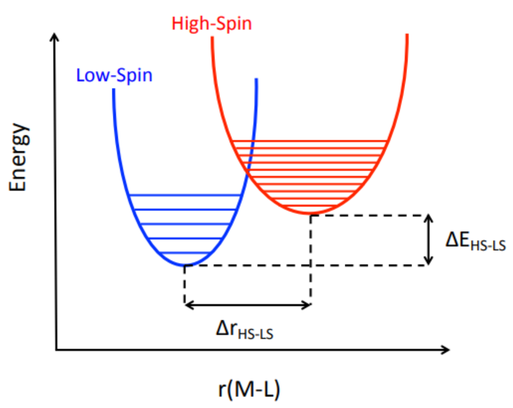
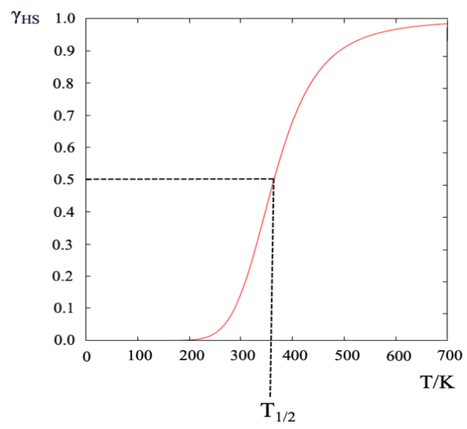
Computational Modelling of [Fe_2] Spin-Crossover Metal-Organic Cages

Laia Navarro, Jordi Cirera
PhD Student in Theoretical Chemistry and Computational Modelling at the UB/IQTCUB
laia.navarro@qi.ub.es

Introduction

Spin-Crossover (SCO) systems are compounds in which two alternative electronic states with similar energies are accessible by means of an external stimulus.





The temperature with equal populations of both spin states is defined as the transition temperature ($T_{1/2}$) and is a key parameter in the physical characterization of such systems. This switching behaviour turns such systems in perfect candidates for molecular-level based applications and has raised a lot of attention from the chemistry and physics community over the last years.[1]

d^6-Fe(II) based SCO systems can alternate between low-spin (S = 0) and high-spin (S = 2) states.

In this work, a computational method to study the SCO behaviour on dinuclear metal-organic cages of general formula $[Fe_2L^R_3]^{4+}$ (L=1,3-bis(3-(pyridin-2-yl)-1*H*-pyrazol-5-yl)benzene, R = -H, -F or CH_3) was carried out, in order to analyse the effect of different guest molecules X = H^-, F^-, Cl^-, Br^-, I^-, $[BF_4]^-$) on the tuning of the $T_{1/2}$.[2-4] Using the TPSSh/TZVP method, we computed the thermochemistry and $T_{1/2}$ for the cages with several guests molecules and different ligand functionalization.[5]

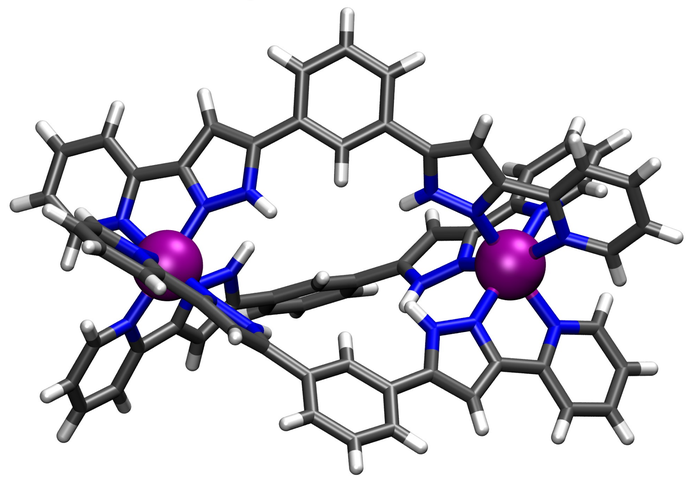


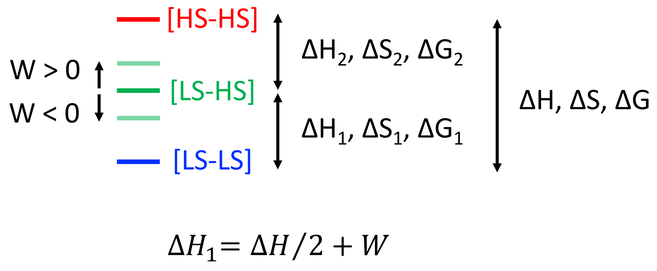
Figure 1. $[Fe_2L^R_3]^{4+}$ (L=1,3-bis(3-(pyridin-2-yl)-1*H*-pyrazol-5-yl)benzene, R = -H).

Modelling the transition

[LS-LS] ⇌ [LS-HS] ⇌ [HS-HS]
x y z

$$\Delta G_T = y(\Delta H_1 - T\Delta S_1) + z(\Delta H - T\Delta S) + \gamma(xy + yz + 2zx) + RT(x\ln(x) + y\ln(y) + z\ln(z))$$

γ = intermolecular interaction

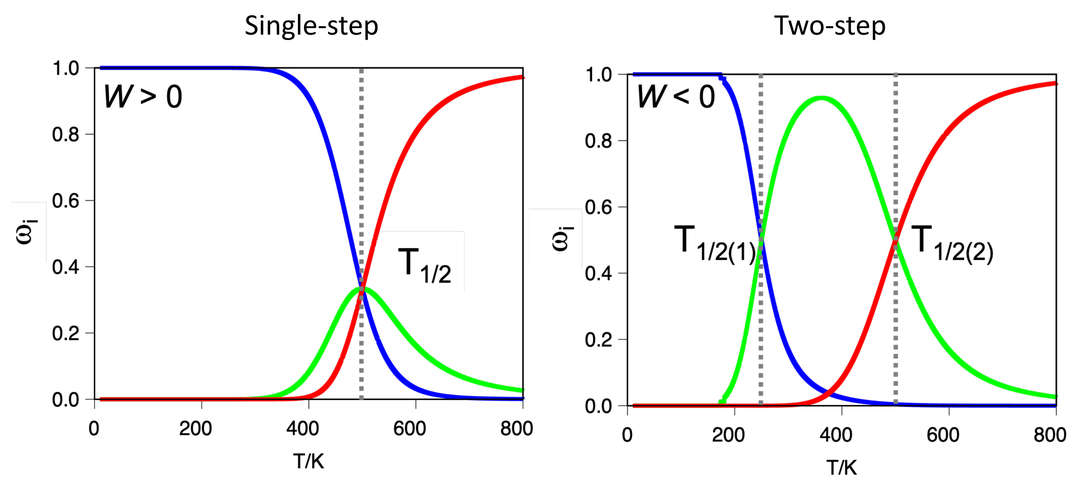


$$\Delta H_1 = \Delta H/2 + W$$

Equilibrium conditions:

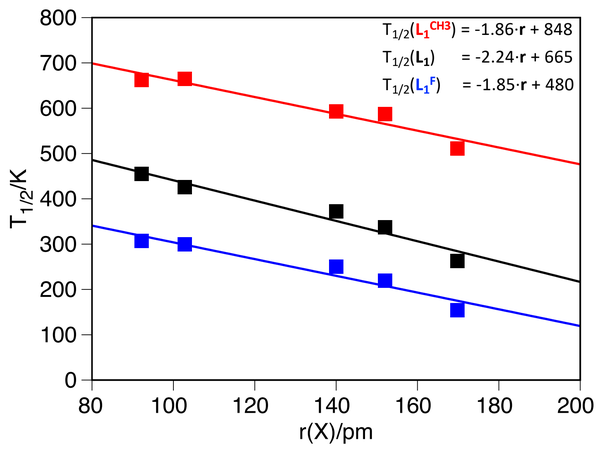
$$\begin{cases} x + y + z = 1 \\ \left(\frac{\partial \Delta G(x,y)}{\partial x}\right)_T = 0 \\ \left(\frac{\partial \Delta G(x,y)}{\partial y}\right)_T = 0 \end{cases}$$

Slichter and Drickamer's model applied to dinuclear species

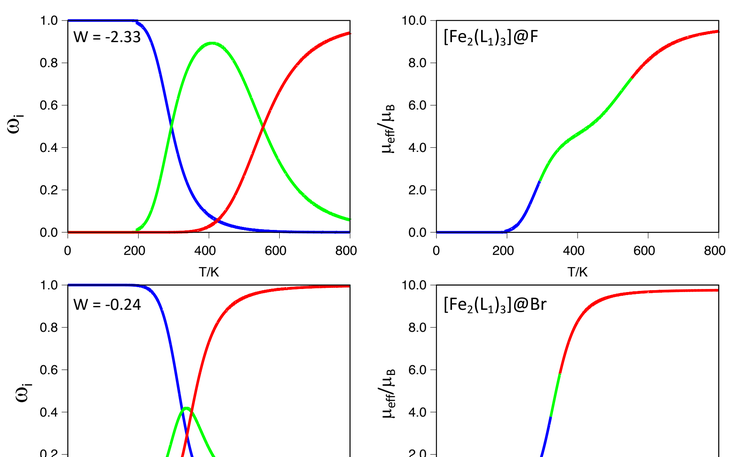


- Modelling the transition from thermochemistry
- Fitting of experimental data to extract thermochemical parameters

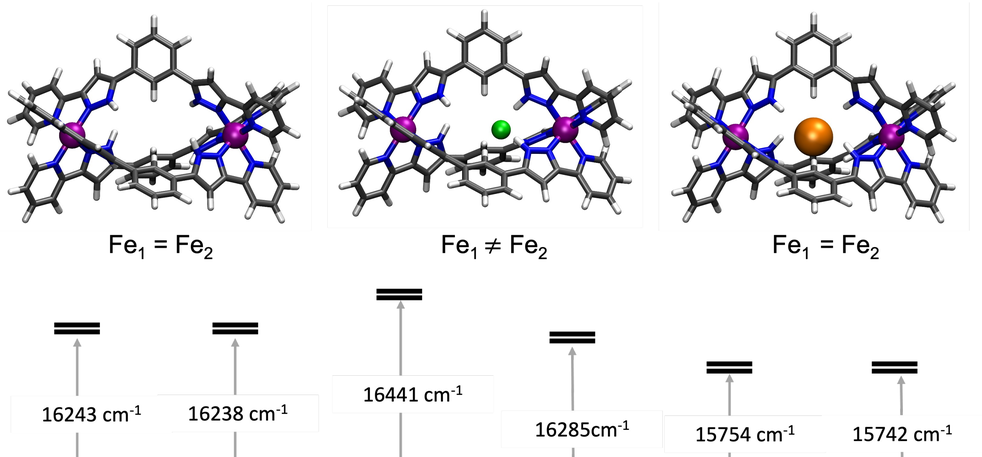
Computational study of the $([Fe_2L_3^R]@X)^{3+}$ systems



- It is possible to adjust $T_{1/2}$ by tuning the ligand field around the metal centre *via* ligand design
- Larger guests lead to smaller $T_{1/2}$



- Smaller guests stabilize [LS-HS] spin state, leading to two-step transitions



- Small guests move inside the cavity
- The closest metal centre gets affected by the guest

Conclusions

1. Electron-donating groups increase the ligand-field around the metal centre, yielding to larger $T_{1/2}$, while electron-withdrawing groups have the opposite effect.
2. Trends on the SCO behaviour upon guest adsorption and ligand functionalization can be observed; the larger the X atom is, the lower $T_{1/2}$, that is, there is a correlation between the size of the guest and the change in $T_{1/2}$.
3. Small guests lead to two-step transition, *via* stabilization of the [HS-LS] intermediate spin-state .

References

1. P. Gütlich and H. A. Goodwin, Spin Crossover in Transition Metal Compounds III, Springer Berlin Heidelberg, Berlin, Heidelberg, 2004, vol. 235.
2. M. D. Darawsheh, L. A. Barrios, et al. *Chem. Eur. J.* 2016, 22, 8635-8645.
3. M. D. Darawsheh, L. A. Barrios, et al. *Chem. Commun*., 2017, 53, 569.
4. M. D. Darawsheh, L. A. Barrios, et al. *Angew. Chem. Int. Ed.* 2018, 57, 13509-13513.
5. J. Cirera, E. Ruiz, *J. Mater. Chem. C*, 2015, 3, 7954.
6. Jian-Biao Liu, W. H. Eugen Scwarz, Jun Li, *Chem. Eur. J.* 2013, 25, 14758-14767.

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