Unique spin crossover pathways differentiated by scan rate in a new dinuclear Fe(II) triple helicate: Mechanistic deductions enabled by synchrotron radiation studies

M.J. Wallis, A.R. Craze,† H. Min, and F. Li

School of Science, Western Sydney University, Locked Bag 1797, Penrith, NSW 2751, Australia, † - current address: Department of Chemistry, University of Oxford, 12 Mansfield road, Oxford, OX1 3TA, UK

17232236@student.westernsydney.edu.au

Keywords: Dinuclear triple helicate, spin crossover, scan rate, phase transition, synchrotron

The achievement of targeted properties in spin crossover (SCO) materials is complicated by often unpredictable cooperative interactions in the solid state. Herein, we report a dinuclear Fe(II) triple helicate, which is a rare example of a SCO material possessing two distinct magnetic behaviors that depend upon the thermal scan rate (Figure 1) [1]. The desolvated material was seen to undergo spin transition (ST) which was complete following slow cooling (1 K min\(^{-1}\)), but incomplete ST (corresponding to 50% conversion) on fast cooling (10 K min\(^{-1}\)). The incomplete ST observed in the latter case was accompanied by a higher temperature onset of ST, differing from TIESST (Temperature-Induced Excited Spin-State Trapping) materials. The two SCO pathways have been shown to arise from the interconversion between two structural phases (a and b), with both phases having associated high spin (HS) and low spin (LS) states. SCXRD (Single Crystal X-ray Diffraction) experiments using controlled cooling rates and a synchrotron light source enabled short collection times (2-3 minutes per dataset) which has enabled the identification of a mechanism by which the slow-cooled material may fully relax. In contrast, fast-cooled materials exhibit disordered arrangements of multiple structural phases, which has in turn revealed that the [HS-LS] ↔ [LS-HS] equilibria are controllable in the solid by varying the scan rate. Such behavior has been previously observed in solution studies, but its control in solids has not been reported up to now. The structural transformations associated with the relaxation of the material by each pathway have been analysed using non-conventional structural parameters describing the orientation of chelate groups and terminal ring moieties. This study demonstrates how intermolecular cooperativity can allow multiple distinct magnetic behaviors, and provides some insight into how [HS-LS] ↔ [LS-HS] equilibria can be controlled in the solid state, which may assist in the design of next-generation logic and signaling devices.

Figure 1. Scan-rate dependent magnetic profile and corresponding structural phase changes in the dinuclear triple helicate material.
