

# Engineering spin transition compounds? A Solvent Game



Marc Hostettler<sup>a</sup>, Karl W. Törnroos<sup>b</sup>, Dmitry Chernyshov<sup>a,c</sup> & Hans-Beat Bürgi<sup>a</sup>

<sup>a</sup> Laboratorium für Kristallographie, Universität Bern, Freiestr. 3, 3012 Bern, Switzerland

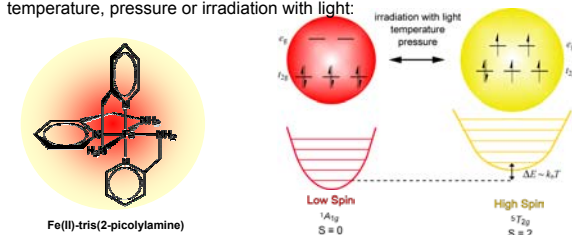
<sup>b</sup> Department of Chemistry, University of Bergen, Allég. 41, 5007 Bergen, Norway

<sup>c</sup> Petersburg Nuclear Physics Institute, Gatchina, St Petersburg 188350, Russia

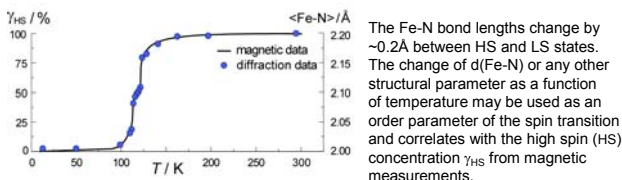


## INTRODUCTION TO SPIN TRANSITION COMPOUNDS

Spin state switching may occur under the influence of a change in temperature, pressure or irradiation with light:



Spin crossover is characterized by a transition curve relating the concentration  $\gamma_{HS}$  of the high spin state to temperature:



The Fe-N bond lengths change by ~0.2Å between HS and LS states. The change of d(Fe-N) or any other structural parameter as a function of temperature may be used as an order parameter of the spin transition and correlates with the high spin (HS) concentration  $\gamma_{HS}$  from magnetic measurements.

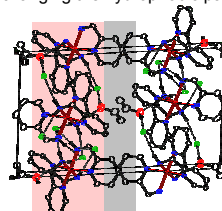
## ENGINEERING A SPIN TRANSITION COMPOUND?

Properties to be engineered and of interest for possible applications [2]:

- $T_{1/2}$ , the temperature at which half of the molecules are in the HS state, is mainly governed by the nature of the ligands and their bonding to a transition metal ion (ligand field theory).
- Abruptness and hysteresis properties of the spin conversion in the crystal. The shape of a spin transition curve depends on the interplay of intermolecular interactions between the metal complex, the counter-ions and the solvate molecules, as governed by the crystal packing [3].
- The control of the shape of the transition curve has not been very successful: in spite of big efforts to synthesize new materials and to derive empirical structure-property correlations, no general trends have yet been formulated.

## A TEST OF THE PARADIGM "STRUCTURE DETERMINES PROPERTY"

Our approach is to modify the weakest intermolecular interactions in the structure type of iron(II) tris-2-picolyamine dichloride alcohol solvates by changing the hydrophobic part of the solvate molecule.



### HIERARCHY OF INTERACTIONS:

- covalent bonds within complex, hydrogen bonds within layer, hydrophilic
- van der Waals contacts between layers, hydrophobic

Fe(II)-tris(2-picolyamine) dichloride ethanol solvate [1]

## CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF 6 SOLVATES

Four new solvates have been obtained in addition to the methanol [4] and ethanol [1] derivatives: 1-propanol, 2-propanol, t-butanol and allyl alcohol. Structures were determined at 200K and magnetic properties (ST) measured with a SQUID magnetometer. The 6 solvates are built from very similar layers, with comparable Fe-Fe distances, the same 2D Hydrogen-bond topology and the same layer-group symmetry  $p 2_1/a 1$ . Even though there are no obvious changes in the molecular packing, the different solvents induce lattice distortions as well as changes in the H-bond geometries.

### SIMILARITIES

Methanol  
Pbcn [4]  
ST: continuous

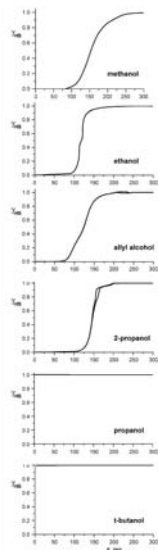
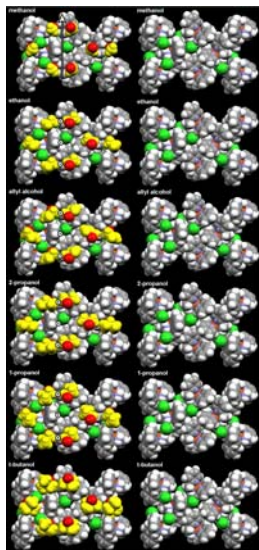
Ethanol  
B2/c [1]  
data @ SNBL  
ST: two steps

Allyl alcohol  
B2/c  
data @ home lab  
ST: two steps

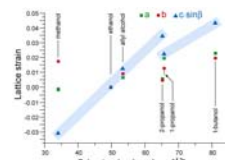
2-propanol  
B2/c  
data @ home lab  
ST: two steps with hysteresis

1-propanol  
B2/c  
data @ home lab  
ST: absent

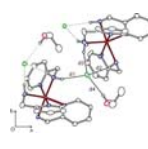
t-butanol  
B2/a  
data @ SNBL  
ST: absent



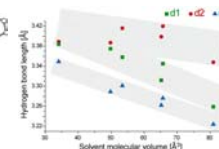
### DIFFERENCES



Strain parameter calculated with reference to the cell parameters of the ethanol derivative.



H-bonding scheme



Change of the H-bond lengths as a function of the solvent volume

## TAKE HOME MESSAGE

Testing the paradigm 'structure determines property':

- six very similar crystal structures show very different spin conversion behaviour
- the dissimilarity of the structures at the microscopic level and the influence of this dissimilarity on spin crossover behaviour are very complex and far from understood.

## REFERENCES

- [1] D. Chernyshov, M. Hostettler, K. W. Törnroos, H.-B. Bürgi, *Angew. Chem. Int. Ed.*, 2003, 42, 3825; D. Chernyshov, M. Hostettler, K. W. Törnroos, H.-B. Bürgi, *ESRF highlights*, 2003, 44.
- [2] O. Kahn, C. J. Martinez, *Science*, 1998, 279, 44.
- [3] P. Gütllich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed.*, 1994, 33, 2024; P. Gütllich, Y. Garcia, H. Spiering, in *Magnetism: Molecules to Materials IV*, J.S. Miller, M. Drillon, eds, Wiley-VCH, 2002.
- [4] A. M. Greenaway, E. Sinn, *J. Am. Chem. Soc.*, 1978, 100, 8080.

**Acknowledgements:** The staff at the Swiss Norwegian Beam Lines (SNBL) at the European Synchrotron Research Facility. University of Berne: Professor Gion Calzaferri, Dr Andreas Sieber.