Structural Investigation of $Fe(btr)(pz)(NCS)_2 \cdot xH_2O$ with Synchrotron Powder X-ray Diffraction

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Being with the dual magnetic properties associated with transition between spin states (of metal atoms) as the consequence of perturbation such as temperature, pressure and/or light irradiation, spin crossover (SCO) systems have drawn a lot of research attention in the past few decades due to the potential of application on storage devices, display chips and molecular switches[1-3]. Modification of ligand field strength and the corresponding cooperative effect within the lattice are especially concerned. $Fe(btr)_2(NCS)_2 \cdot H_2O$ is one of the typical SCO complexes, for which an abrupt spin transition with a hysteresis loop of about 21 K is characterized in the temperature dependent magnetic measurement (Figure 1)[4-5]. Within the lattice, the 2D framework structure composed by the coordination between Fe atoms and btr ligands are responsible for the corresponding strong cooperativity and the correlative magnetic behavior.

In the present work, pyrazine is introduced to replace one of the btr ligands to retain the 2D framework structure by taking the high possibility of acting as a bridge ligand as well. The speculated formula is $Fe(btr)(pz)(NCS)_2 \cdot xH_2O$. However the expected strong cooperative effect is not observed, according to the corresponding magnetic measurement where a gradual spin transition is presented (Figure 1). Besides, the relatively large residual HS component reveals the existence of multiple crystallographically unique Fe sites in the lattice. Structure of $Fe(btr)(pz)(NCS)_2 \cdot xH_2O$ was studied with the single crystal X-ray diffraction measurement but failed due to the unpreventable problem of twin crystal. Thus, synchrotron powder X-ray diffraction experiment is performed.

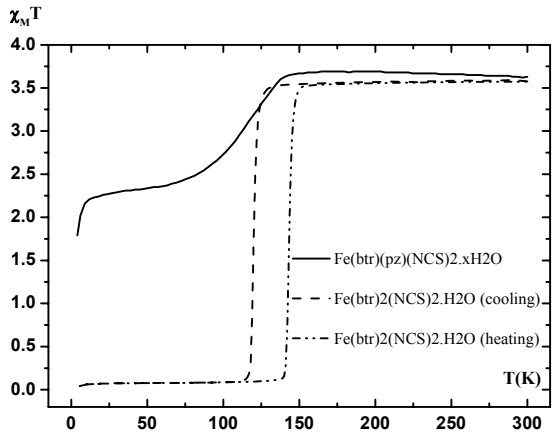

Figure 1. Magnetic measurement of $Fe(btr)_2(NCS)_2 \cdot H_2O$ and $Fe(btr)(pz)(NCS)_2 \cdot xH_2O$.

The corresponding patterns collected at both 298 K for HS (high spin) state and 7 K for LS (low spin) state are shown in Figure 2. Crystalline phase of the powder sample of $Fe(btr)(pz)(NCS)_2 \cdot xH_2O$ is well illustrated with the intensive peaks (with acceptable S/N ratio) appearing even at high 2θ angle around 60°. With decreased temperature, shifts of reflection peaks (toward lower 2θ angle) expected for the unit cell shrinkage due to both temperature effect and spin crossover behavior is not obvious, which might be attributed to the poor overall resolution. Nevertheless, unit cell indexing is in progress. However, a more accurate and precise data collection with the fully optimized instrumental alignment is necessary for the eventual structure determination.

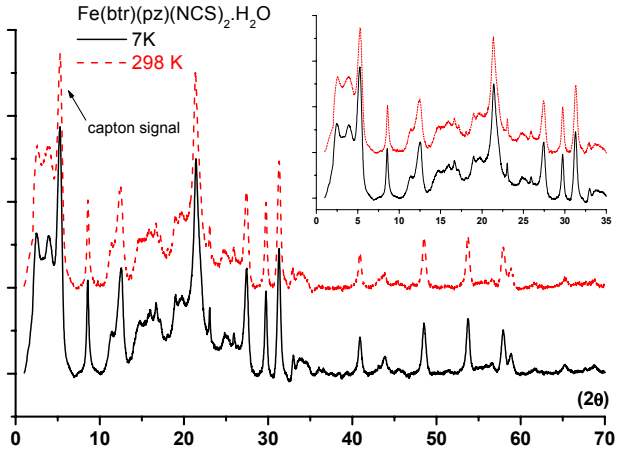

Figure 2. Powder patterns of $Fe(btr)(pz)(NCS)_2 \cdot xH_2O$ collected at 298 K (dash line) and at 7 K (solid line).

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