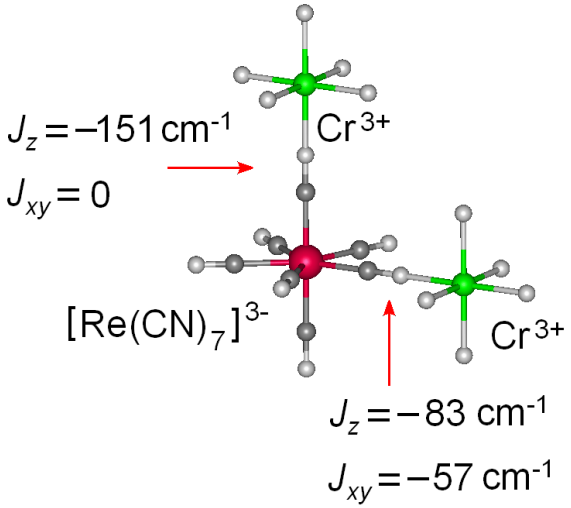


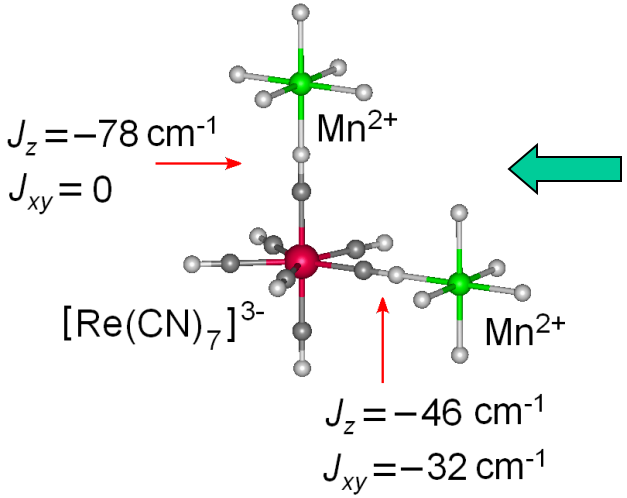
The spin-orbit splitting of the ground orbital doublet $^2\Phi(5d^3)$ of Re^{IV}

The ground Kramers doublet with the effective spin S = 1/2

$$\boldsymbol{H} = -J_z S^z_{5d} S^z_{3d} - J_{xy}(S^x_{5d} S^x_{3d} + S^y_{5d} S^y_{3d})$$





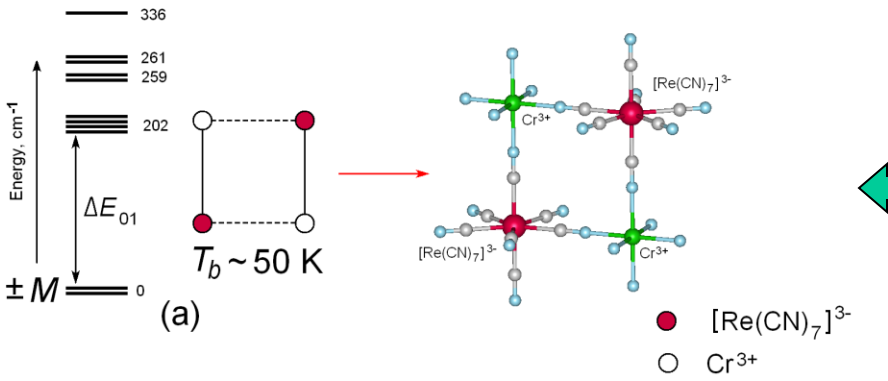


Re-CN-M(3*d*) exchange interactions are highly anisotropic with large exchange parameters. This corresponds to a large *Jr* factor

Jr ~ 100-150 cm^{-1}

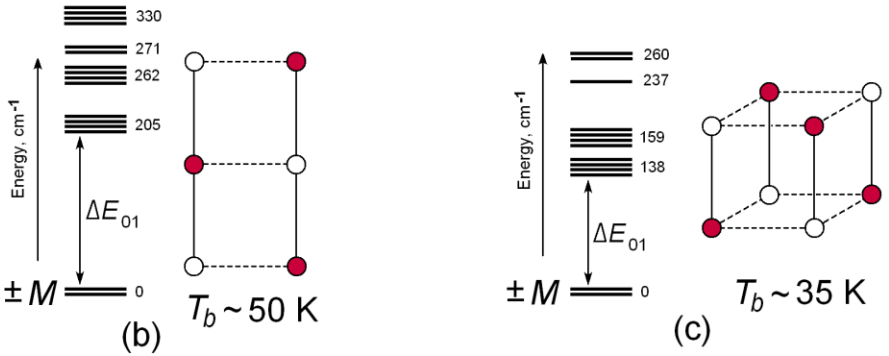
V.S. Mironov, *Dokl. Akad. Nauk* **408**, 130 (2006)

5*d*-3*d* spin clusters with orbitally degenerate $[Re^{IV}(CN)_7]^{3-}$ complexes: Potential high-T single-molecule magnets



In mixed $(Re_n\text{-}Cr)_n$ (n =2,3,4) cyano-bridged clusters with orbitally-degenerate $[Re(CN)_7]^{3-}$ building blocks the energy gap ΔE_{01} can reach a value of 200 cm^{-1}. This corresponds to the blocking temperature of T_b ~ 25-50 K:

$\Delta E_{01} \approx 200\ cm^{-1}$, $T_b \approx 25\text{-}50$ K.

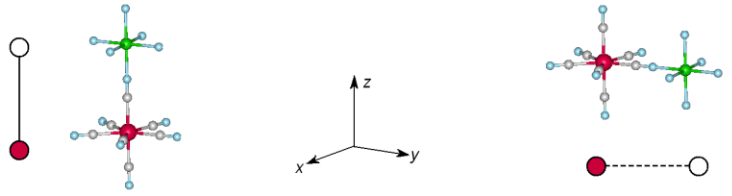


T_b is estimated from the ratio

$$\Delta E_{01}/kT_b \sim 5\text{-}10$$

In $Mn_{12}Ac$:

$\Delta E_{01} \approx 9\ cm^{-1}$ (13 K), $T_b \approx 3$ K.



$J_z = -151\ cm^{-1}$

$J_{xy} = 0$

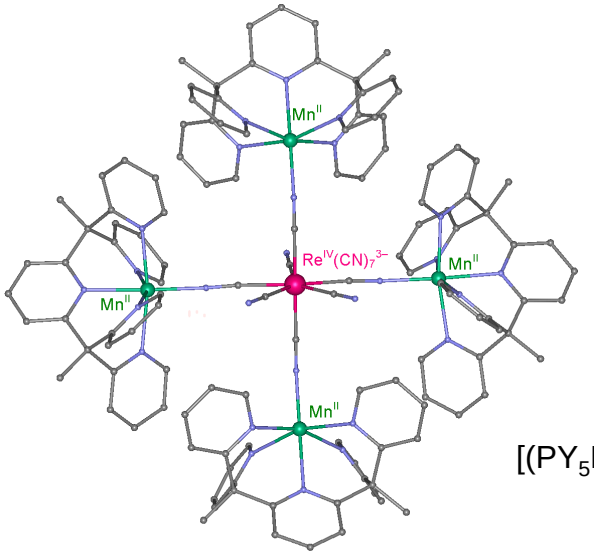
$J_z = -83\ cm^{-1}$

$J_{xy} = -57\ cm^{-1}$

$$\hat{H} = -J_z S^z_{5d} S^z_{3d} - J_{xy}(S^x_{5d} S^x_{3d} + S^y_{5d} S^y_{3d})$$

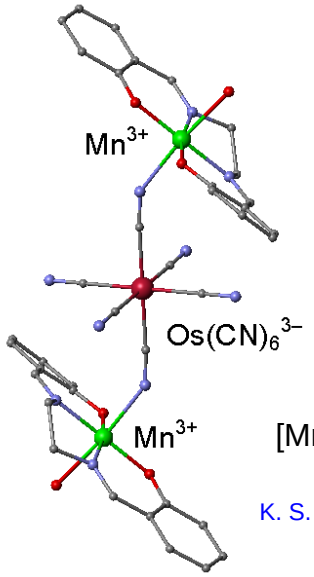
V.S. Mironov, *Dokl. Akad. Nauk* **408**, 130 (2006)

Experimentally characterized molecular spin clusters based on 4*d* and 5*d* orbitally-degenerate complexes $Mo^{III}(CN)_7^{4-}$, $Re^{IV}(CN)_7^{3-}$, and $Os^{III}(CN)_6^{3-}$



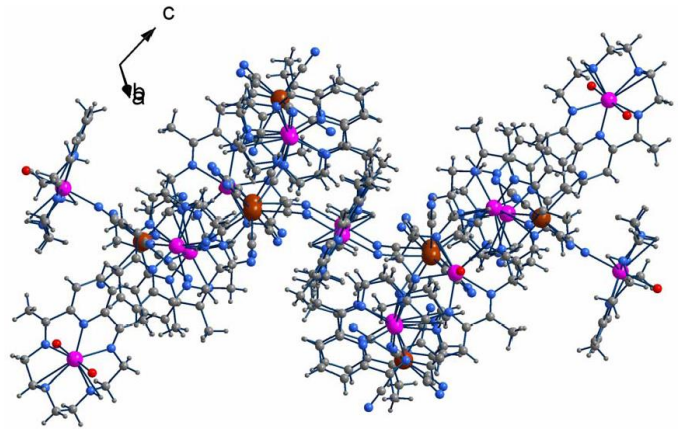
$[(PY_5Me_2)_4Mn_4Re(CN)_7]^{4+}$

$[PY5Me_2)_4Mn_4Re(CN)_7]^{4+}$ cluster
D.E. Fredman, D.M. Jenkins A.T. Iavarone, and J.R. Long,
J. Am.Chem.Soc. **130**, 2884 (2008).



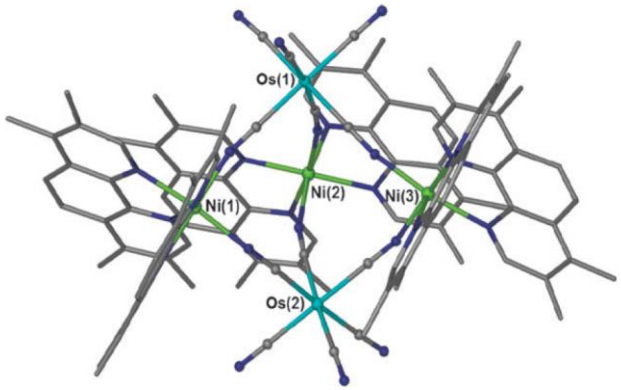
$[Mn^{III}_2(5\text{-Brsalen})_2Os^{III}(CN)_6]$

K. S. Pedersen et al. *Chem. Eur. J.* **2010**, 16, 13458



$[Mn(dpop)(H_2O)_2]_2\{[Mo(CN)_7]_8[Mn(dpop)]_{10}[Mn(dpop)(H_2O)]_4\}$

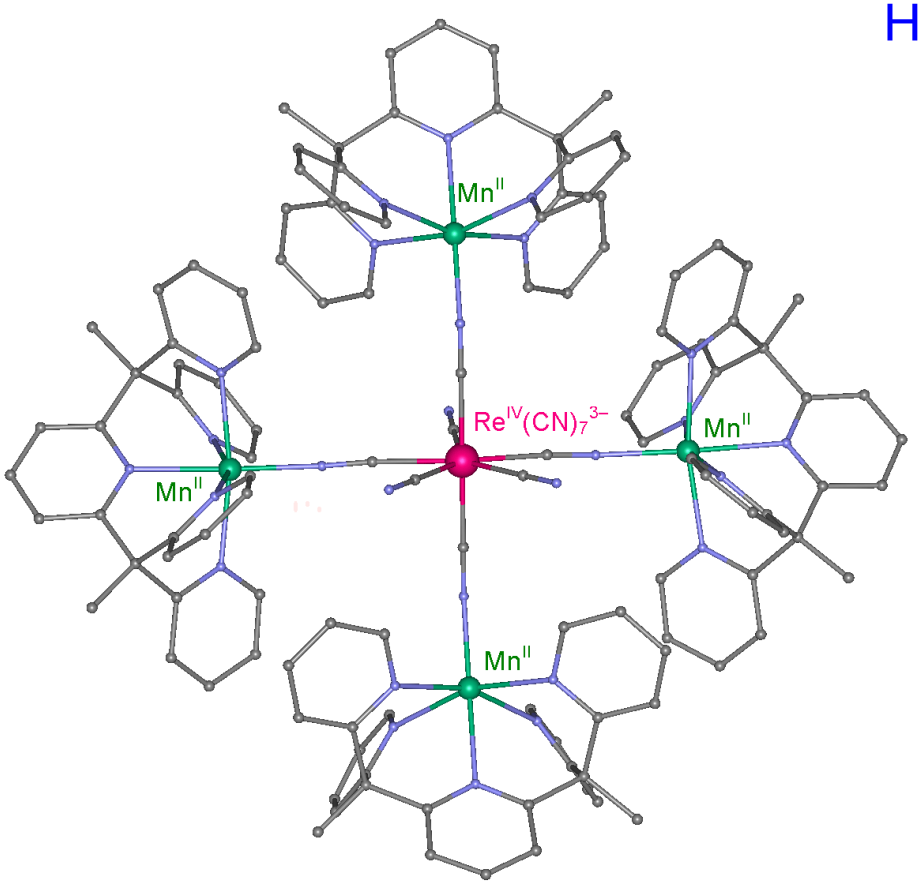
K.R.Dunbar et. al. *Angew. Chem. Int. Ed.* **2010**, 49, 5013.



$Ni_3[Os(CN)_6]_2$

M.G.Hilfiger et. al. *Chem. Commun.* **2008**, 5752.

Direct experimental evidence : the $[(PY5Me_2)_4Mn_4Re(CN)_7]^{4+}$ cyano-bridged SMM cluster



$[PY5Me_2)_4Mn_4Re(CN)_7]^{4+}$ cluster
D.E. Fredman, D.M. Jenkins A.T. Iavarone, and J.R. Long, *J. Am.Chem.Soc.* **130**, 2884 (2008).

High spin-reversal barrier, U_{eff} ~ 33 cm^{-1}

U_{eff} is the largest among small SMM clusters!

Important !!!

The $[(PY5Me_2)_4Mn_4Re(CN)_7]^{4+}$ cluster has no one-center (ZFS) contribution to the molecular magnetic anisotropy since the ZFS energies on Re and Mn sites are too small:

SDS = 0 for $Re(CN)_7^{3-}$, S = 1/2

SDS < 1 cm^{-1} for Mn^{2+}, S = 5/2

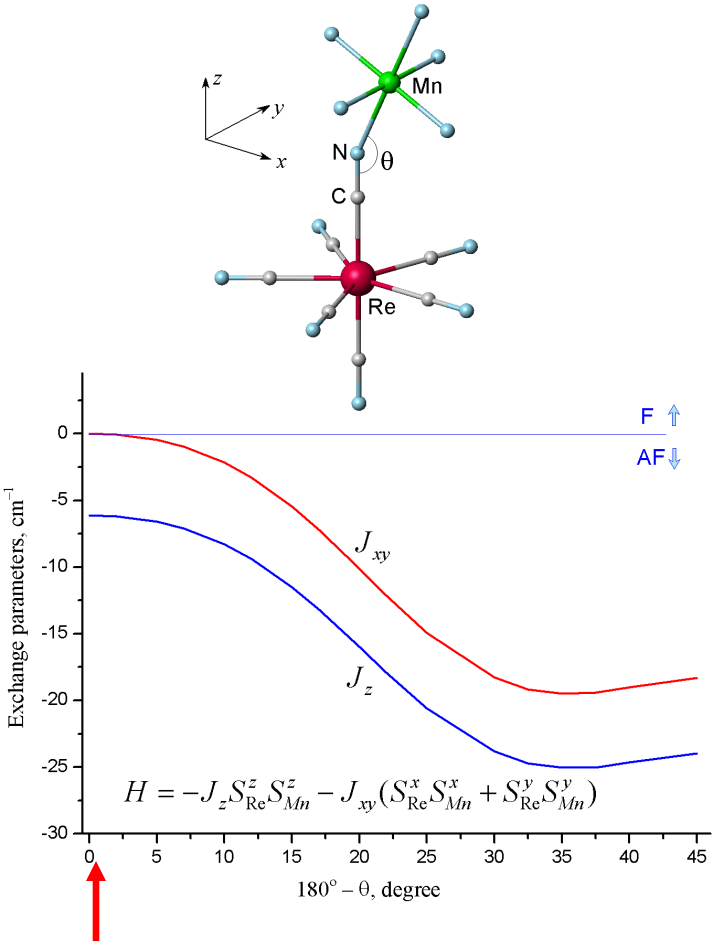
Conclusion:

The spin-reversal barrier of U_{eff} ~ 33 cm^{-1} is entirely due to anisotropic exchange interactions of the Re^{IV}-CN-Mn^{II} linkages

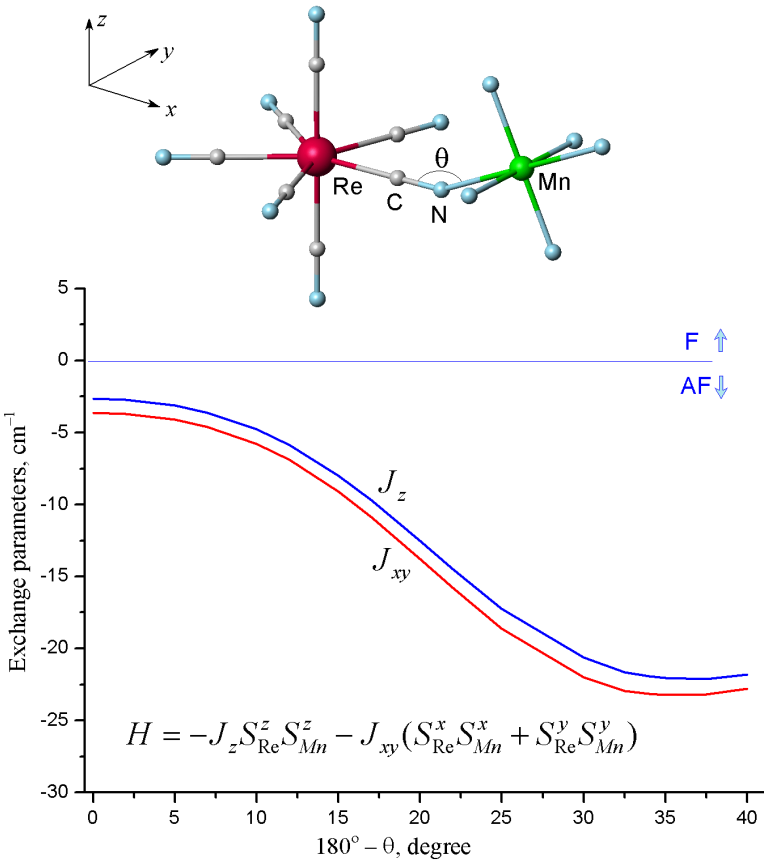
Anisotropic exchange parameters are sensitive to the bending of the CN bridging groups

$[Re^{IV}(CN)_7^{3-}]$ – Mn^{3+} anisotropic exchange interaction

$$H = -J_z S_{Re}^z S_{Mn}^z - J_{xy}(S_{Re}^x S_{Mn}^x + S_{Re}^y S_{Mn}^y)$$



Ising-like spin coupling $J_z S_{Re}^z S_{Mn}^z$ occurs only for the apical Re-CN-Mn pairs with the linear geometry

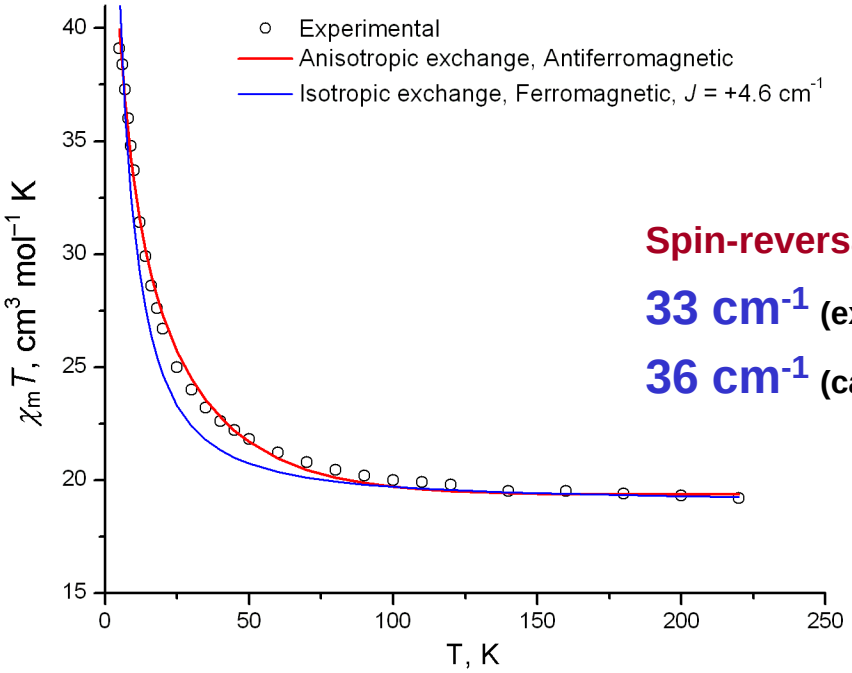


Exchange interaction is nearly isotropic in the equatorial Re-CN-Mn pairs, $J_z \approx J_{xy}$

V.S. Mironov, JACS., *submitted*

Modeling magnetic and SMM properties of the $[(PY5Me_2)_4Mn_4Re(CN)_7]^{4+}$ cluster

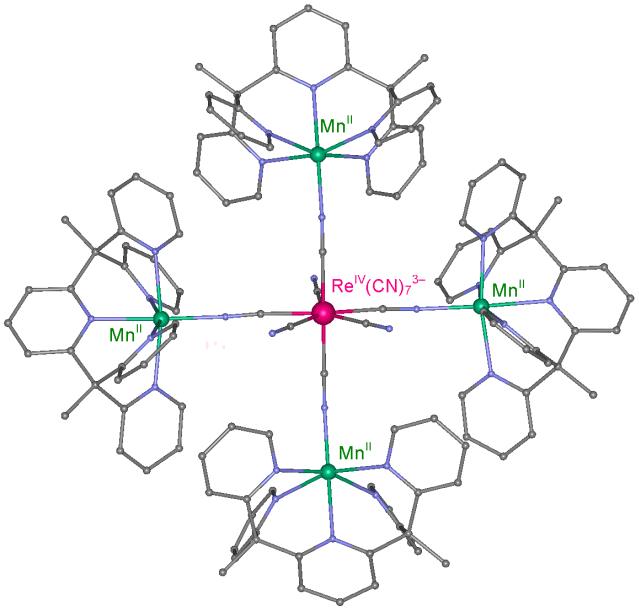
Formally, magnetic behavior looks as weakly ferromagnetic, J =+4.6 cm^{-1}



Spin-reversal barrier U_{eff} :

33 cm^{-1} (experimental)

36 cm^{-1} (calculated)



$[PY5Me_2)_4Mn_4Re(CN)_7]^{4+}$ cluster
D.E. Fredman, D.M. Jenkins A.T. Iavarone, and J.R. Long, *J. Am.Chem.Soc.* **130**, 2884 (2008).

Actually, Re^{IV}-CN-Mn^{II} exchange interactions are highly anisotropic

$$H = -J_z S^z_{\mathrm{Re}} S^z_{Mn} - J_{xy}\left(S^x_{\mathrm{Re}} S^x_{Mn} + S^y_{\mathrm{Re}} S^y_{Mn}\right)$$

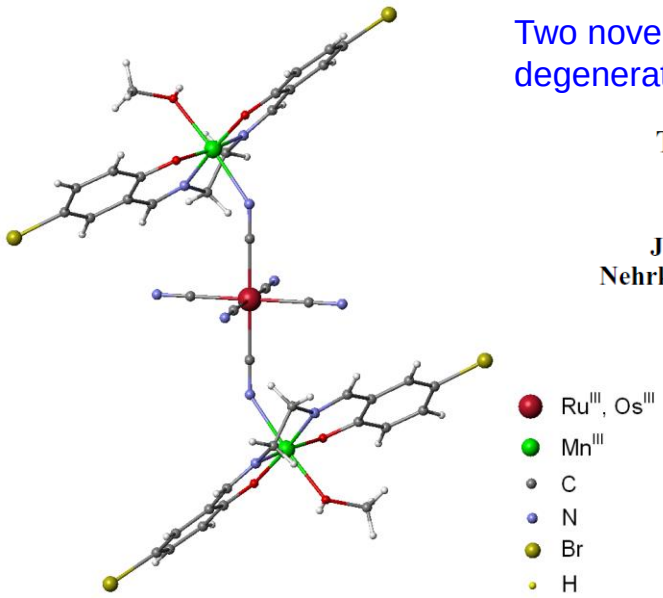
Anisotropic exchange parameters J_z, J_{xy} are all antiferromagnetic !!!

J_z = -32, J_{xy} = -11 cm^{-1} apical Re-CN-Mn pairs

J_z = -6.5, J_{xy} = -9.0 cm^{-1} equatorial Re-CN-Mn pairs

V.S. Mironov, JACS., *submitted*

Trinuclear SMMs $[Mn^{III}_2(5\text{-Brsalen})_2(MeOH)_2M^{III}(CN)_6]$ (M=Ru, Os)



Two novel trinuclear Mn-Ru-Mn and Mn-Os-Mn SMM clusters based on orbitally degenerate $Ru^{III}(CN)_6^{3-}$ and $Os^{III}(CN)_6^{3-}$ complexes are obtained and characterized:

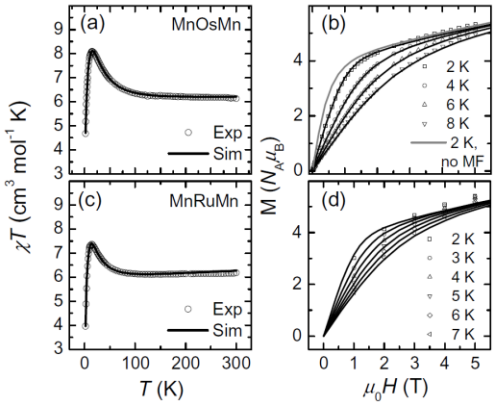
Three-Axis Anisotropic Exchange Coupling in the Single-Molecule Magnets $(NEt_4)[Mn^{III}_2(5\text{-Brsalen})_2(MeOH)_2M^{III}(CN)_6]$, M = Ru, Os

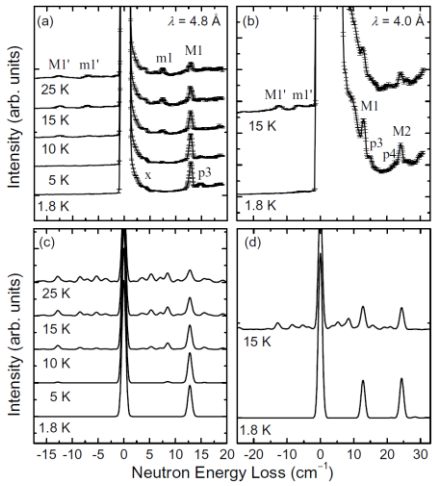
Jan Dreiser,*[a,b] Kasper S. Pedersen,[c] Alexander Schnegg,[d] Karsten Holldack,[e] Joscha Nehrkorn,[a] Marc Sigrist[f], Philip Tregenna-Piggott,[g]† Hannu Mutka,[f] Høgni Weihe,[c] Vladimir S. Mironov,[h] Jesper Bendix,[c] and Oliver Waldmann*[a]

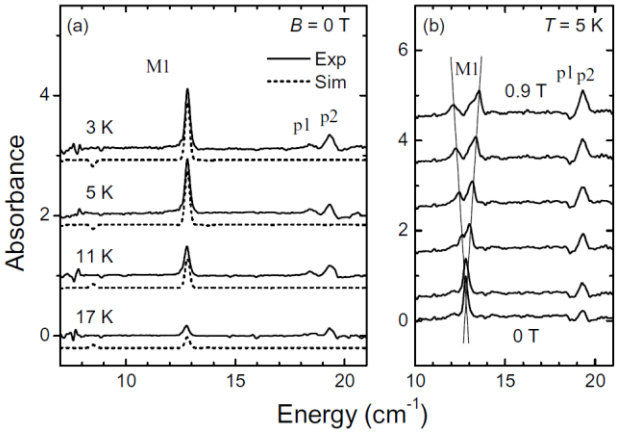
Chem. Eur. J., 19, 3693 (2013)

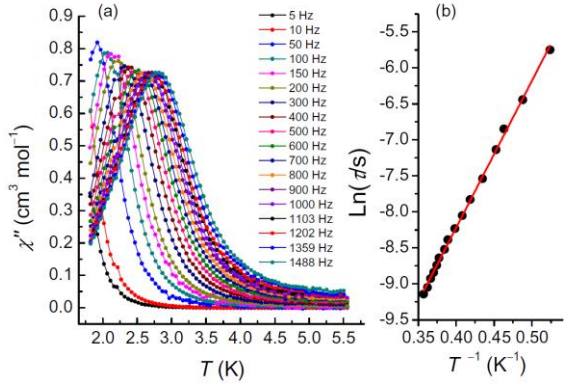
- Magnetic susceptibility
- Field-dependent magnetization
- INS spectroscopy
- THz EPR spectroscopy
- Relaxation AC measurements

U_{eff} = 11.8 cm^{-1} (Ru), 14.2 cm^{-1} (Os)





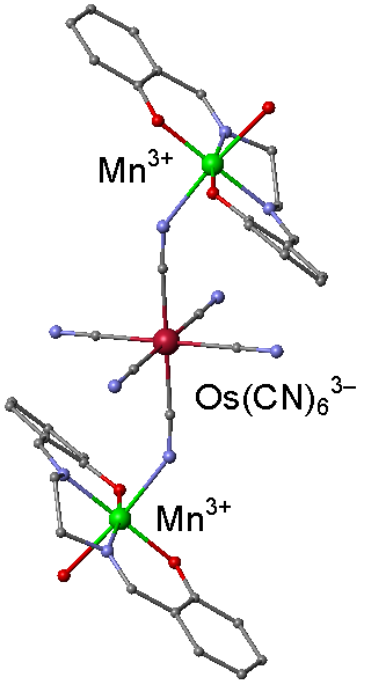




Extremely anisotropic three-axis spin coupling in Ru^{III}-CN-Mn^{III} and Os^{III}-CN-Mn^{III} pairs

$$H = -J_x S^x_{Os} S^x_{Mn} - J_y S^y_{Os} S^y_{Mn} - J_z S^z_{Os} S^z_{Mn}$$

Exchange parameters J_x , J_z and J_y have opposite signs!



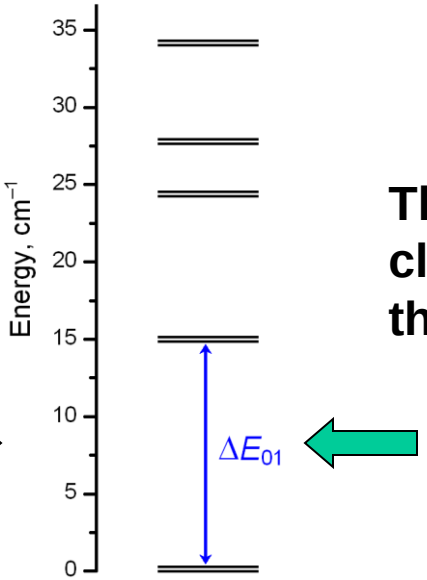
Ru^{III}-CN-Mn^{III}

J_x = -20 cm^{-1} AF
J_y = +25 cm^{-1} Ferro
J_z = -26 cm^{-1} AF

Os^{III}-CN-Mn^{III}

J_x = -18 cm^{-1} AF
J_y = +35 cm^{-1} Ferro
J_z = -33 cm^{-1} AF

The spin energy spectrum differs drastically from the usual DS^2 pattern

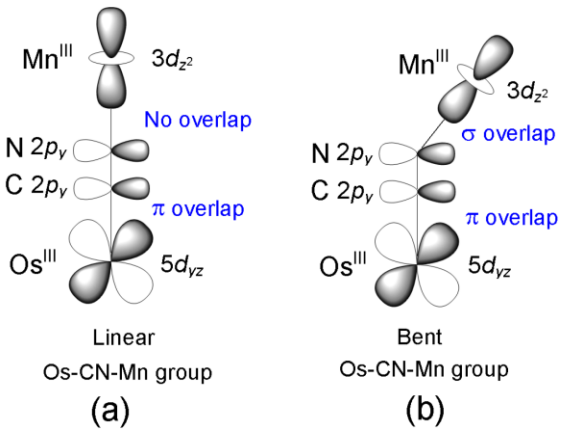


The spin-reversal barrier U_{eff} is very close to the energy position ΔE_{01} of the first excited spin state

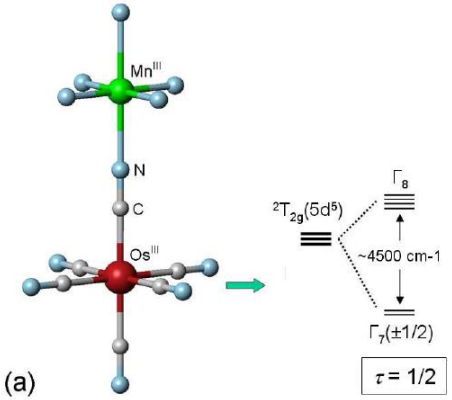
U_{eff} = 11.8 cm^{-1} MnRuMn
U_{eff} = 14.2 cm^{-1} MnOsMn

Three-axis exchange anisotropy is due to bending of the Os-CN-Mn group

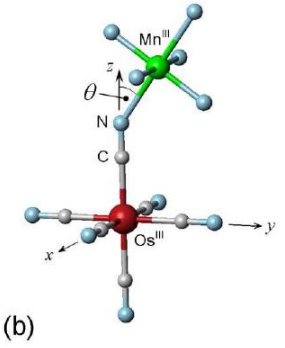
The key reason: a very efficient superexchange pathway of mixed σπ-type opens up in the bent Os-CN-Mn group



Uniaxial Ising-like spin Hamiltonian transforms to a three-axis spin Hamiltonian upon bending the Os-CN-Mn bridging group



$$H_{eff} = -J_{\perp}(\tau^x S^x + \tau^y S^y) - J_{zz}\tau^z S^z$$



$$H_{eff} = -J_{xx}\tau^x S^x - J_{yy}\tau^y S^y - J_{zz}\tau^z S^z$$

Orbitally-dependent exchange spin Hamiltonian for the ground $^2T_{2g}(5d^5)$ orbital triplet of $Os(CN)_6^{3-}$

Anisotropic exchange spin Hamiltonian H_{eff} for the ground Kramers doublet $\Gamma_7(\pm 1/2)$ of $Os(CN)_6^{3-}$

$$H = -\begin{pmatrix} J_1 & 0 & 0 \\ 0 & J_2 & 0 \\ 0 & 0 & J_3 \end{pmatrix} \boldsymbol{S}_{Os}\boldsymbol{S}_{Mn} \quad \Rightarrow \quad H_{eff} = -J_x\tau^x_{Os}S^x_{Mn} - J_y\tau^y_{Os}S^y_{Mn} - J_z\tau^z_{Os}S^z_{Mn}$$

$J_x = (-J_1+J_2+J_3)/3$, $J_y = (J_1+J_2-J_3)/3$, $J_z = (J_1+J_2+J_3)/3$

Linear Os-CN-Mn group → $J_1=J_3$, $J_2\approx 0$ → $J_z = 2J_1/3$, $J_x = J_y \approx 0$ → AF Ising-like exchange

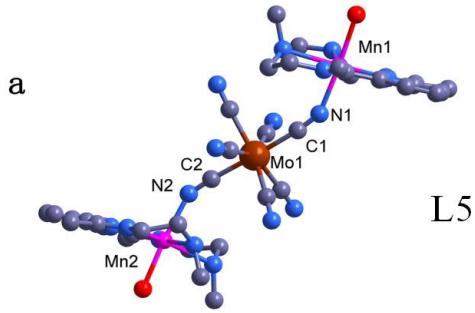
Bent Os-CN-Mn group → $J_3 >> J_1, J_2$ → $J_x \approx J_z = J_3/3 < 0$, $J_y \approx -J_3/3 > 0$ → Three-axis exchange

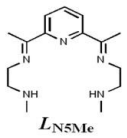
These results are in perfect agreement with the experimental data

Complete experimental evidence of the high-T SMM concept: Trinuclear [Mn^{II}(L5)-$Mo^{III}(CN)_7$- Mn^{II}(L5)] clusters

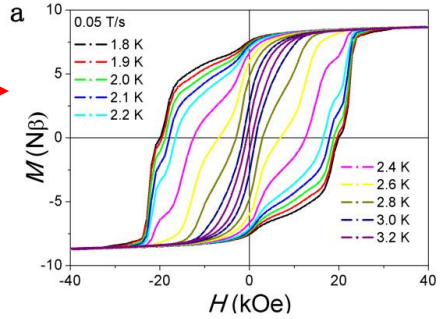
Three novel trinuclear Mn^{II}-Mo^{III}-Mn^{II} cyano-bridged clusters based on the orbitally degenerate $Mo^{III}(CN)_7^{4-}$ bipyramidal complex are recently obtained and characterized:

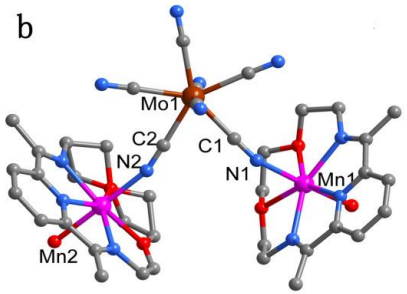
Xin-Yi Wang, Kun Qian, Xing-Cai Huang, Chun Zhou, Xiao-Zeng You, Vladimir S. Mironov, and Kim R. Dunbar, *Nature Chem.*, *submitted*

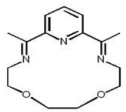


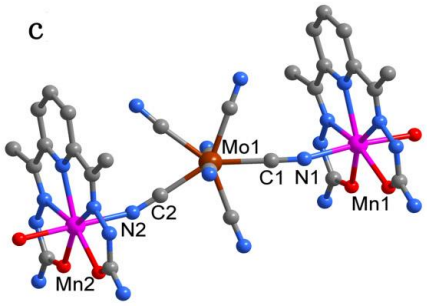
L5 = 

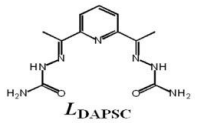
Only isomer (a) with two Mn^{II}(L5) centers attached to the central $Mo^{III}(CN)_7^{4-}$ complex via two apical positions exhibits SMM behavior with U_{eff} = 40.5 cm^{-1} and T_b = 3.2 K.



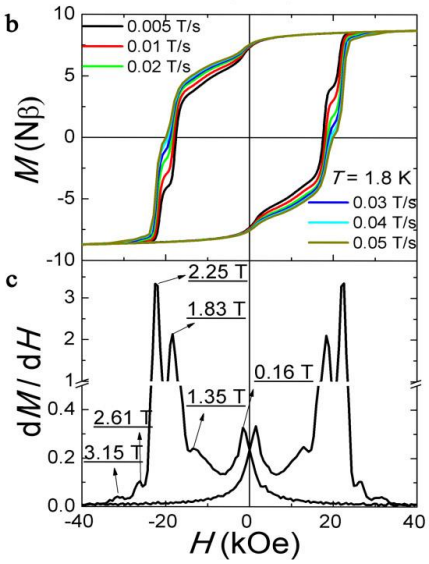


L5 = 



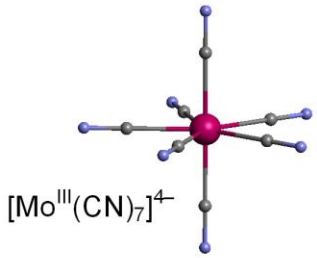
L5 = 

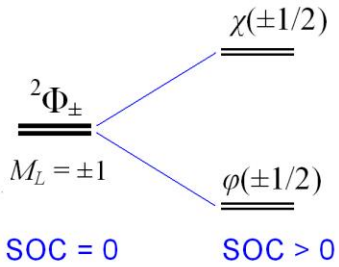
Quite different SMM behavior despite the same molecular building blocks !!!

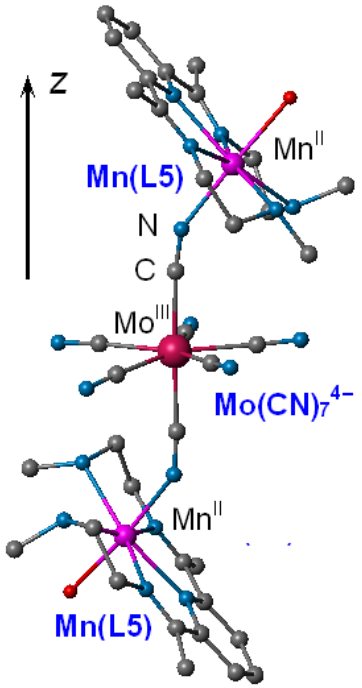


The isomers (b) and (c) with two Mn^{II}(L5) centers attached via the equatorial positions exhibit no SMM behavior !!!

Anisotropic spin coupling in Mo^{III}-CN-Mn^{II} linkages







Isotropic orbitally-dependent Mo^{III}-Mn^{II} spin coupling

$$^2\Phi_\pm - S_{Mn}$$

+ SOC Mo^{III}

Anisotropic Mo^{III}-Mn^{II} spin coupling

$$\varphi(\pm 1/2) - S_{Mn}$$

$$\hat{H} = \hat{A} + \hat{J}\,\boldsymbol{S}_{Mo}\boldsymbol{S}_{Mn}$$

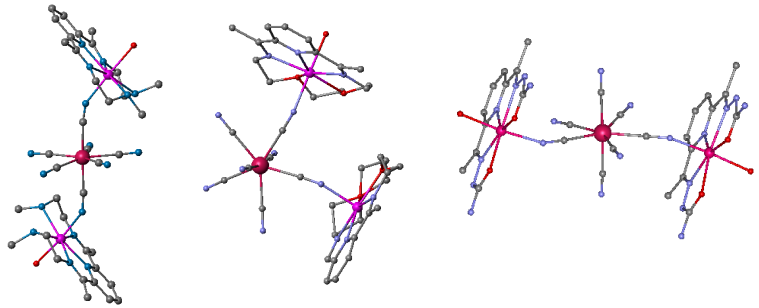
$$\hat{H} = \begin{pmatrix} J_1 & 0 \\ 0 & J_2 \end{pmatrix} \boldsymbol{S}_{Mo}\boldsymbol{S}_{Mn}$$

Projection onto the $|m, M_S\rangle = \varphi(m)\times|S, M_S\rangle$ space

$$\hat{H}_{eff} = -J_{xy}(S^x_{Mn}S^x_{Mo} + S^y_{Mn}S^y_{Mo}) - J_z S^z_{Mn}S^z_{Mo}$$

$$J_z = (J_1 + J_2)/2 \qquad J_{xy} = (J_1 - J_2)/2$$

The spin Hamiltonian of anisotropic spin coupling always has an axial symmetry, regardless of the specific geometry of the Mo^{III}-CN-Mn^{II} linkages and the coordination mode of attached Mn^{II} ions

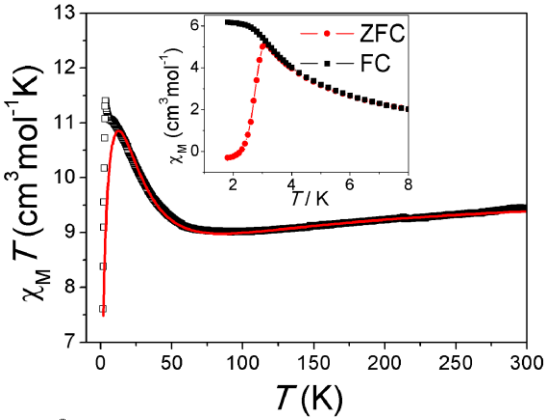


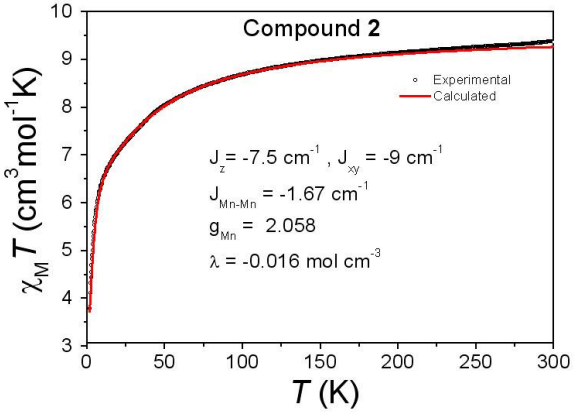
For the regular $Mo^{III}(CN)_7^{4-}$ bipyramid the symmetry of the spin Hamiltonian is higher than the actual local symmetry of Mo-CN-Mn groups !

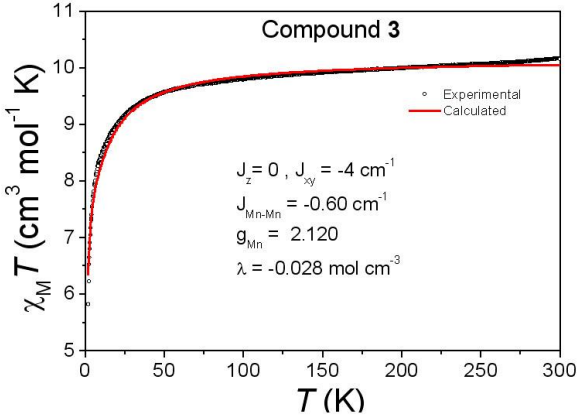
The difference in the SMM behavior of Mn-Mo-Mn isomers (a), (b), and (c) is due to different relation between J_z and J_{xy} exchange parameters

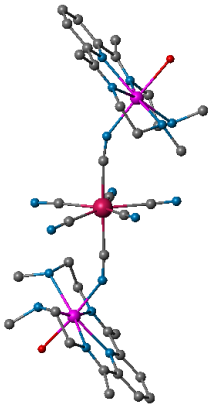
$$\hat{H} = -\sum_{i=1,2}\left(J_{xy}(S^x_{\mathrm{Mn}(i)}S^x_{\mathrm{Mo}} + S^y_{\mathrm{Mn}(i)}S^y_{\mathrm{Mo}}) + J_z S^z_{\mathrm{Mn}(i)}S^z_{\mathrm{Mo}}\right) - J_{\mathrm{Mn-Mn}}\boldsymbol{S}_{\mathrm{Mn}(1)}\boldsymbol{S}_{\mathrm{Mn}(2)}$$

$$+ \mu_B g_{\mathrm{Mn}}(\boldsymbol{S}_{\mathrm{Mn}(1)} + \boldsymbol{S}_{\mathrm{Mn}(2)})\boldsymbol{H} + \mu_B(g_x S^x_{\mathrm{Mo}}H_x + g_y S^y_{\mathrm{Mo}}H_y + g_z S^z_{\mathrm{Mo}}H_z)$$

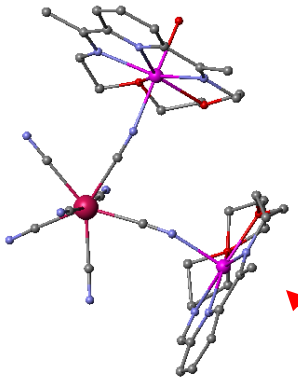






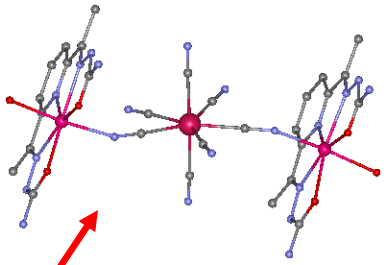


J_z = -34 cm^{-1}
J_{xy} = -11 cm^{-1}



J_z = -7.5 cm^{-1}
J_{xy} = -9 cm^{-1}

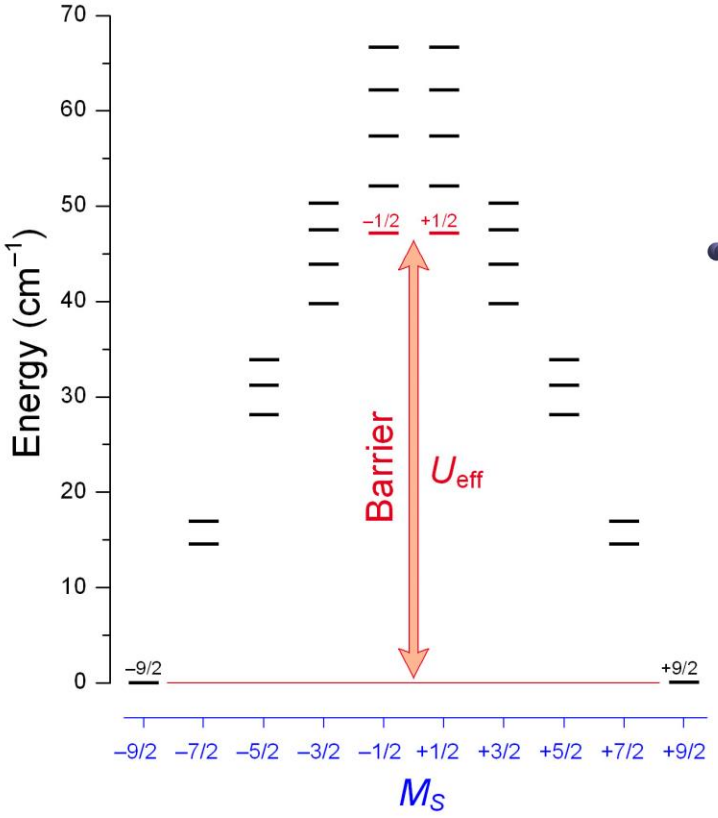
J_z = 0
J_{xy} = -4 cm^{-1}

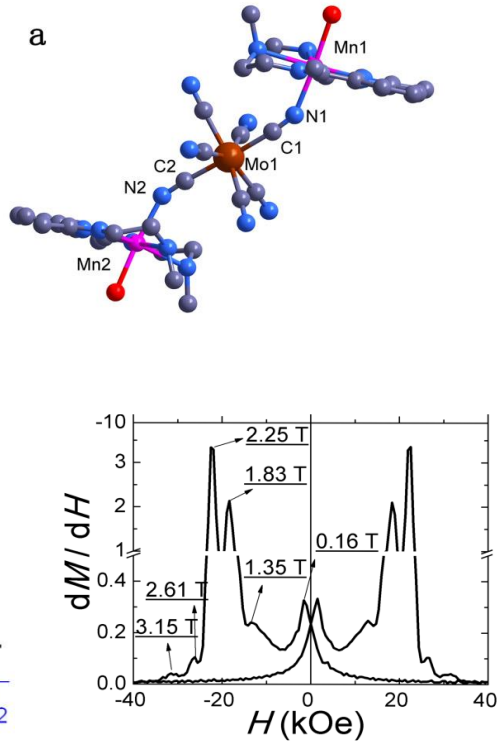


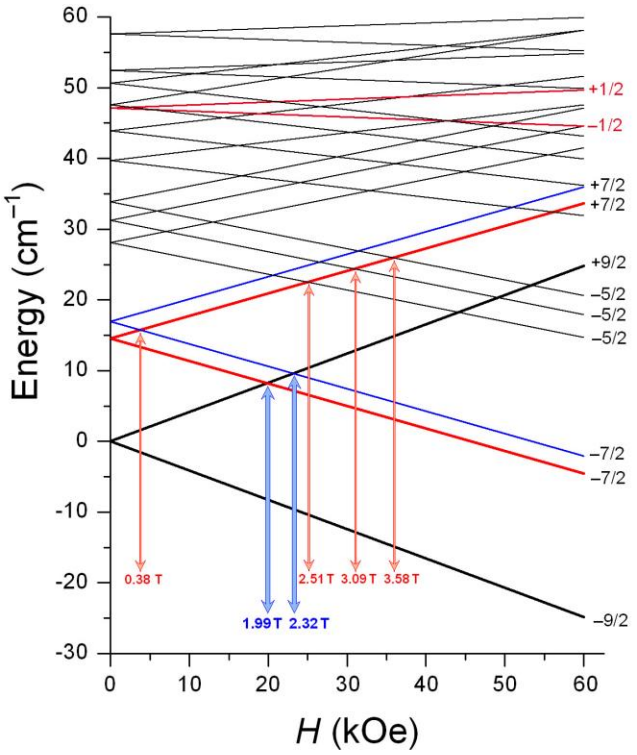
z-type (Ising-like) anisotropy
SMM behavior
U_{eff} = 40.5 cm^{-1}, T_B = 3.2 K

xy-type anisotropy
No SMM behavior

Calculated and experimental energy barrier U_{eff} and resonance magnetic field values in Mn-Mo-Mn isomer (a)







Spin-reversal barrier U_{eff} :

40.5 cm^{-1} (experimental)

47 cm^{-1} (calculated)

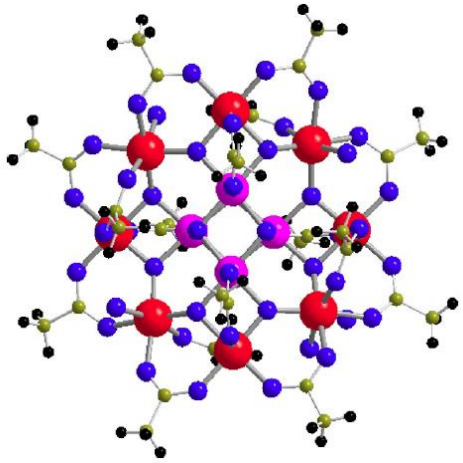
Resonance magnetic field values :

1.83 and 2.25 T (experimental)

1.99 and 2.32 T (calculated)

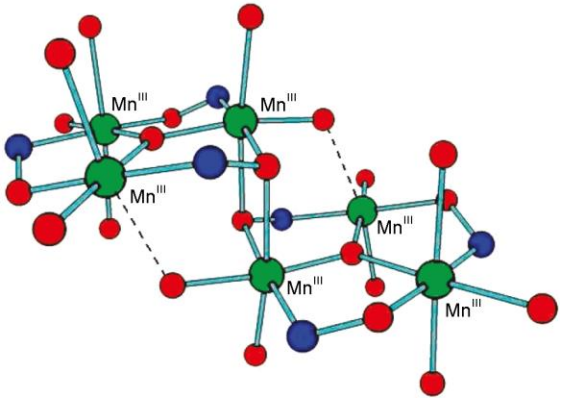
Xin-Yi Wang, Kun Qian, Xing-Cai Huang, Chun Zhou, Xiao-Zeng You, Vladimir S. Mironov, and Kim R. Dunbar, *Nature Chem.*, *submitted*

Efficiency of anisotropic spin coupling in enhancing U_{eff} and T_B values: A comparison with conventional 3d-metal based SMMs



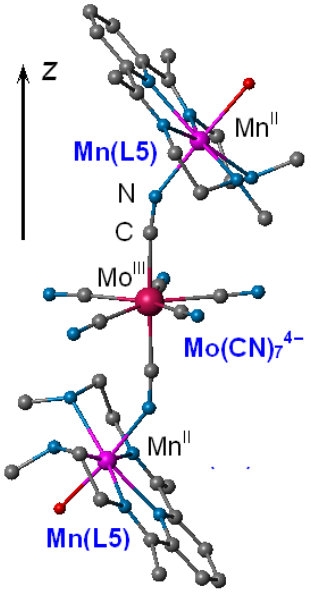
$Mn_{12}Ac$
U_{eff} = 65 K
T_b = 3 K
S = 10 (1993)

Single-ion ZFS on Mn^{III} ions



Mn_6
U_{eff} = 89 K
T_b = 4.5 K
S = 12 (2007)

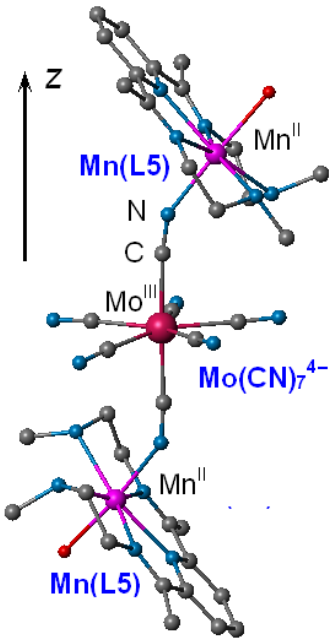
Single-ion ZFS on Mn^{III} ions



Mn-Mo-Mn
U_{eff} = 58 K
T_b = 3.2 K
S = 9/2 (2013)

Ising-like anisotropic spin coupling Mo^{III}-CN-Mn^{II}

Small trinuclear Mn-Mo-Mn cluster with S=9/2 has nearly the same U_{eff} and T_B values as those of a large $Mn_{12}Ac$ cluster with S=10. In fact, SMM characteristics of Mn-Mo-Mn are even comparable with the record U_{eff} and T_B values for the Mn_6 cluster



No single-ion ZFS contributions to the molecular magnetic anisotropy!

The spin-reversal barrier U_{eff} ~ 40 cm^{-1} is entirely due to anisotropic spin coupling of the Mo^{III}-CN-Mn^{II} linkages

Basic idea of high-T SMM concept based on anisotropic spin coupling was suggested in 2003. It has taken a decade to prove it experimentally

The barrier U_{eff} is directly proportional to the exchange parameter J_z. This approach has high potentialities since J_z can easily be scaled to very high values :

Mo^{III}-CN-Mn^{II} :

$|J_z|$ = 34 cm^{-1} → U_{eff} = 40 cm^{-1}, T_B = 3.2 K

Mo^{III}-CN-V^{II} :

$|J_z|$ > 200 cm^{-1} → U_{eff} > 200 cm^{-1}, T_B > 10 K

J|A|C|S
ARTICLES
Published on Web 07/22/2003

Mechanism of a Strongly Anisotropic Mo^{III}−CN−Mn^{II} Spin−Spin Coupling in Molecular Magnets Based on the [Mo(CN)$_7$]$^{4-}$ Heptacyanometalate: A New Strategy for Single-Molecule Magnets with High Blocking Temperatures

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Contribution from the Institute of Crystallography Russian Academy of Sciences, Leninskii prosp. 59, 117333 Moscow, Russian Federation and Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Received November 28, 2002; E-mail: mirsa@icp.ac.ru

Abstract: Unusual spin coupling between Mo^{III} and Mn^{II} cyano-bridged ions in bimetallic molecular magnets based on the [Mo^{III}(CN)$_7$]$^{4-}$ heptacyanometalate is analyzed in terms of the superexchange theory. Due to the orbital degeneracy and strong spin−orbit coupling on Mo^{III}, the ground state of the pentagonal-bipyramidal [Mo^{III}(CN)$_7$]$^{4-}$ complex corresponds to an anisotropic Kramers doublet. Using a specially adapted kinetic exchange model we have shown that the Mo^{III}−CN−Mn^{II} superexchange interaction is extremely anisotropic: it is described by an Ising-like spin Hamiltonian $JS^z_{Mo}\,S^z_{Mn}$ for the apical pairs and by the $J_zS^z_{Mo}\,S^z_{Mn} + J_{xy}(S^x_{Mo}\,S^x_{Mn} + S^y_{Mo}\,S^y_{Mn})$ spin Hamiltonian for the equatorial pairs (in the latter case J_z and J_{xy} can have opposite signs). This anisotropy resulted from an interplay of several Ising-like ($S^z_{Mo}\,S^z_{Mn}$) and

General strategy for designing high-T single-molecule magnets

- Search for new orbitally degenerate 4*d* and 5*d* molecular building blocks with a high *Jr* factor

  Conditions:

  - Unquenched orbital momentum ($L \neq 0$)
  - Strong exchange interactions

- Searching favorable combinations of magnetically anisotropic 4*d* (5*d*) complexes and attached high-spin 3*d* ions

  Conditions:

  - Strong exchange anisotropy, preferably of the Ising-type
  - Large exchange parameters

- Molecular design and tuning of the SMM structure

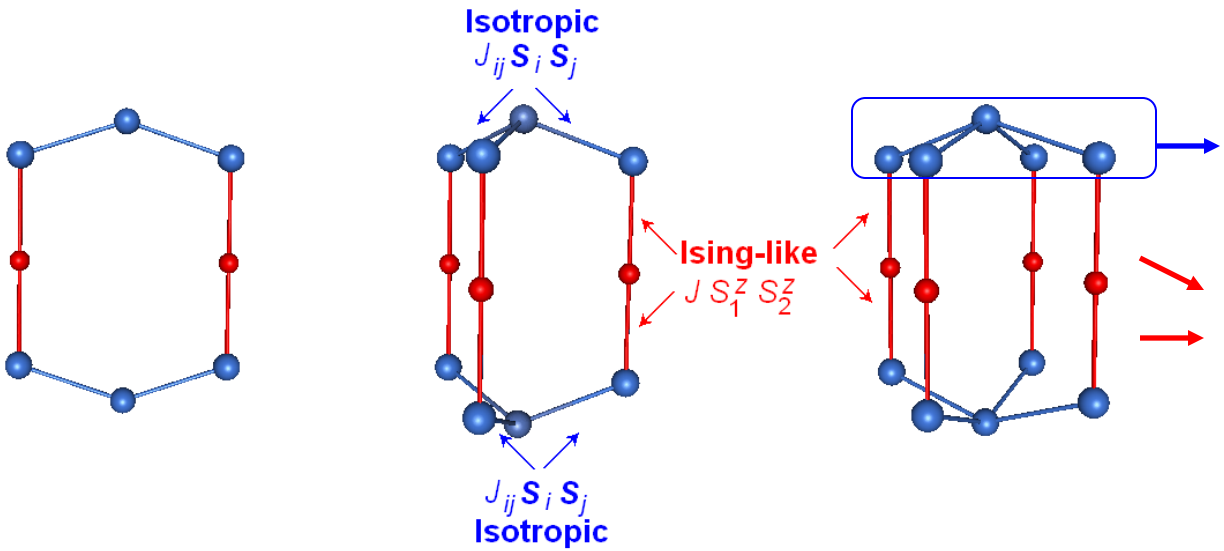
  Key factors controlling and tuning SMM characteristics T_b and U_{eff}:

  - Chemical composition
  - Structure, nuclearity, and symmetry of the SMM cluster
  - Topology of anisotropic and isotropic exchange linkages
  - Orientation of principal magnetic axes

- Theory

  Development of the theory of SMMs with highly anisotropic spin couplings and elaboration of computational approaches are crucially important for designing high-T SMMs

Prospects for designing high-T SMM based on orbitally-degenerate 4d and 5d complexes

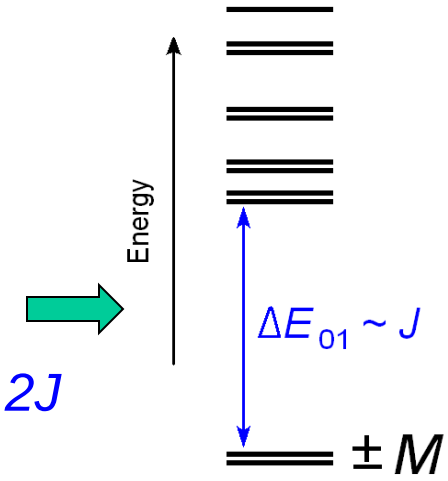


Isotropic exchange interactions $J_{ij}S_iS_j$ (AF or F) between high-spin 3*d* centers form high ground-state magnetic moment of a SMM cluster

Anisotropic (Ising-like) exchange interactions $J_{ij}S_i^zS_j^z$ between 5*d* and 3*d* centers form high molecular magnetic anisotropy. The local magnetic anisotropy axes must be parallel

- Ordinary (spin-only) magnetic sites (Cr^{3+}, Mn^{2+}, Fe^{3+})
- Orbitally-degenerate magnetic sites - $[Os(CN)_6]^{3-}$, $[Re(CN)_7]^{3-}$

In specially organized SMM clusters with orbitally-degenerate 5*d* centers the energy barrier U_{eff} can reach a value of $U_{eff} \sim 1.5J - 2J$



Anisotropic 5*d*-3*d* exchange interactions may be as strong as $J \sim 200\text{-}400$ cm^{-1} :

Therefore, $U_{eff} \sim 500$ cm^{-1} (700 K) and $T_b \sim 30\text{-}50$ K are potentially feasible!

Search for new 4*d* and 5*d* molecular building blocks for high-T single-molecule magnets

New molecular building blocks with an extremely high ***Jr*** factor are required for designing high-T SMMs

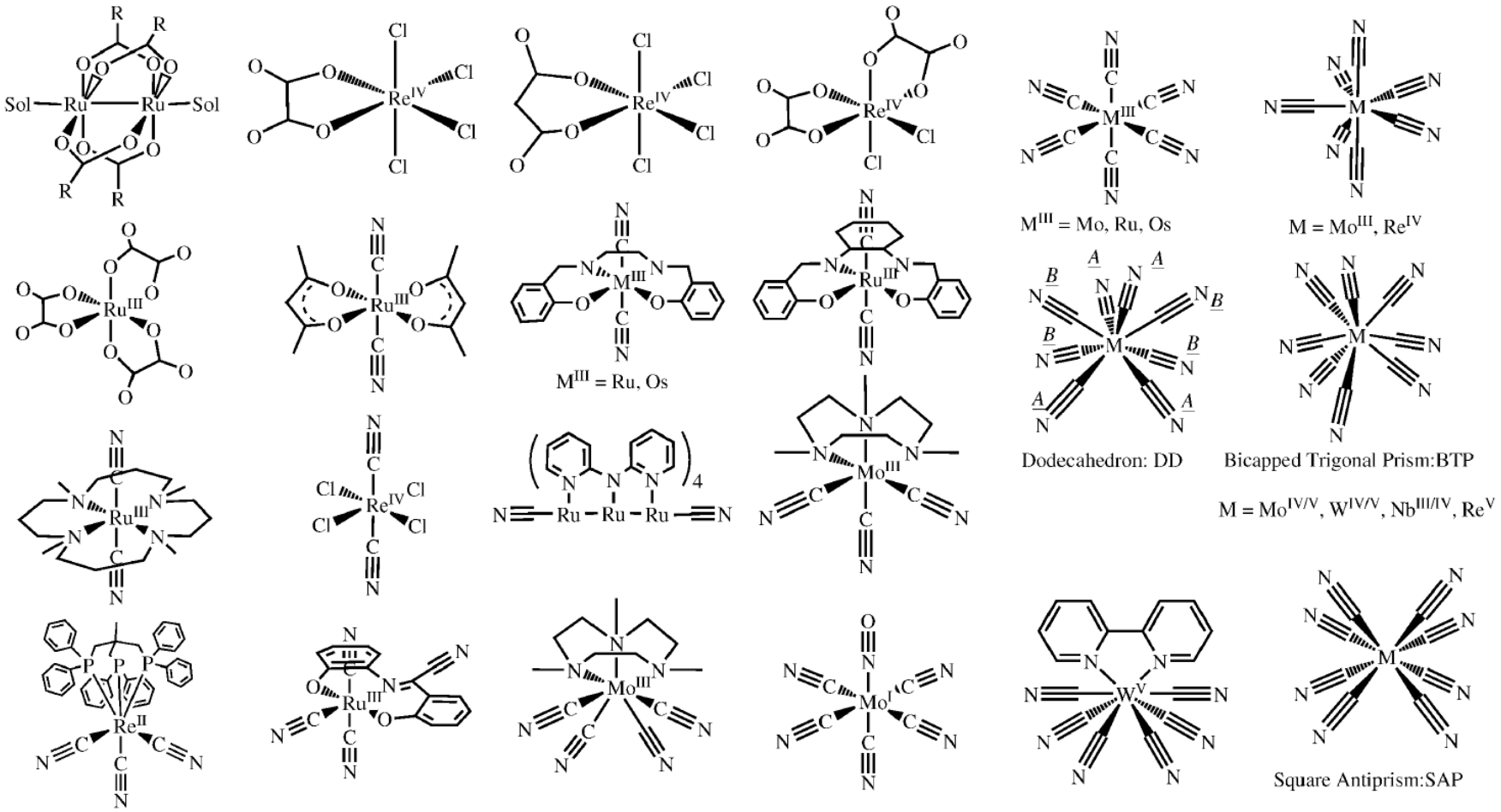
T_b ~ 30-50 K ***Jr*** > 400 cm^{-1}

T_b > 100 K ***Jr*** > 1000 cm^{-1}

General conditions:

- Ising-like ($JS_1^zS_2^z$) exchange anisotropy is highly preferable
- Very high 4(5)*d* – 3*d* exchange parameters (J > 300 cm^{-1}) in combination with suitable high-spin 3d ions

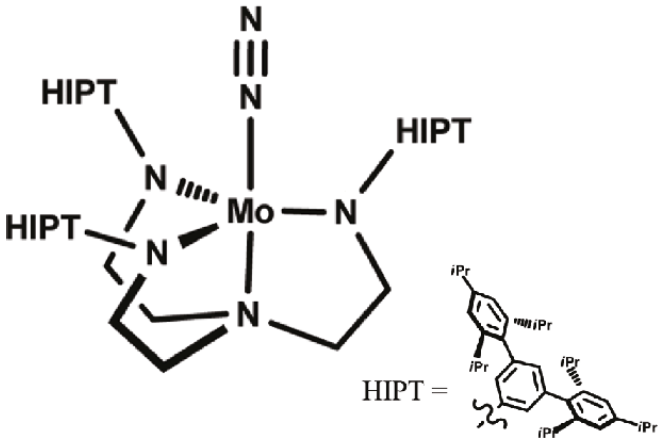
Examples of paramagnetic 4*d* and 5*d* molecular building blocks

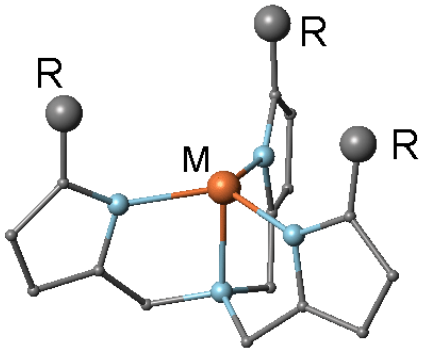


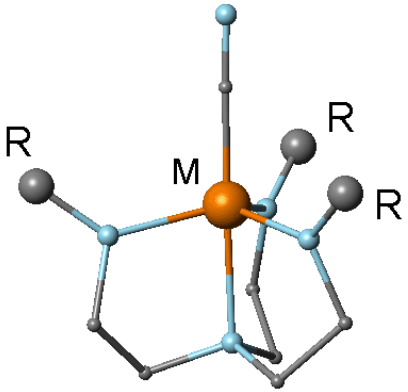
Most of them are spin-only complexes with $L = 0$

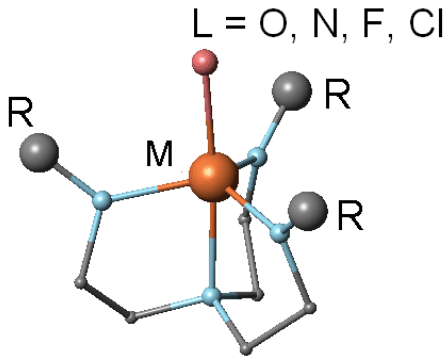
Orbitally-degenerate trigonal-pyramidal 4d and 5d complexes with macrocyclic ligands

A variety of trigonal-pyramidal 4*d* and 5*d* complexes with triamidoamine macrocyclic ligands are reported in the literature. Many of them are very promising for designing high-T SMMs









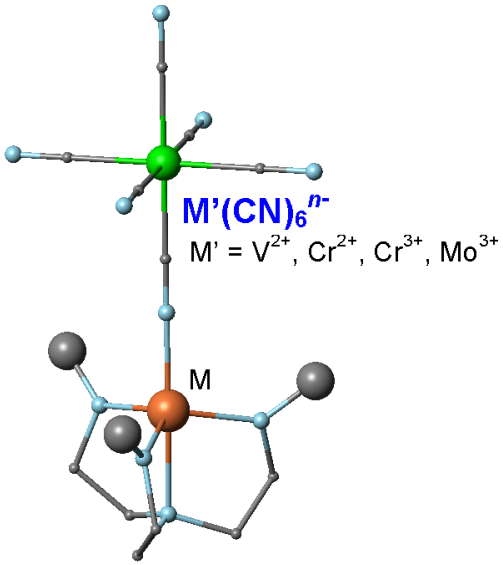
M = Mo^{V}, Mo^{III}, W^{V}, W^{III}, Nb^{IV}, Ta^{IV}
R = Aryl, Alkyl

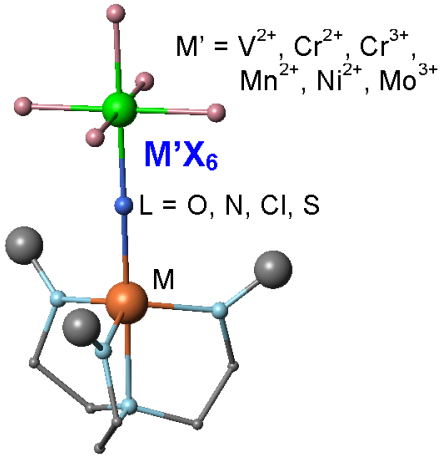
N
C

Advantages:

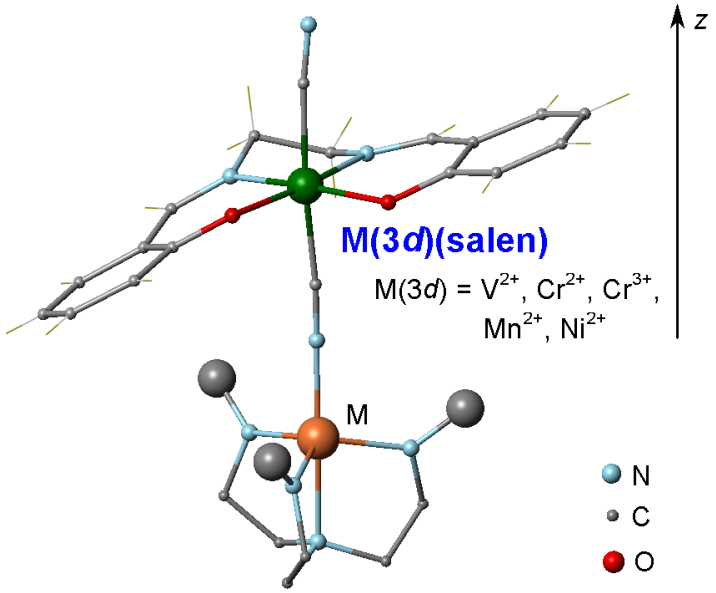
- The ground state of d^1 and d^3 complexes is an orbital doublet with unquenched angular momentum;
- Strong spin-orbit coupling keeps the orbital momentum unquenched upon distortions; Jahn-Teller distortions are small;
- All unwanted equatorial coordination positions are blocked;
- Apical coordination positions provide highly anisotropic spin coupling with attached high-spin; ions;
- Molecular spin clusters and spin chains are easily obtained;
- A variety of promising metal-ligand combinations are available.

Ising-like spin coupling between trigonal-pyramidal 4d and 5d complexes and attached high-spin 3d ions





M = Mo^{V}, Mo^{III}, W^{V}, W^{III}, Nb^{IV}, Ta^{IV}, Re^{IV}



$$H = -J_z S^z_{5d} S^z_{3d} - J_{xy}(S^x_{5d} S^x_{3d} + S^y_{5d} S^y_{3d})$$

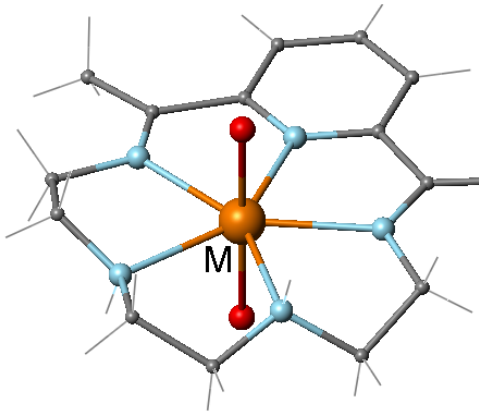
J_z ~ 100-300 cm^{-1} (AF)
$J_{xy} \sim 0$

These *4d*-3*d* and 5*d*-3*d* combinations provide a very high *Jr* factor, up to ***Jr* ~ 300 cm^{-1}** !

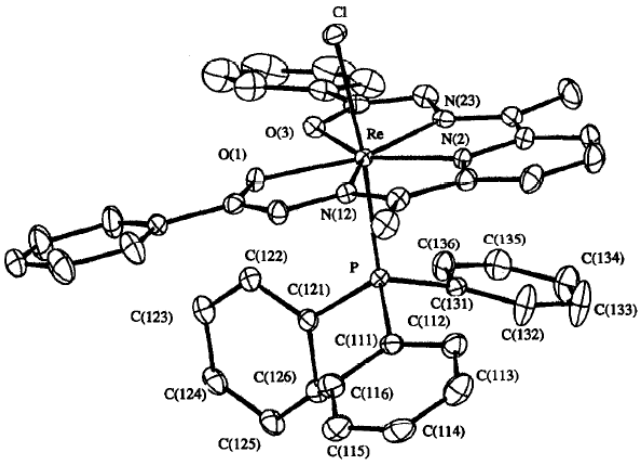
V.S. Mironov, *submitted in Inorganic Chemistry*

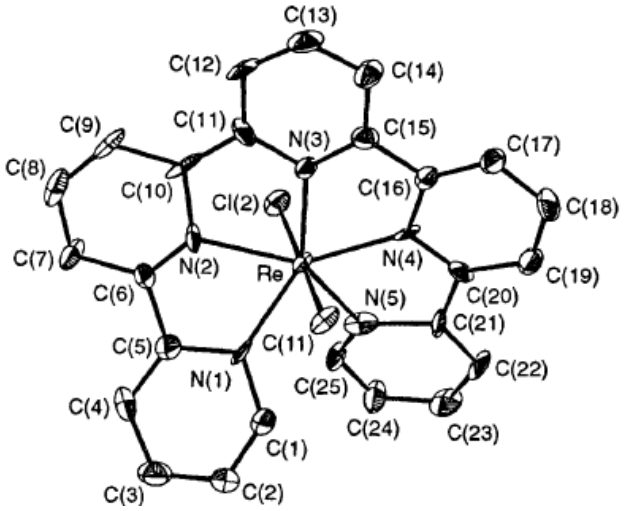
Orbitally-degenerate pentagonal-pyramidal 5d complexes with macrocyclic ligands

Very interesting are pentagonal-pyramidal 4*d* and 5*d* complexes pentadentate macrocyclic ligands L5. They are most promising molecular building blocks for designing high-T SMMs



M = Mo^{V}, Mo^{III}, W^{V}, W^{III}, Nb^{IV}, Ta^{IV}, Re^{IV}

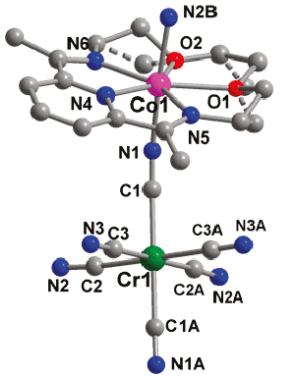


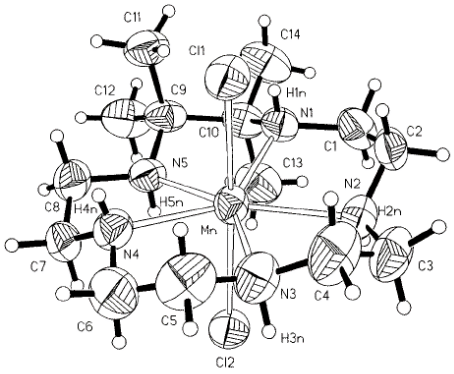


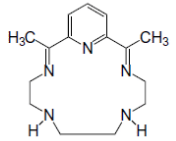
Advantages:

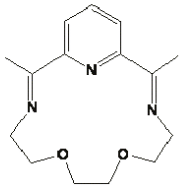
- The ground state of d^1 and d^3 complexes is an orbital doublet with unquenched angular momentum;
- Strong spin-orbit coupling keeps the orbital momentum unquenched upon distortions; Jahn-Teller distortions are small;
- All unwanted equatorial coordination positions are blocked;
- Apical coordination positions provide highly anisotropic spin coupling with attached high-spin; ions;
- Molecular spin clusters and spin chains are easily obtained;
- A variety of promising metal-ligand combinations are available.

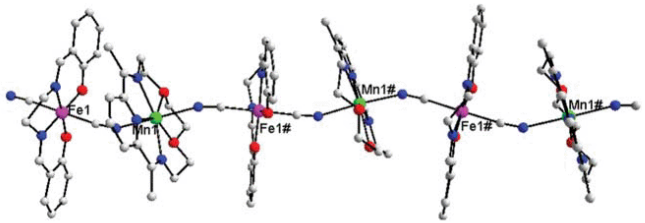
Pentadentate macrocyclic ligands and related pentagonal-bipyramidal complexes

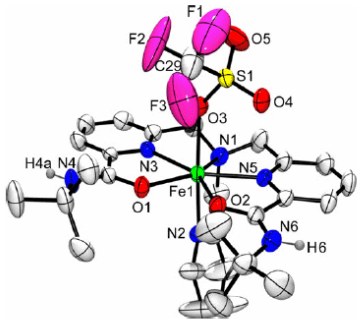


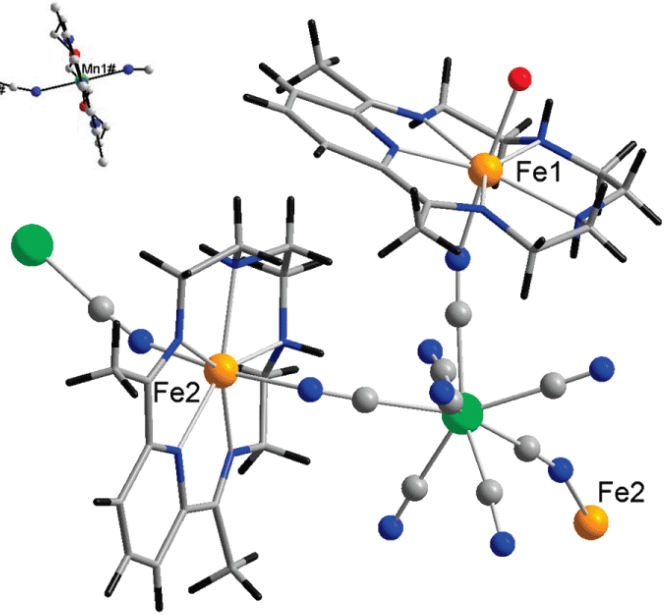


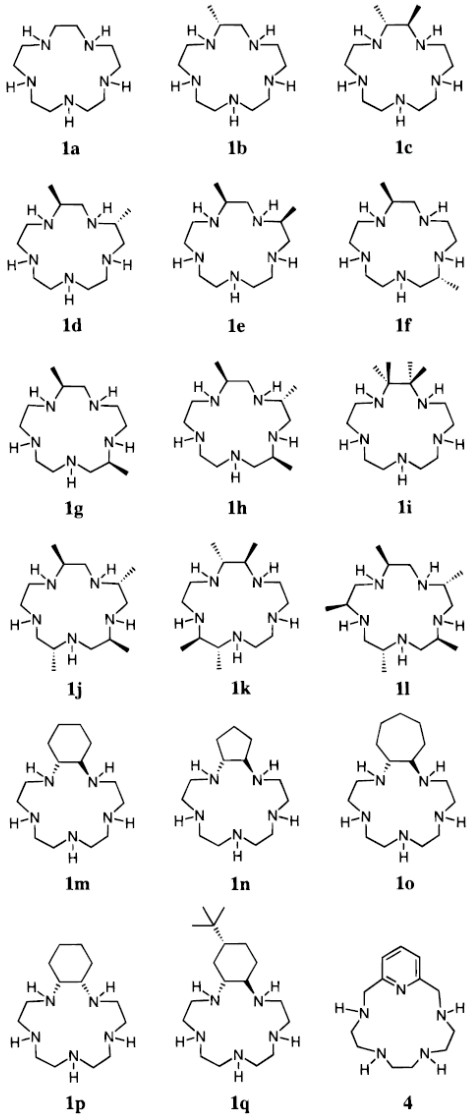








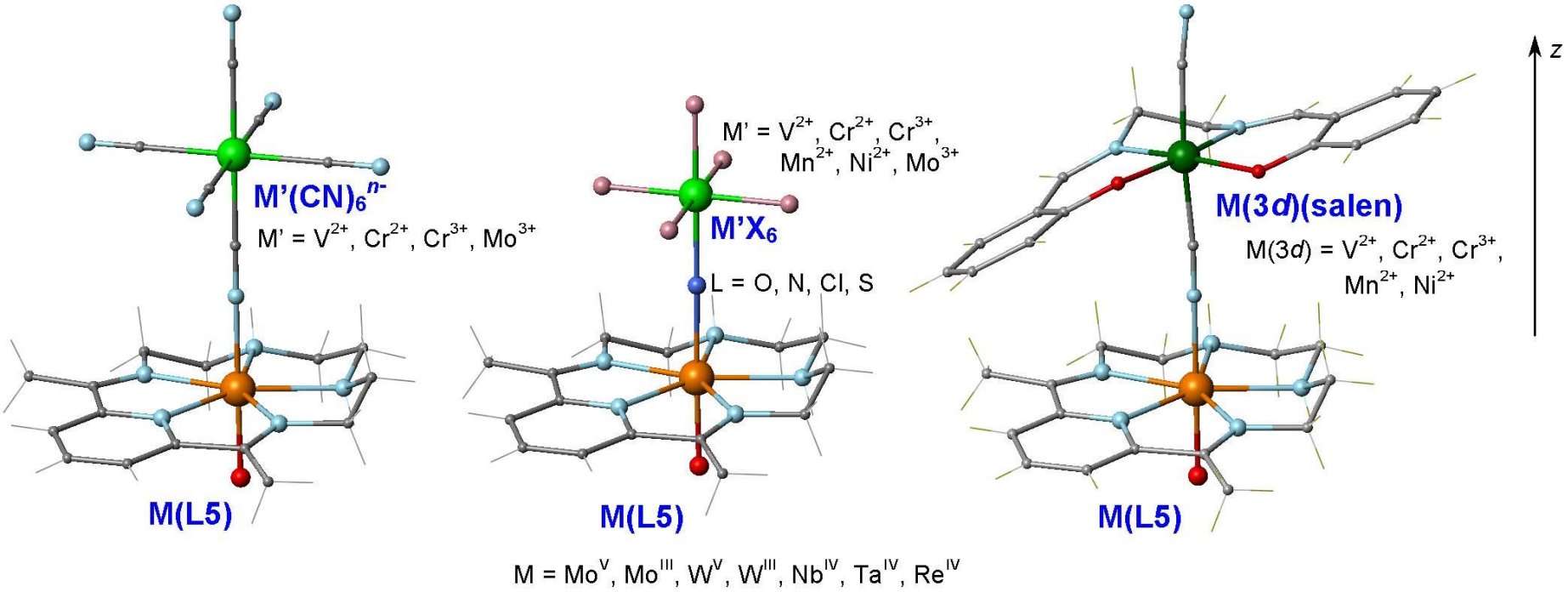




Spin coupling between M(L5) complexes and attached high-spin transition-metal ions is highly anisotropic

$$H = -J_z S_{5d}^z S_{3d}^z - J_{xy}(S_{5d}^x S_{3d}^x + S_{5d}^y S_{3d}^y)$$

J_z ~ 100-600 cm^{-1},
J_{xy} ~ 0



M = Mo^{V}, Mo^{III}, W^{V}, W^{III}, Nb^{IV}, Ta^{IV}, Re^{IV}

These complexes provide a very high *Jr* factor

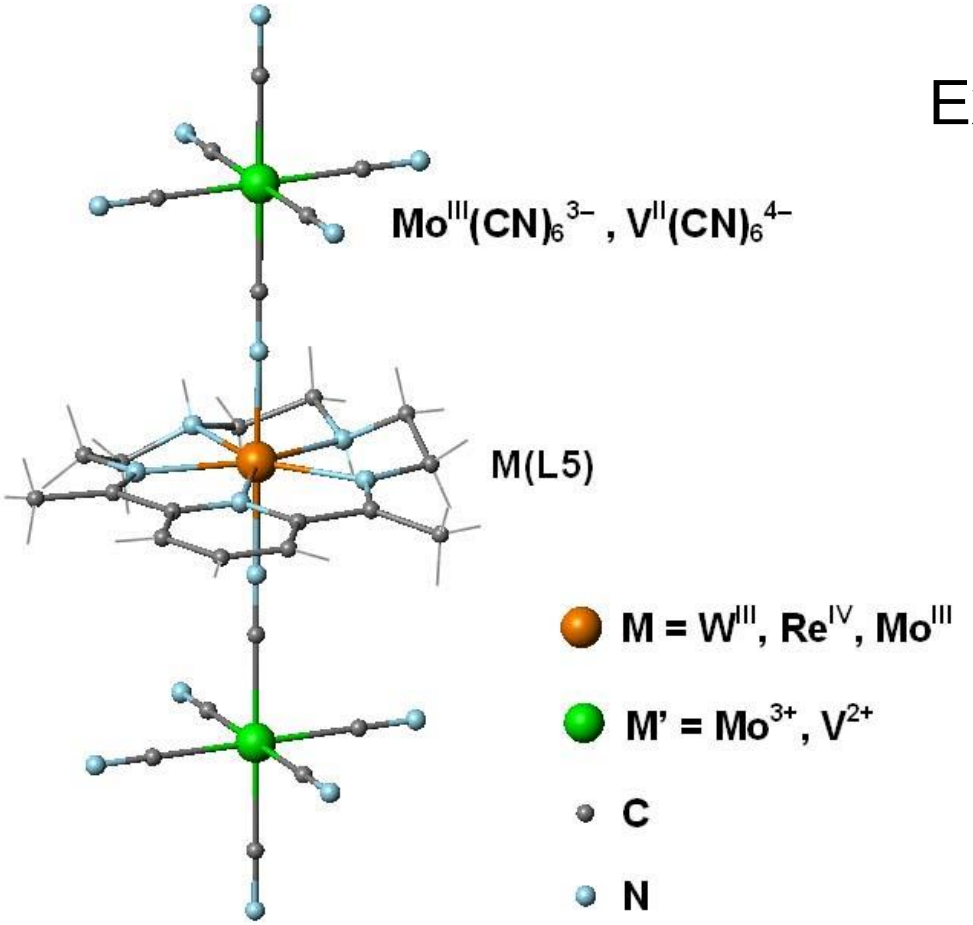
Jr ~ 600 cm^{-1} ⇒ $T_b \approx$ 50-70 K

A prototype of high-T single-molecule magnet based on 4d and 5d complexes M(L5) with planar pentadentate macrocyclic ligands L5

Ising-like 4d/5d – 3d spin coupling with very large J_z

$$H = -J_z S^z_{5d} S^z_{3d} - J_{xy}(S^x_{5d} S^x_{3d} + S^y_{5d} S^y_{3d})$$

→ J_z ~ 400 cm^{-1}, $J_{xy} << J_z$

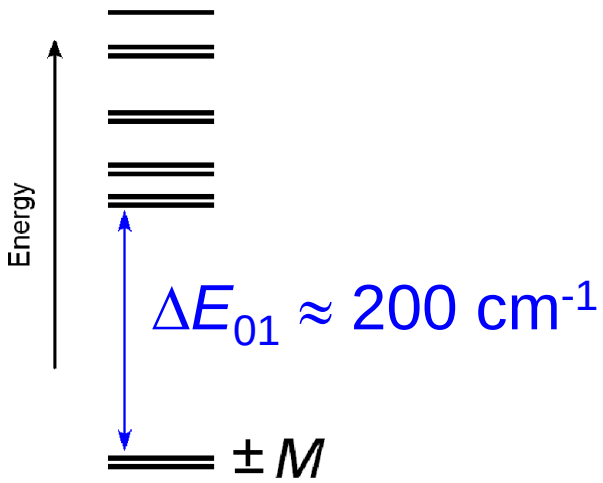


Expected SMM characteristics:

$S = 7/2$

$U_{eff} \approx 400$ cm^{-1}

$T_B > 15$ K



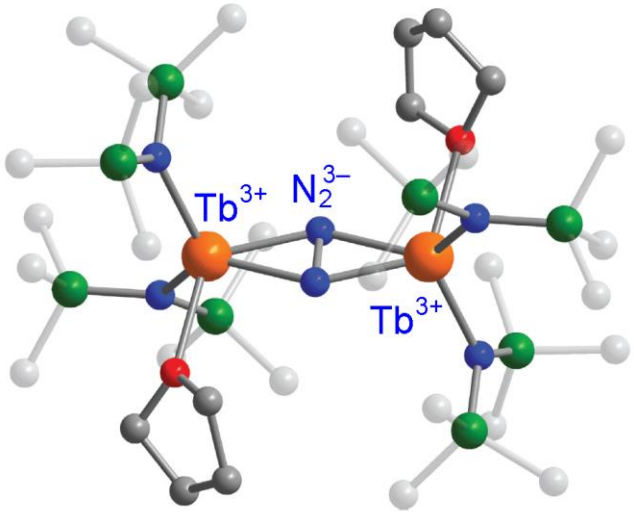
Lanthanide-based SMMs

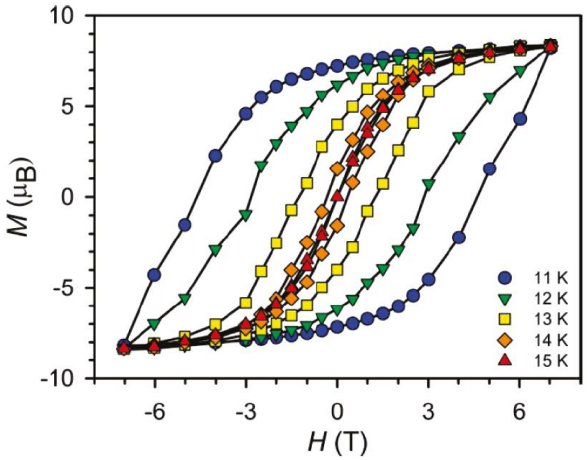
Numerous lanthanide-based SMMs were obtained and characterized in recent years

Several lanthanide-radical SMMs with record characteristics were reported

$Tb_2(N_2^{3-})$ SMM cluster with record U_{eff} and T_b

Bridging anion-radical N_2^{3-} (S = 1/2) enters the coordination sphere of two Tb^{3+} ions resulting in high exchange parameters (J ~ 30 cm^{-1})!





U_{eff} = 326 K
T_b = 14 K

J.D. Rinehart et al, *JACS*, 133, 14236 (2011)

Summary and Conclusions

- **All presently known SMM clusters based on 3*d* ions have a low blocking temperature (T_b ~3-5 K) - little progress for the past decade;**
- **In molecular SMM clusters with ordinary (spin-only) 3*d* ions the blocking temperature T_b is limited by ~10-15 K due to fundamental factors;**
- **Strong exchange anisotropy of orbitally-degenerate magnetic centers represents a very efficient tool to increase the molecular magnetic anisotropy of SMM clusters;**
- **In clusters with orbitally-degenerate 5*d* complexes, the blocking temperature T_b can be raised by an order of magnitude, from T_b = 3 - 5 K to ~30-50 K;**
- **General selection rules for molecular magnetic building blocks are formulated;**
- **Specific magnetically anisotropic molecular building blocks are selected and explored. Orbitally degenerate 4*d* and 5*d* complexes with macrocyclic ligands are found to be especially promising;**
- **Geometry factors are extremely important in designing SMM clusters. Right angles between Ising axes of anisotropic spin couplings and bent bridging groups must be strictly avoided.**