



	Experiment title: Measurement and interpretation of diffuse x-ray scattering from a mixed high spin-low spin phase of an Iron(II) spin-crossover complex	Experiment number: CH-1316
Beamline: BM01A	Date of experiment: from: 11 Sept. 2002 to: 14 Sept. 2002	Date of report: 08 April 2003
Shifts: 9	Local contact(s): Dr. Silvia Capelli	<i>Received at ESRF:</i>
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Report:

The compound $[\text{Fe}^{\text{II}}(2\text{-picolyamine})_3]\text{Cl}_2 \cdot \text{EtOH}$ (Fig. 1) exhibits a temperature dependent spin crossover with an intermediate regime represented by a plateau in the spin transition curve, spanning the temperature range 113-123 K and showing an approximately equal concentration of high- and low-spin molecules (Fig. 2b). The purpose of the experiment was to investigate the postulated short range order of different spin states [1] by analysing the diffuse scattering.

Diffuse scattering was observed for several crystals coming from a sample several years old. Since the diffuse signals do not show any significant temperature dependence, it is very improbable that they reflect spin disorder. So far we can not say whether this scattering is linked to an aging process or if it has a mechanical origin (the samples had to be cut prior to the diffraction experiment). The diffraction pattern of freshly grown single crystals of the compound revealed no diffuse scattering at any temperature, neither in the plateau, nor close to the steps. This is surprising since there are two types of disorder in the structure: firstly, the disordered arrangement of the HS and LS complexes mentioned above, and secondly, a distribution of the alcohol oxygen atoms over two positions. The lack of observable diffuse scattering strongly suggests that the spin transition does not induce short-range order of any importance.

Instead of short-range order and contrary to all previous diffraction studies [2] we have observed two successive structural phase transitions at $T_1 = 123$ K and $T_2 = 113$ K. The two transitions and the three associated phases have been characterized by structure determinations at 16 different temperatures in the range 300 to 12 K. In all three phases the crystal structures are built from hydrogen-bonded layers of complex cations, chloride anions and alcohol molecules. The layers are stacked via hydrophobic contacts between the hydrocarbon parts of the ligand and alcohol molecules.

In the HS and LS phases all iron atoms are crystallographically equivalent and the two spin states appear to be distributed randomly in the crystal. The unit cell dimensions are similar and the space groups are the same ($B2_1/c$). Superficially the two structures look the same. Closer inspection shows that there are discontinuous differences in the unit cell constants, the atomic coordinates and their variation with temperature. Figure 3a shows the change of the monoclinic angle β with temperature, figure 3b shows the evolution of the x-coordinate of the iron atoms. Analogous behavior is observed for most other structural parameters. If the evolution of the HS into the LS structure was not interrupted by an intermediate phase (IP),

the changes in structural parameters would be associated with a so-called *isostructural* phase transition [3], which is always of first order, i.e. associated with a latent heat.

In the intermediate ordered structure the unit cell volume doubles and there are now two independent iron sites in the unit cell, because the B-centering is lost (P2₁/c). The atoms occupy neither the HS nor the LS positions, but are displaced significantly from both (figure 3b). The average Fe-N distances plotted in figure 2a show that upon entering the IP one site becomes predominantly HS, the other one predominantly LS.

In summary, this work corrects misinterpretations of earlier diffraction data and provides the most detailed structural description of the spin and order-disorder transitions of [Fe(2-pic)₃]Cl₂·EtOH and probably of any spin transition compound. The crystal structures at high and low temperatures clearly show that the HS and LS phases are different; their relationship being isostructural. The IP with its partial order shows that the intermediate plateau in the two-step transition of this compound is associated with a two-sublattice structure as observed for other compounds with two-step behavior. The combination of the isostructural HS and LS phases with the partially ordered IP leads to a reentrant phase transition behavior, a relatively rare phenomenon. The quantitative characterization of the degree of disorder in the iron complex and the ethanol molecule will serve as a basis for analysing the experimentally determined specific heat and the entropy of the compound.

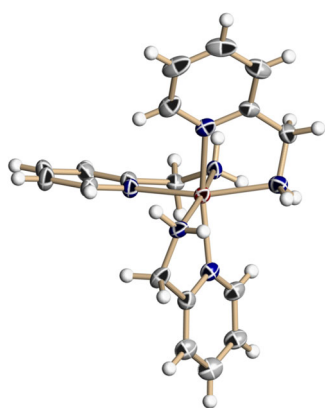


Fig 1. The cationic Fe^{II}(2-picolyamine)₃ complex molecule.

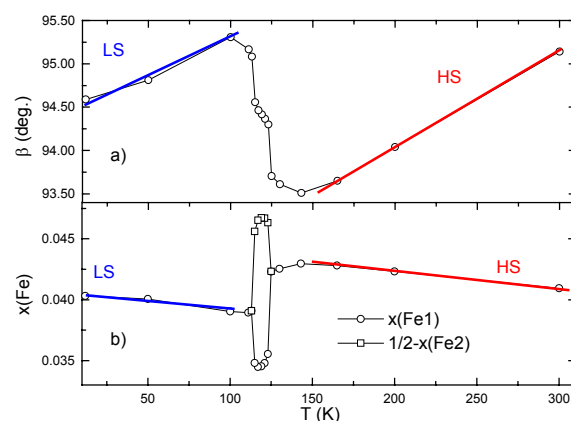


Fig. 3. a) Temperature dependence of the monoclinic angle β . b) x-coordinate of the Fe-atoms as a function of temperature. The coordinate of Fe2 in the IP is given as $\frac{1}{2} - x(\text{Fe}2)$ for easier comparison with $x(\text{Fe}1)$. The blue and red lines highlight the temperature dependence of $x(\text{Fe})$ in the HS and LS structures. Standard uncertainties are approximately equal to symbol sizes in both figures.

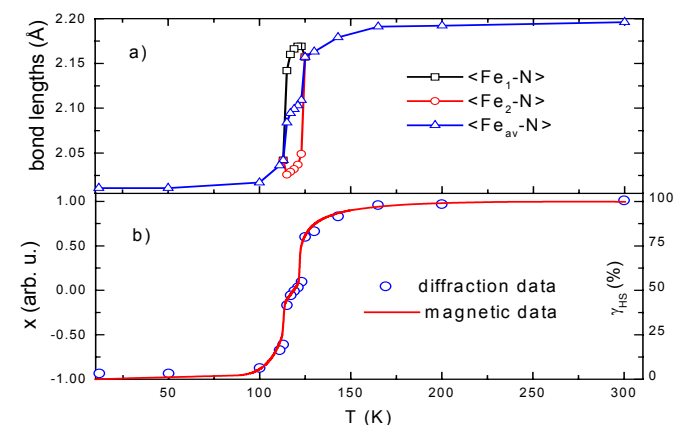


Fig. 2. a) Temperature dependence of the average $\langle \text{Fe-N} \rangle$ bond lengths. The IP shows two different bond lengths associated with two different iron sites; they are close, but not equal to the HS and LS values (the lines are guides to the eye). b) Comparison of spin transition behavior from diffraction and magnetisation experiments

References

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