

Communication

Multistability at room temperature in a bent-shaped spincrossover complex decorated with long alkyl chains

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Multistability at room temperature in a bent-shaped spin-crossover complex decorated with long alkyl chains

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S Supporting Information

ABSTRACT: A novel iron(II) pyridyl-benzohydrazonate based complex decorated with long alkyl chains is reported as a rare spin-crossover compound displaying a wide thermal hysteresis spanning room temperature. On heating mode, this compound exhibits a spin transition between a LS ground state and an ordered HS-LS phase with symmetry breaking from monoclinic P_{21}/n into orthorhombic $P_{21}_{21}_{22}$ space groups. During the cooling, the compound first transits into a magnetically distinguishable HS-LS phase with monoclinic P_{21} symmetry before returning into the LS phase. The interconversion between the two distinct HS-LS phases is the result of subtle structural changes in the alkyl chains and produces a second minor thermal hysteresis that superposes to the large one. This unprecedented result shows that the combination of a conventional cooperative spin transition and ligand-driven magnetic changes can promote magnetic tristability at room temperature.

>pin-crossover (SCO), which involves an interconversion between the low-spin (LS) and high-spin (HS) states of a metal ion, is considered as one of the most appealing phenomena for the development of molecule-based switchable materials.¹ Remarkably, the spin-state switching can be triggered by a large panel of means (e.g. temperature, pressure, light, magnetic/electric fields or chemical stimuli) and in the meantime affords a broad variety of detectable changes associated with magnetic, optical, dielectric and mechanical properties. Experimentally, the SCO process can be gradual in temperature, following Boltzmann population of the excited HS state (i.e. a thermal spin conversion), or it can involve a first order phase transition (i.e. a spin transition) that can be abrupt, stepwise or hysteretic, providing ideal conditions for potential applications in either sensors, switches or memories.² Controlling the nature of the SCO behavior and its characteristic temperature through molecular design and crystal engineering is one of the main focuses in moleculebased magnetism, and in this frame, materials displaying wide thermal hysteresis (> 30 K) centered at room temperature (RT) are the most wanted.³ Spin transitions have been successfully promoted by creating covalent linkage between SCO centers in coordination polymers⁴ or through supramolecular approaches⁵ by generating for instance efficient hydrogen bonding networks. However, SCO systems fulfilling both large hysteresis and RT transition criteria still remain extremely uncommon.^{2a,5,6} In other hand, major research efforts have been recently dedicated to nanostructuring and processing SCO compounds as fundamental steps toward their possible implementation into technological devices.⁷ In this respect, modification of ligands or counter-ions with long alkyl chains appears as one of the best and straightforward options since the low melting temperature, high solubility and amphiphilic character of resulting materials provide opportunities to produce liquid-crystals,⁸

gels,9 surfactant-free Langmuir Blodgett films¹⁰ and other wet-method based self-assemblies.11 While transferring the SCO property to these soft materials is usually successfully achieved, preserving its hysteretic character is more challenging, owing to the reduction of size or thickness of the self-assemblies and/or the loss of 3D structural order. Even when occasionally these alkylated complexes crystalize and display a spin transition,¹² its hysteretic character is less pronounced than in non-alkylated analogues since the flexible alkyl chains absorb the intrinsic deformations of the SCO cores without being able to efficiently propagate them across the lattice. Nonetheless, these materials can count on other sources of cooperativity, which rely on the ability of the flexible substituents to promote phase transitions as exemplified at solid / liquid-crystal¹³ or solid / isotropic liquid¹⁴ first order transitions. In crystalline phases, entropy-driven conformational isomerization of alkyl chains such as *anti/gauche* changes or order/disorder transitions can also affect magnetic properties¹⁵ and promote spin-state switching as strikingly illustrated in Co^{II}/terpyridine compounds featuring "reverse" spin transition.¹⁶ Herein, we report on a novel iron(II) pyridyl-benzohydrazonate based complex functionalized with decyl chains, $[Fe(C_{10}-pbh)_2]$ (1; C_{10} -pbh = (1Z,N'E)-4-(decyloxy)-N'-(pyridin-2-ylmethylene)-benzohydrazonate), displaying spin transition with a wide thermal hysteresis around RT. Furthermore, we demonstrate for the first time that a spin transition and the concomitant presence of a monotropic phase lead to magnetic tristability at room temperature.

Complex 1 was prepared by combining stoichiometric amounts of $Fe^{II}(ClO_4)_2$ and C_{10} -pbhH ligand in hot methanol in presence of a base (Et₃N). In a few hours, black prismatic crystals form in good yield (~80%; Supporting Information). At 315 K, 1 crystallizes in the orthorhombic P21212 space group (Tables S1-S3) for which the asymmetric unit consists of two crystallographically unique halves of $[Fe(C_{10}-pbh)_2]$ (Figure 1), located on a 2-fold rotation axis that crosses the corresponding Fe site along c-axis. Both Fe sites feature a distorted octahedral N4O2 coordination sphere provided by two tridentate ligands in mer configuration. The Fe-ligand distances for Fe1 ($d_{\text{Fe1-O}} = 2.08$ and $\langle d_{\text{Fe1-N}} \rangle = 2.16$ Å) and Fe2 ($d_{\text{Fe2-O}} = 1.98$ and $\langle d_{\text{Fe2-N}} \rangle = 1.91$ Å) are in fair agreement with values previously reported for Fe(II)/pbh analogues with HS and LS configurations,^{14,17} respectively, indicating that 1 forms an ordered HS-LS phase. The coexistence of HS and LS species is also supported by the octahedral distortion parameter (Σ) ,¹⁸ which is much larger for Fe1 (154.1°) than Fe2 (79.2°) .¹⁷ The long alkyl chains attached to the aryl moieties afford a bent geometry to the complexes, which self-assemble in a bilayer lamellar organization along the *b*-axis with an upside-down arrangement between two subsequent layers; the interlamellar distance, corresponding to b/2, is 21.05 Å (Figures 2, S2-S4). The bending angles δ_i , defined by the metal center and the two terminal carbons of the alkyl



Figure 1. Balls and sticks view of crystallographically unique complex(es) **1** in the $P2_12_12$ (315 K), $P2_1$ (290 K) and $P2_1/n$ (220 K) phases viewed along the *c*-axis. Color scheme: Fe^{II}_{HS} green, Fe^{II}_{LS} orange, N blue, O red, C grey, H Pink.

chains ($\delta_{HS} = 107.6^\circ$, $\delta_{LS} = 101.8^\circ$), are similar despite a much stronger octahedral distortion of the HS Fe(II) site, allowing therefore a near ideal lipid-like assembly with an optimal interdigitation. The rigid-core sheets consist of alternating HS/LS moieties where the Fe(II) centers are perfectly co-planar (*ac* plan). The cohesion within Fe(II) layers is essentially assured through C-H…X (X = N, O, π) short contacts. Among those, C-H…O interactions, which range between 2.38 and 2.67 Å for oxygen atoms belonging to the Fe(II) coordination spheres, appear as the most relevant to explain cooperative effects within the 2D metal ion array (Figure S4, Table S4).

Upon cooling to 290 K, unit-cell parameters of 1 remain nearly constant except for β that increases to 91.3°, leading to a change of symmetry from orthorhombic P21212 into monoclinic P21 space group. This phase transition is not related to a SCO phenomenon since no significant evolution of the Fe(II) coordination sphere and distortions (Σ , Θ) was detected for the two independent complexes (Table S2). A close examination of structure suggests that the symmetry change is due to an entropydriven transition,^{15,16,19} involving a conformational isomerization occurring in decyloxy chains of the HS molecules. Indeed, the oxy-pentylene fragments adopt a gauche-anti-gauche (gag) conformation at 315 K (the rest of the chain being all anti), while the comparative fragments at 290 K embrace an energetically more stable anti-anti-anti (aaa) geometry (Figure 1).^{15,19b} Although this transition does not provoke spin-state switching, the twisting in the *ac* plan and loss of C₂ symmetry elements modify the intermolecular interactions within the 2D metal layers. Especially, the HS Fe(II) ion establishes shorter contacts with a pyridyl ring of a neighboring LS molecule (C-H...Fe 3.20 Å), while noticeable changes in C-H-O interactions involving Fe(II) coordination spheres are also observed (Figure S4 and Table S4). As revealed by the magnetic properties below, such local changes, which slightly affect the coordination geometry of metal ion and its resulting g factor, induce a substantial alteration of the magnetic susceptibility, giving rise to non-SCO magnetic bistability.^{15,19a}



Figure 2. Crystal packing of 1 at 315 K viewed along the *a*-axis. Fe^{II}_{LS} and Fe^{II}_{HS} are shown as orange and green octahedra, respectively.

When further cooling, a second transition occurs around 270 K as shown by the brutal change of lattice parameters (Figure S1, Tables S1, S3). At 220 K, a centrosymmetric $P2_1/n$ space group is found revealing a second crystallographic symmetry breaking. In this low temperature phase, the asymmetric unit contains a single Fe(II) site for which the coordination bond distances reveal unambiguously its LS state (Figure 1, Table S2). Remarkably, the geometry of the molecule is strongly modified with a bending angle of 87.5° (Figure S2). This δ angle is close to the ideal value for an octahedral center and contrasts with the larger values (98.6-107.6°) found for the HS-LS phases due to the strong octahedral distortion of the HS complexes. This structural change leads to an impressive shrinkage (about 11 %) of the interlamellar distance from 20.99 Å (290 K) to 18.80 Å (220 K). While shorter Fe-ligand bonds and the 2D organization of the molecule rigid cores (within ac plan) should favor a concerted contraction of the network, an increase of the first neighbor Fe…Fe distance from 6.49 Å (290 K) to 7.19 Å (220 K) and an expansion of the ac lattice surface (about 7 %) are observed. This counter-intuitive effect can be easily rationalized considering the strong decrease of the bending angle and the resulting shortening of the interlamellar distance, which mechanically implies an expansion within the 2D metal array in order to preserve an optimum interdigitation of alkyl chains. These observations support that the overall deformation of the crystal packing is driven by the "breathing" of the alkyl chains relaying the octahedral distortion of the Fe coordination sphere. As a result, important rearrangements and a weakening of the supramolecular interactions are seen within the metal ion layers (Table S4, Figure S4). Reciprocally in the P21 and P21212 phases, stronger intermolecular constraints resulting from *ac* plan contraction is believed to be responsible for the partial spin transition and thus the stabilization of a HS-LS state.

As in many other switchable materials, the strong deformations inherent to the present first order phase transitions unfortunately affect the quality of the single-crystals, preventing further single-crystal X-ray diffraction experiments on heating mode. Thus, to probe the reversibility of the thermal behavior and eventual hysteretic effects, differential scanning calorimetry (DSC) measurements were performed. DSC data revealed a perfectly reproducible thermal behavior over cycling, while no significant effect of the sweeping rates from 1 to 10 K/min was evidenced (Figures 3 and S7). During the cooling, two exothermic peaks are found at 296 and 267 K confirming the two successive $P2_12_12 \rightarrow P2_1$ and $P2_1 \rightarrow P2_1/n$ phase transitions, respectively (Figure S1). The enthalpy and entropy changes associated to spin transition at 267 K, $\Delta H =$ -13.9 kJ mol⁻¹ and ΔS = -52.1 J K⁻¹ mol⁻¹, are relatively high considering that only one of the two complexes experiences spin-state switching. Nevertheless, these values can be rationalized considering that strong deformations of the overall crystal packing (vide supra) are associated to the spin transition. The enthalpy and entropy of high-temperature transition (296 K), $\Delta H = -10.1$ kJ mol⁻¹ and $\Delta S = -34.1$ J K⁻¹ mol⁻¹, fall in the expected range for anti/gauche conformational isomerizations taking 1

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into account that four of them are present in the HS complex.¹⁵ Hence, the gag/aaa isomerization appears unambiguously the primary cause behind this crystallographic phase transition. During the warming (Figures 3 and S7), only one sharp endothermic peak is found at 301 K with ΔH = 22.6 kJ mol⁻¹ and ΔS = 75.1 J K⁻¹ mol⁻¹. These values, which roughly correspond to the $\varDelta H$ and $\varDelta S$ sums obtained from the two exothermic peaks, and the high symmetry of the peak, suggest that both spin transition and isomerization of alkyl chains occur in a concerted fashion $(P2_1/n \rightarrow P2_12_12)$. As a consequence, the $P2_1$ phase is unequivocally a monotropic polymorph, which appears only in a metastable domain between the thermodynamic $P2_1/n$ (LS) phase and the entropic $P2_12_12_1$ (HS-LS) phase. When warming from the $P2_1$ phase, the reverse $P2_1 \rightarrow$ $P2_12_12$ transition is observed at 299 K ($\Delta H = 10.2$ kJ mol⁻¹ and $\Delta S = 34.1$ J K⁻¹ mol⁻¹), revealing a hysteresis of about 3 K. Hence, between 296 and 299 K, three distinct phases can be observed depending on the thermal history of 1, conferring to this material an unprecedented tristability.



Figure 3. Differential scanning calorimetry (DSC) traces for **1** in the range 350-230 K (black) and 350-285 K (red), showing the monotropic thermal behavior (10 K/min).

This intriguing thermal behavior was also monitored by powder X-ray diffraction (PXRD) experiments. The sample was first cooled to 77 K to reach the LS phase and then PXRD patterns were collected on warming mode between 273 and 383 K (Figure 4 left, Figure S5a). The diffractograms below and above 303 K are in good agreement with simulated powder patterns for the $P2_1/n$ and $P2_12_12$ phases (Figure S6), respectively. No evidence for the P21 phase was detected including during the transition, confirming DSC data and the monotropic nature of this phase. On the subsequent cooling/heating cycle between 383 and 273 K (Figure 4, center and right), the $P2_12_12 \rightarrow P2_1$ transition is detected somewhere between 298 and 293 K, while the reverse transition is found between 298 and 303 revealing a slightly hysteretic behavior. It is noteworthy that the monotropic phase remains stable down to 273 K, showing a bistable $P2_1/n - P2_1$ domain of at least 25 K. The tristability of **1** is illustrated by the subsequent collections at 298 K (central pink diffractogram in Figure 4), which can be assigned to the three distinct phases, $P2_1/n$, $P2_12_12$ and $P2_1$, from left to right parts of Figure 4.

Magnetic susceptibility measurements recorded between 1.8 and 400 K are shown as $\chi T vs. T$ plot in Figure 5. Below 300 K, the χT value is close to zero (at 100 K: 0.08 cm³ K mol⁻¹) as expected for a diamagnetic material like **1** in its LS ground state. Above 300 K, a first-order spin transition centered at 303 K is observed. At 320 K, the χT product (normalized per Fe(II) complex) reaches 1.55 cm³ K mol⁻¹ in agreement with a HS-LS phase containing a 1:1 mixture of two isolated Fe(II) magnetic centers, one being LS (S = 0) and one HS (S = 2). Up to 400 K, no further marked evolution of the χT product is observed confirming the incomplete SCO behavior. When cooling, the χT product decreases slowly from 1.67 cm³ K mol⁻¹ at 400 K to 1.49 cm³ K mol⁻¹ at 300 K, upon which its value jumps to 1.58 cm³ K mol⁻¹ (295 K), reaching a plateau down to about 273 K. This magnetic anomaly coincides with the

 $P2_12_12 \rightarrow P2_1$ transition between HS-LS phases detected by DSC and Xray diffraction techniques. Therefore, the variation of the susceptibility is undoubtedly induced by the slender modification of supramolecular contacts around the HS iron(II) site (*vide supra*).

Figure 4. Variable-temperature PXRD patterns of **1** recorded between 273 and 383 K on heating-cooling-heating modes, showing the $P2_1/n \Rightarrow P2_12_12$ (left), $P2_12_12 \Rightarrow P2_1$ (center), $P2_1 \Rightarrow P2_12_12$ (right) transitions.

Figure 5. Temperature dependence of the χT product at 1 T for 1 over the 1.8-400 K range (0.2 K/min). Inset: expanded view between 292 and 306 K emphasizing the P2₁ / P2₁2₁2 transition (0.05 K/min).

Upon further cooling, the transition into the diamagnetic $P2_1/n$ phase is observed at 268 K, revealing a thermal hysteresis of about 35 K, which is reproducible over cycling and almost scan rate independent (0.2 to 12 K/min; Figure S9). It should be emphasized that the hysteresis is much wider than in any pbh based analogues,¹⁷ making of this compound one of the rare examples displaying an improvement of the cooperativity upon functionalization with alkyl chains.^{11a,16} Remarkably, 1 is also one of the very few SCO compounds displaying this type of properties in the RT region, which is considered as a prerequisite for numerous practical applications. In agreement with calorimetric and X-ray diffraction experiments, the warming from the HS-LS P21 phase reveals a weak hysteresis loop (ΔT = 1.2 K; 0.05 K/min) centered at 298.8 K associated with the $P2_1 / P2_12_12$ transition (Figures 5 inset, S10). Although the shape and small width of the hysteresis loop prevent from reaching the maximal amplitude of the magnetic signal at the same temperature, three distinct χT values (e.g. at 298.8 K: 0.14, 1.51 and 1.57 cm³ K mol⁻¹) can be measured depending on the thermal history of the material. It is noteworthy, that a similar small jump of the magnetic moment occurring in a spin transition hysteresis loop was previously described in a Co(II) terpyridine complex, however the crystal structures on both sides of the transition, as well as its potential hysteretic character, were not reported.^{16a}

In summary, we have reported the synthesis, structural and magnetic characterizations of a new alkyl-chain-functionalized Fe(II) SCO complex exhibiting a cooperative spin transition at room temperature. The

choice of the bent molecular geometry rather than the usual calamitic shape, along with the high deformability of the Fe(II)/pbh core afford favorable conditions for these cooperative properties. The single-crystal X-ray diffraction investigations revealed that the alkyl groups magnify the coordination sphere distortion provoking a huge deformation of the overall crystal packing that is manifested by a crystallographic symmetry breaking. Furthermore, thanks to the intrinsic conformational changes of the flexible alkyl chains, which impact the magnetic behavior at a temperature concomitant to the spin transition, we demonstrate for the first time that the association of these two phenomena can be used to promote magnetic tristability at room temperature.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files (CIFs), experimental details, additional crystallographic, DSC, PXRD and magnetic data. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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