

Ordering in a spin crossover compound

Uncovering the nature of the intermediate phase of Fe(II) tris(2-picolyamine) dichloride ethanol

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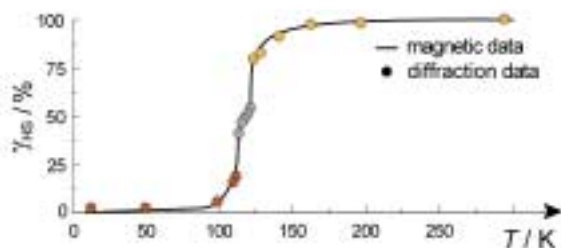
INTRODUCTION

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

Spin crossover is characterized by a transition curve relating the concentration of the HS state to temperature. The three temperature domains of a double step transition are associated with a HS phase, an intermediate phase (IP) and a LS phase.

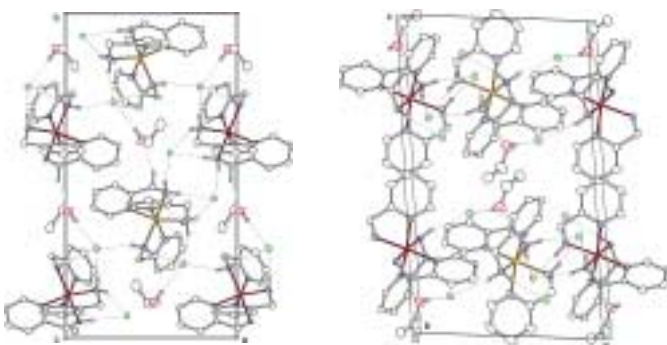
Optical and magnetic data of the title compound show a plateau between $T_1=122$ K and $T_2=114$ K, while the crystal structure has been reported to be the same in the three phases with no change of crystal symmetry [1].

SPIN TRANSITION CURVE



CRYSTAL STRUCTURE OF THE IP

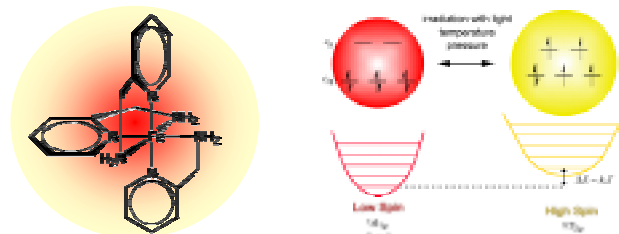
Hydrogen bonded layer Hydrophobic interlayer contacts



In the HS and LS phases the two different iron, chlorine and ethanol sites become indistinguishable.

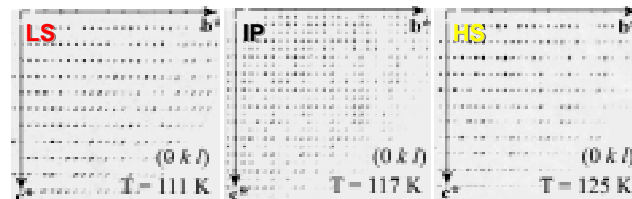
WHAT HAVE WE LEARNT?

- To measure a spin transition curve using X-ray diffraction
- Spin crossover is associated with an *isostructural transition*
- The observed ordered IP combined with the isostructural HS and LS phases implies a *re-entrant transition behaviour*



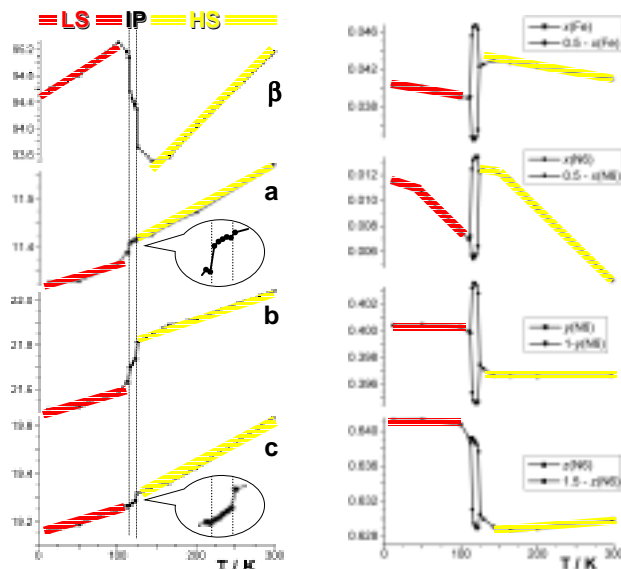
16 DIFFRACTION EXPERIMENTS BETWEEN 12 AND 298 K

We have reinvestigated the title compound to characterize the expected short-range-correlations in the plateau [2]. Instead of diffuse scattering we have discovered additional Bragg reflections disclosing an ordered IP between two transitions [3].



T - DEPENDENCE OF CRYSTAL STRUCTURE

Lattice parameters (left), fractional coordinates (right) from X-ray experiments carried out at the SNBL (ESRF):



REFERENCES

- [1] Gütlich P., Garcia Y., Spiering H., *Magnetism: Molecules to Materials IV*, J.S. Miller, M. Drillon, eds, Wiley-VCH, 2002.
- [2] Gütlich P., Hauser A., Spiering H., *Angew. Chem. Int. Ed.*, 1994, **33**, 20.
- [3] Chernyshov D., Hostettler M., Törnroos K. W., Bürgi, H.-B., *Angew. Chem. Int. Ed.*, 2003, **42**, 3825.