Theoretical Study of low-spin S=1/2 Mononuclear Single-Molecule Magnets

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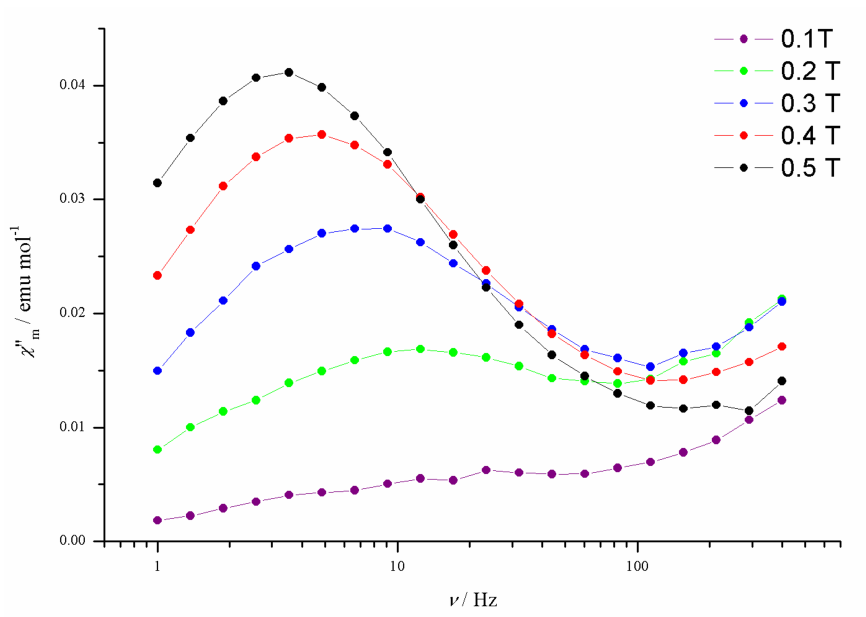
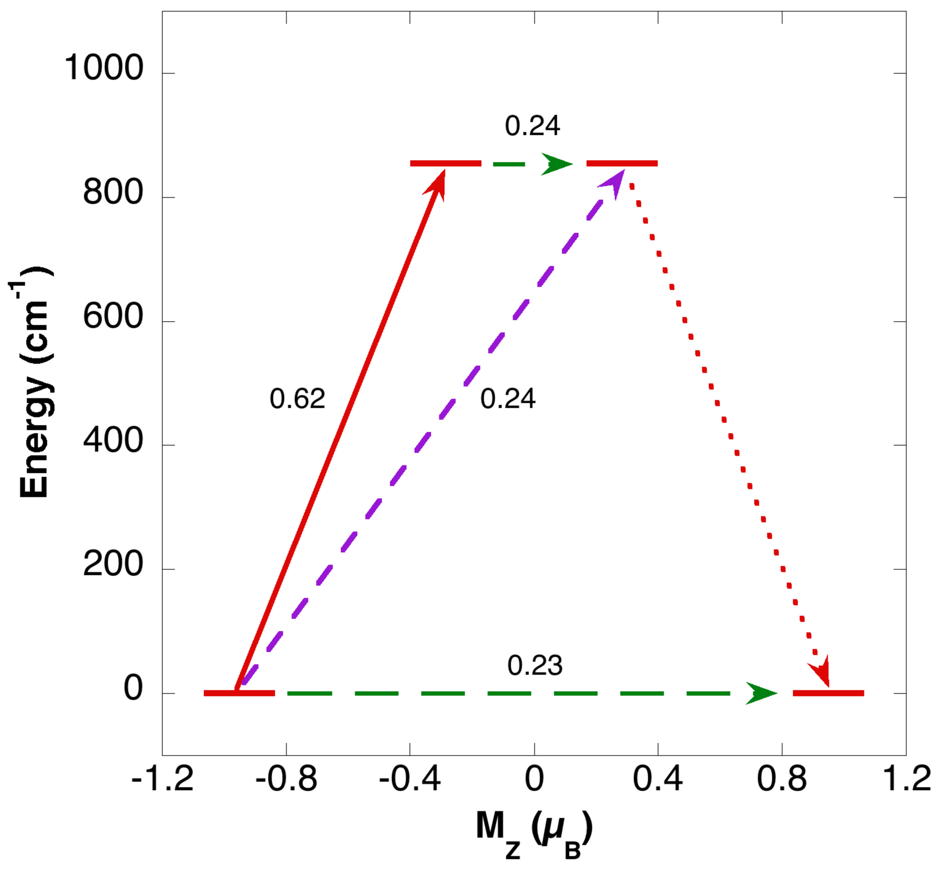
Introduction

We have theoretically studied some transition metal mononuclear single-molecule magnets with a spin total value of S=½ and compare with the available experimental data. We demonstrate that the simplest Fe^{III} sandwich-type complex has a field-induced mononuclear SMM behavior and reasoned why it analogous complex with Co^{II} it is not.

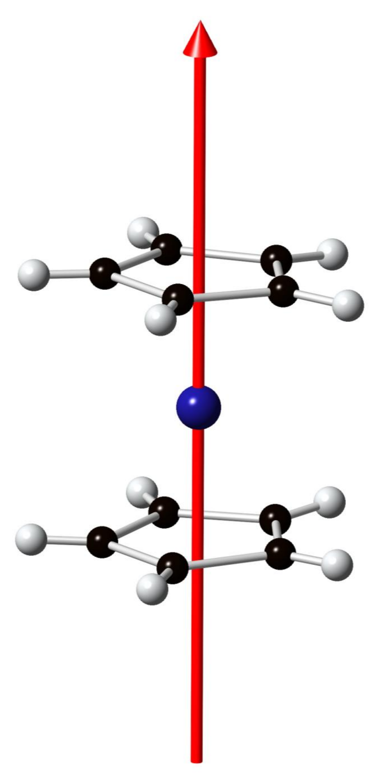
Fe^{III} sandwich complex (Ferrocenium)

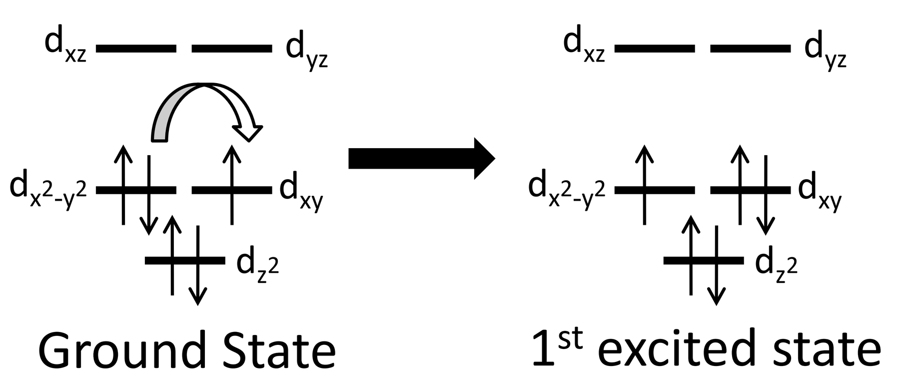


χ "$_M$ vs frequency for $[FeCp_2]PF_6$ but only in the presence of an static field.



Calculated ab initio effective barrier with the probability of the different transitions between states (red, thermal relaxation; green, tunneling relaxation; violet, Orbach relaxation) with a high relaxation through the ground state (probability > 0.1).

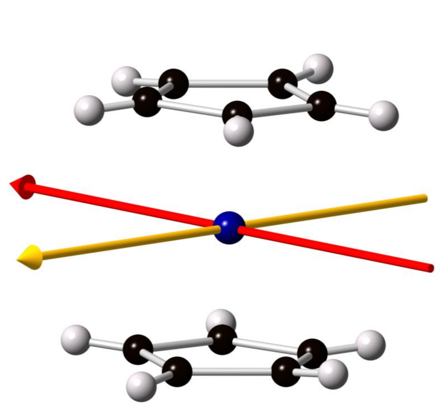




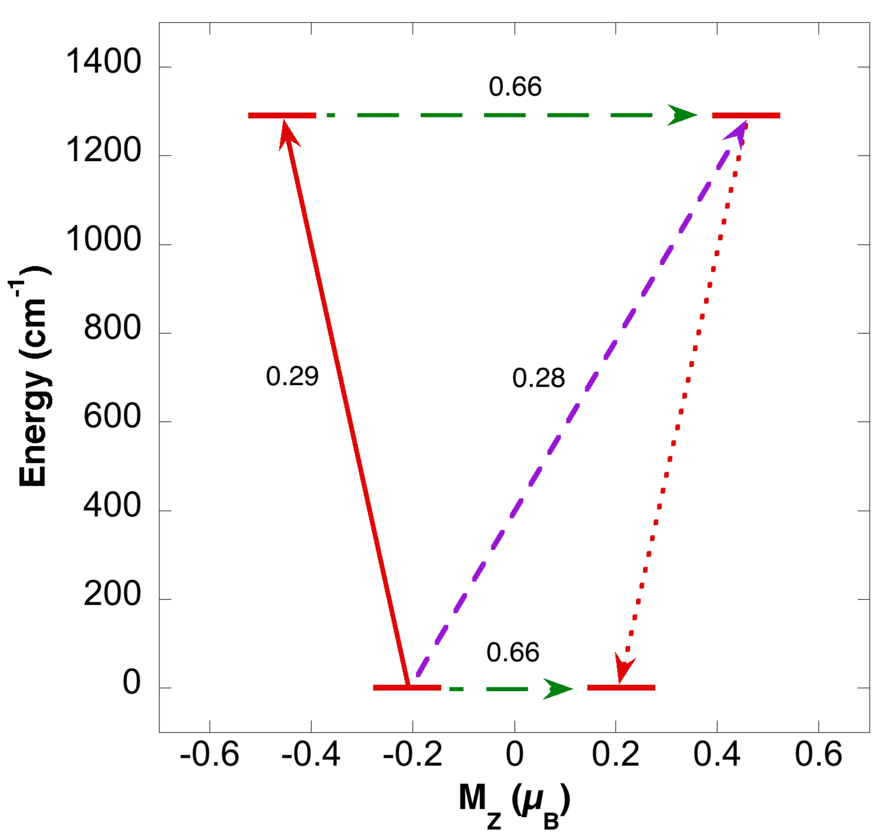
Calculated G-tensor		
g_x	g_y	g_z
0.70	0.70	5.72

A $d_{x^2-y^2}{}^2$ $d_{z^2}{}^2$ $d_{xy}{}^1$ orbital occupation from where the low-energy excitation from the doubly-occupied $d_{x^2-y^2}$ to singly-occupied d_{xy} orbital results according Eq.1 in a large positive g_z. **It is a SMM.**

Co^{II} sandwich complex (Cobaltocene)



Calculated G-tensor		
g_x	g_y	g_z
2.07	1.86	1.27



Cobaltocene ground state corresponds to a $d_{x^2-y^2}{}^2$ $d_{z^2}{}^2$ $d_{xy}{}^2$ $d_{xz}{}^1$ orbital occupation occupation**. The low-energy excitation from the singly-occupied d_{xz} to singly-occupied d_{yz} results in a low negative g_z. It is not a SMM.**

Acknowledgements

Spanish Ministerio de Economía y Competitividad (grants MAT2012-38319-C02 and CTQ2015-64579-C3-1-P). M.A. acknowledges the Ministerio de Educación, Cultura y Deporte for an FPU predoctoral grant. E.R. thanks Generalitat de Catalunya for an ICREA Academia grant. The authors thankfully acknowledge the computer resources, technical expertise and assistance provided by the CSUC.

Methodology

CASSCF/CASPT2+RASSI+SINGLE_ANISO calculations MOLCAS 8.0 with ANO-RCC basis.
CASSCF/NEVPT2+QDPT calculations ORCA 3.0.1 with def2-TZVPP basis (g-tensor components.)
Active space used: Ferrocenium (5,5); Cobaltocene (7,5); Mn^{IV} T_d complex (9,8)

G-tensor

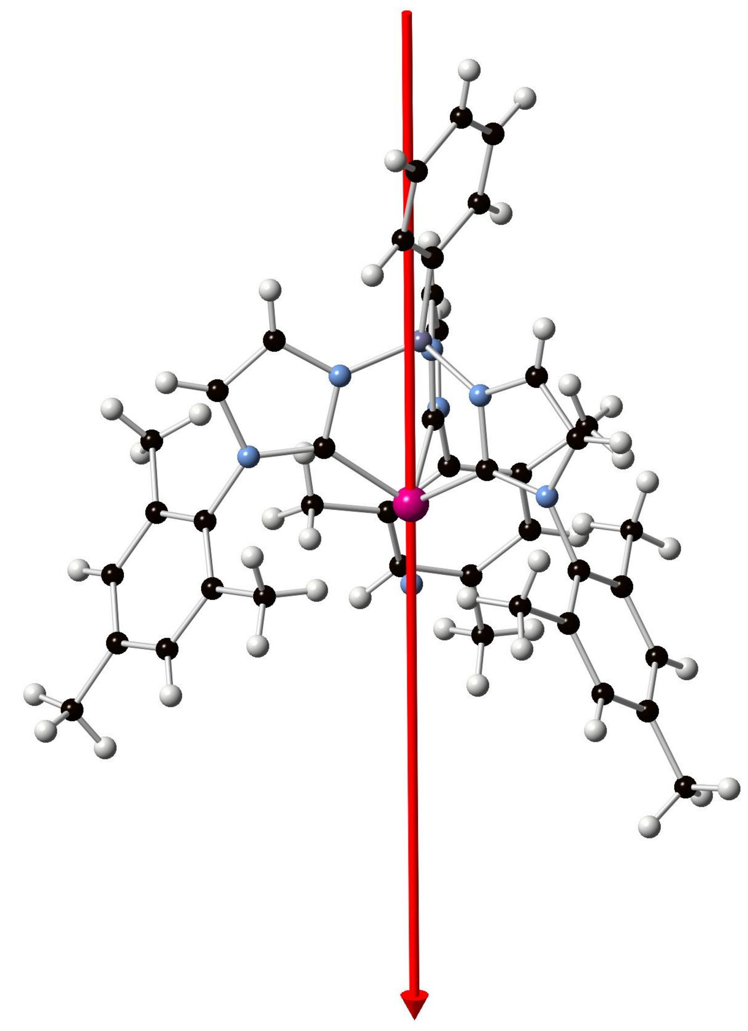
To understand the different values of the component we have that each component g_{kl}:

$$g_{kl} = g_e + \frac{\zeta_{eff}}{2S}\sum_{i,p}\frac{\langle\varphi_i|l_k|\varphi_p\rangle\langle\varphi_p|l_l|\varphi_i\rangle}{\varepsilon_p-\varepsilon_i} - \frac{\zeta_{eff}}{2S}\sum_{p,a}\frac{\langle\varphi_p|l_k|\varphi_a\rangle\langle\varphi_a|l_l|\varphi_p\rangle}{\varepsilon_a-\varepsilon_p} \qquad [1]$$

where ζ_{eff} is the spin-orbital coupling constant, l_k is the k-component of the angular momentum operator and φ are the molecular orbitals (with orbital energy ε) with the subindex *i*, *p* or *a* to indicate double-occupied, singly-occupied or empty orbitals, respectively.

Low-spin Mn^{IV} T_d Complex

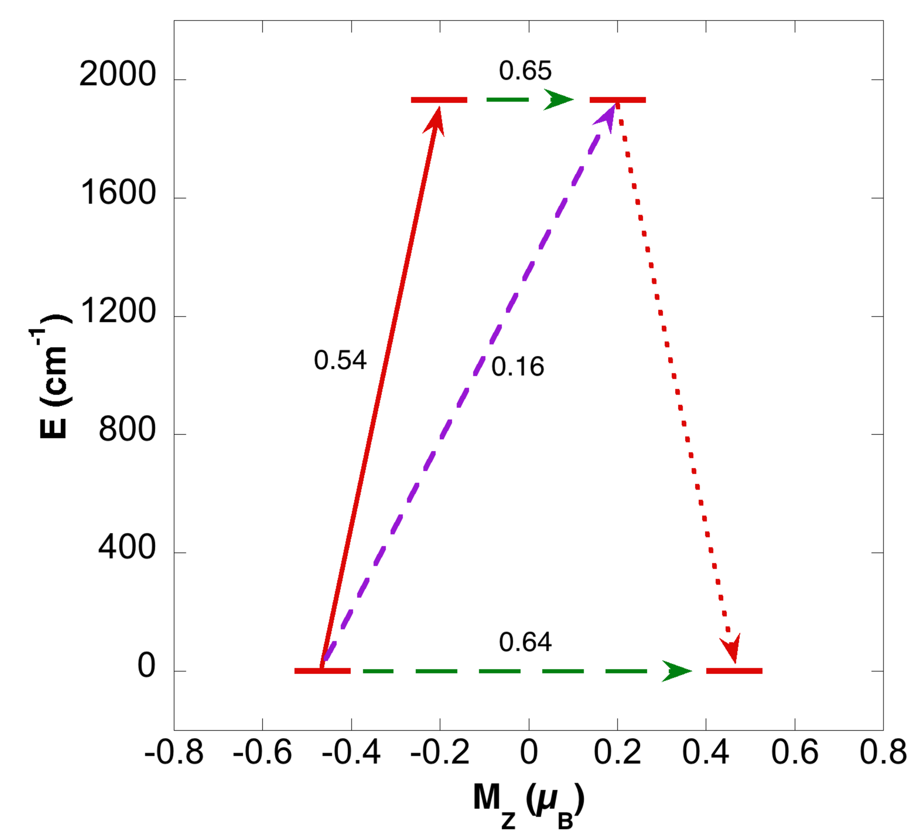
Collaboration with Rodolphe Clérac (Bordeaux) and Jeremy M. Smith (Indiana): PhB(MesIm)3Mn≡N



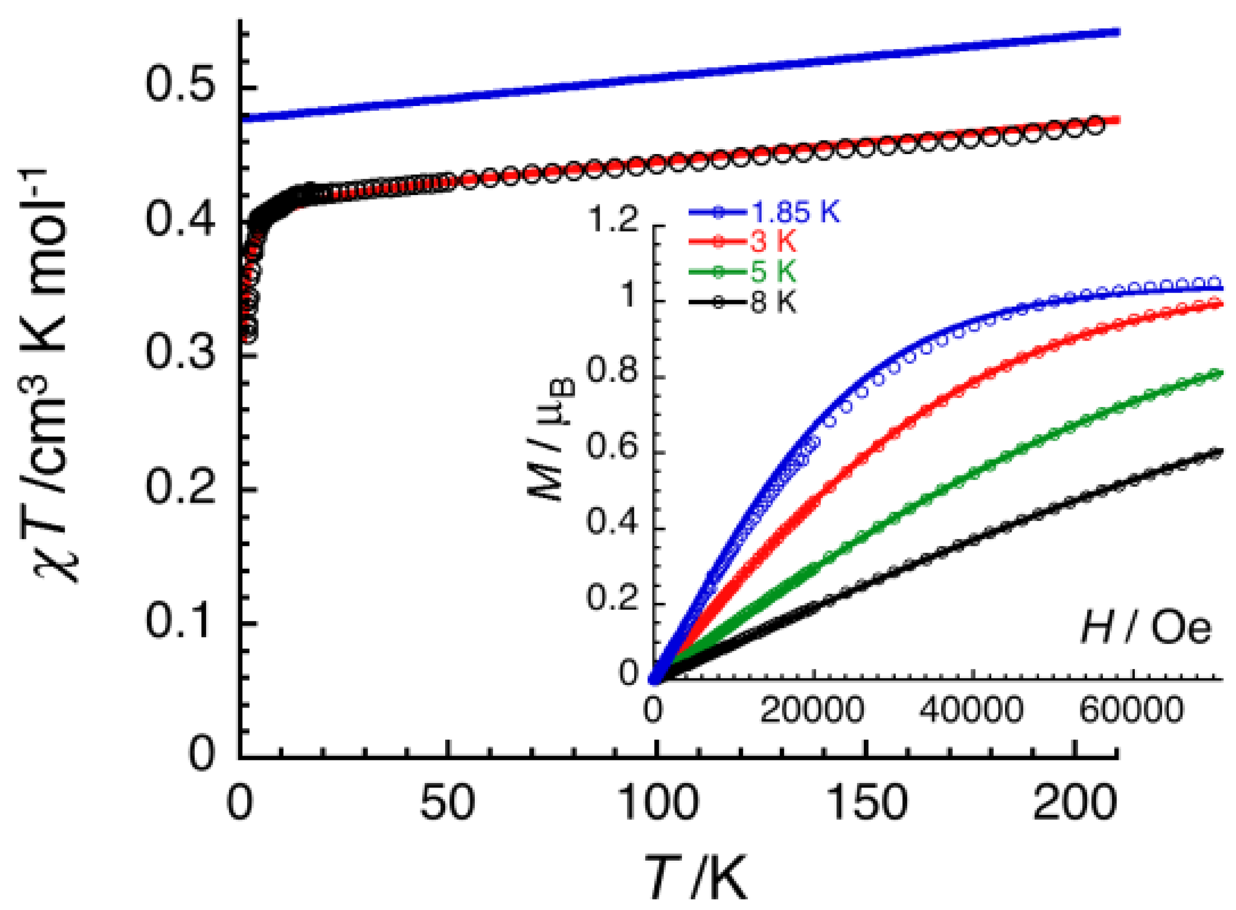
G-tensor		
g_x	g_y	g_z
1.927 (1.965)*	1.933 (1.973)*	2.790 (2.350)*

*Experimental values

Ising Axis give by the g_z component of the g-tensor.



Calculated ab initio probability of the different transitions between doublet states (red, thermal relaxation; green, QTM; violet, Orbach relaxation). Large tunneling through the ground states (>0.1) no zero-field slow relaxation.



Temperature dependence of the χT product at 0.1 T and field dependence of magnetization at different temperatures. Solid lines are simulations obtained from SINGLE_ANISO package from MOLCAS.

Overestimation of χT curve due to the difference between the calculated and the experimental g-tensor values.

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