Anionic spin-crossover complex of Fe(III) with space symmetry transition and thermal hysteresis around room temperature

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The 2D spin-crossover potassium salt of the $N_2S_2O_2$-coordination Fe(III) anion K[Fe(5Cl-thsa)$_2$] (5Cl-thsa−5-chlorosalicylaldehyde thiosemicarbazone) is synthesized and characterized structurally and magnetically over a wide temperature range [1]. The salt exhibits a complete three-step cooperative SCO transition in the temperature range 2-440 K both in the heating and cooling modes: the first step occurs in a temperature range from 2 K to 50 K, the second abrupt hysteretic step occurs from 200 K to 250 K with $T_{1/2}$=½·($T_{1/2}$↑+ $T_{1/2}$↓)=230 K ($T_{1/2}$ = temperature of 50 % HS to LS conversion) and a 6 K hysteresis loop, the third gradual step occurs from 250 K to 440 K.

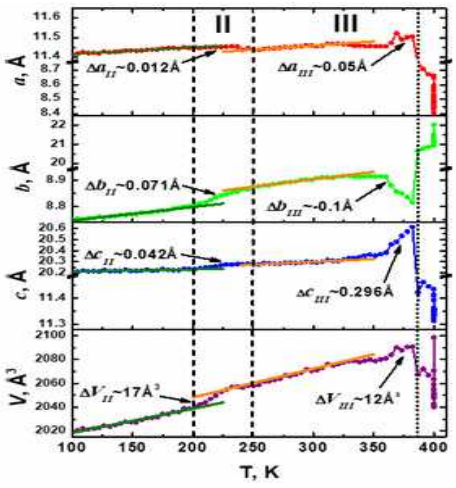

Figure 1. The dependences of K[Fe(5Cl-thsa)$_2$] salt unit cell parameters based on XRPD data in the temperature range 100-400 K for *a*, *b*, *c* and *V*. Roman numerals **II** and **III** indicate the SCO step numbers according to magnetic measurements. The short dashed lines (---) mark borders of the distinct SCO steps. The dotted line (⋯) at ~387 K indicates the orthorhombic-to-monoclinic structural phase transition (*Pbcn*→*P2$_1$/n*). Note that the Y-axes for *a*, *b*, and *c* parameters contain breaks.

A peculiar effect of structural lagging was revealed (Fig. 1), associated with the discrepancy between the expected significant increase in the iron(III)-ligand bond lengths with an increase in the HS concentration by 57% at the second stage of SCO transitions. This non-trivial phenomenon was investigated in detail applying magnetization measurements, ^{57}Fe Mössbauer spectroscopy, and DFT calculations.

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[1] N.G. Spitsyna, M.A. Blagov, V.A. Lazarenko, *et. all*., *Inorganic Chemistry*. **2021**, *60*, pp. 17462-17479.