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### Coupled Crystallographic Order–Disorder and Spin State in a Bistable Molecule: Multiple Transition Dynamics

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Abstract: A novel bispyrazolylpyridine ligand incorporating lateral phenol groups, H<sub>4</sub>L, has led to an Fe<sup>II</sup> spincrossover (SCO) complex,  $[Fe(H_4L)_2]$ - $[ClO_4]_2 \cdot H_2O \cdot 2(CH_3)_2CO$  (1), with an intricate network of intermolecular interactions. It exhibits a 40 K wide hysteresis of magnetization as a result of the spin transition (with  $T_{0.5}$  of 133 and 173 K) and features an unsymmetrical and very rich structure. The latter is a consequence of the coupling between the SCO and the crystallographic transformations. The high-spin state may also be thermally trapped, exhibiting a very large  $T_{\text{TIESST}}$  ( $\approx 104$  K). The structure of 1 has been determined at various temperatures after submitting the crystal to different processes to recreate the key points of the hysteresis cycle and thermal trapping; 200 K, cooled to 150 K and trapped at 100 K (high spin, HS), slowly cooled to 100 K and warmed to 150 K (low spin, LS). In the HS state, the system always exhibits disorder for some components (one  $\text{CIO}_4^-$  and two acetone molecules) whereas the LS phases show a relative  $\approx 9\%$  reduction in the Fe–N bond lengths and anisotropic contraction of the unit cell. Most importantly,

**Keywords:** bistability • hysteresis • iron • magnetic properties • order-disorder transitions • spin crossover

### Introduction

The phenomenon of spin crossover (SCO) provides for a versatile means of achieving molecular bistability, driven or addressed through external stimuli, and thus constitutes a promising avenue for research into molecular devices.<sup>[1]</sup> Compounds based on Fe<sup>II</sup> ions are particularly attractive;

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bistability of crystallographic the order-disorder coupled to SCO is demonstrated here experimentally for the first time. The variation in the cell parameters in 1 also exhibits hysteresis. The structural and magnetic thermal variations in this compound are paralleled by changes in the heat capacity as measured by differential scanning calorimetry. Attempts to simulate the asymmetric SCO behaviour of 1 by using an Ising-like model underscore the paramount role of dynamics in the coupling between the SCO and the crystallographic transitions.

in the LS state all the species are

always found to be ordered. Therefore,

their transition occurs between a diamagnetic low-spin (LS, S=0) and a paramagnetic high-spin (HS, S=2) state and is often accompanied by drastic changes in optical or dielectric responses.<sup>[2,3]</sup> The focus of the renewed interest in SCO systems for applications in nanotechnology is directed toward their nanostructure, such as incorporation into soft-matter phases,<sup>[4,5]</sup> nanoparticles<sup>[6]</sup> or surfaces.<sup>[7]</sup> In this context, issues of supramolecular or long-range interactions are of special relevance. Indeed, although the origin of the SCO phenomenon is molecular, the kinetics of this transformation are intimately related to the mode of connection between the centres that undergo the transition. The latter is crucial because it determines the conditions or feasibility of bistability by controlling both the abruptness of the transitions and the properties of any possible hysteretic behaviour. It is, therefore, of paramount importance to understand the fundamentals of this relationship as a possible means of controlling the dynamics of the SCO and its various manifestations. In most systems, various types of intermolecular interactions occur simultaneously to produce the whole network. The modelling of these systems, however, is usually oversimplified by combining them into one single phenomenological parameter that describes the interaction between the spin-active centres.<sup>[8]</sup> The structures of SCO solids normally also contain spin-inactive components, such as solvents and counterions. In some cases, temperature-induced crystallographic ordering of some of these components has been detected in concomitance with the spin transition.<sup>[9-12]</sup> In a remarkable example, two degrees of ordering have been detected at one given temperature (25 K), depending on whether the sample has been brought to that temperature by slow cooling or by quench-cooling.<sup>[13]</sup> Recently, this coupling has been modelled for the cases in which the spinactive and inactive components belong to either one or two sublattices (i.e., for one- and two-step SCO, respectively).<sup>[8]</sup> The issue of bistability in the context of coupled phase transitions involving crystallographic ordering has so far not been treated at this level, perhaps because it has not yet been revealed experimentally.

One of the most versatile groups of ligands in SCO research is that based on 2,6-bis(pyrazol-x-yl)pyridine (x-bpp; x=1, 3.<sup>[14,15]</sup> Both regioisomers are capable of chelating transition metals in an N-based tridentate fashion. Within the broad family of resulting complexes, especially those of Fe<sup>II</sup>, many exhibit SCO behaviour of varying natures, often depending on spin-inactive components (counterions, solvent molecules and the extent of hydration).<sup>[11,16]</sup> Also, derivatives of 1-bpp and 3-bpp have been prepared by introducing substituents onto almost every accessible site of the ligand framework.<sup>[17]</sup> This has allowed correlations between local geometric distortions and the SCO properties of related chromophores to be established<sup>[17]</sup> and permitted the study of the effect of order-disorder phase transitions on the spin transition.<sup>[11,18]</sup> Very recently, several intermediate states were observed upon warming in the thermal SCO of the  $[Fe(1-bpp)_2]^{2+}$  cation, resulting from the different forms adopted by the  $[Ni(mnt)_2]^-$  anions (mnt = maleonitriledithiolate) in the system and leading to multiple bistability.<sup>[19]</sup> Indeed, the coupling of simple SCO molecular complexes, such as the  $[Fe(bpp)_2]^{2+}$  type, with lattice components constitutes a potential way to design cooperative SCO systems. With the aim of studying in detail the interrelation between the phenomenon of spin transition and the properties of the crystal lattice hosting it, we have prepared a functionalised derivative of 3-bpp (2,6-bis{5-(2-hydroxyphenyl)pyrazol-3yl}pyridine,  $H_4L$ )<sup>[20]</sup> by introducing two hydroxyphenyl groups on the sides of the bpp unit. These substituents were expected to facilitate the establishment of a large variety of intermolecular interactions. Indeed, extensive variable-temperature structural, magnetic and thermal studies of the molecular complex  $[Fe(H_4L)_2][ClO_4]_2 \cdot H_2O \cdot 2(CH_3)_2CO$  (1) reveal the occurrence of SCO behaviour and a large bistable domain. Its striking asymmetric nature is related to a crystallographic order-disorder transition involving most of the intermolecular interactions at work in the compound.



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### **Results and Discussion**

**Synthesis:** Ligand H<sub>4</sub>L has been prepared through a less conventional method for making bpp derivatives, that is, the aza-cyclation of bis-1,3-diketones<sup>[21]</sup> by excess hydrazine as previously described by us.<sup>[22]</sup> The aerobic reaction in acetone of H<sub>4</sub>L with Fe(ClO<sub>4</sub>)<sub>2</sub>•4H<sub>2</sub>O in the presence of a small amount of ascorbic acid leads to an orange solution that, upon layering with diethyl ether, gives the complex [Fe-(H<sub>4</sub>L)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O·2(CH<sub>3</sub>)<sub>2</sub>CO (**1**) after approximately one week. It is interesting to note that the presence in this reaction system of anions (X<sup>-</sup>; X=SCN, Cl, Br) that can potentially act as terminal ligands triggers the oxidation of Fe<sup>II</sup> to Fe<sup>III</sup> and the degradation of ascorbate to oxalate, which leads to oxalate-bridged [Fe<sup>III</sup><sub>2</sub>] complexes that incorporate X<sup>-</sup> as axial ligands.<sup>[20]</sup> Thus, the poor coordination ability of perchlorate seems crucial here for the stability of complex **1**.

Description of the structure: At 200 K, compound 1 crystallizes in the triclinic space group  $P\overline{1}$  (Table 1) and the unit cell is composed of the main complex cation  $[Fe(H_4L)_2]^{2+}$ (Figure 1) together with two ClO<sub>4</sub><sup>-</sup> ions, two lattice molecules of acetone and one lattice molecule of water. The cation of 1 consists of an Fe<sup>II</sup> centre bound to two neutral H<sub>4</sub>L ligands, each of which uses its three central N-atoms for coordination, which leads to a distorted octahedral geometry. Each ligand lies in approximately one plane (especially the bpp fragments). In one ligand, both phenol groups point in the same direction (syn,syn conformation with respect to the central coordination pocket) whereas in the other ligand the phenol groups are oriented opposite to each other (syn, anti; Figure 1). The angle ( $\theta$ ) between the idealized [Fe1,N2,N3,N4] and [Fe1,N7,N8,N9] meridian planes is 84.69°, whereas the N3-Fe1-N8 angle ( $\phi$ ) is 177.00(5)°. The Fe-N bond lengths are in the range 2.118(2)-2.206(2) Å, with an average of 2.167 Å. These values fall within the range expected for Fe<sup>II</sup> centres in the HS state (see Tables 1 and S1 for other metric parameters).

The components of 1 are engaged in an extensive network of intermolecular interactions in the three crystal dimensions, involving  $\pi \cdots \pi$  and C-H $\cdots \pi$  contacts as well as hydrogen bonds (Table 1). In this network, the 2-hydroxyphenyl groups introduced as substituents of the bpp units play a very significant role (vide infra). Thus the cations are aligned in the *ac* direction with their pyridyl rings approximately oriented towards each other and establishing interactions through  $\pi \cdots \pi$  stacking (Figures 2 and S1). In this direction, the complexes are connected by means of hydrogen bonds through the intermediacy of ClO<sub>4</sub><sup>-</sup> anions to form supramolecular chains. Each ClO<sub>4</sub><sup>-</sup> group establishes hydrogen bonds with one [N-H] of one H<sub>4</sub>L ligand and one [O-H] of another ligand from an opposite complex. This pattern occurs twice between each pair of adjacent complex cations (Figures 2 and S1), and takes place alternately within each of the two approximate planes defined by the ligands along the chain. In the ab direction zig-zag chains are formed through  $\pi \cdots \pi$  interactions between pairs of phenol/pyrazolyl

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Table 1. Crystallographic data and crystallographic parameters related to the intermolecular interactions (See Figure 3 and 4 for letter codes) and to the local environment of the SCO centres of complex 1 ( $C_{52}H_{48}Cl_2FeN_{10}O_{15}$ ), and occupancies of disordered species at various temperatures and spin states.

T [K]	200 (HS)	150 (HS)	150 (LS)	100 (LS)	100 (HS, trapped)
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	12.310(3)	12.275(3)	12.364(3)	12.326(3)	12.247(2)
b [Å]	13.442(3)	13.407(3)	13.523(3)	13.513(3)	13.385(3)
c [Å]	17.399(4)	17.386(4)	17.312(4)	17.269(4)	17.355(4)
a [°]	104.57(3)	104.61(3)	106.69(3)	106.63(3)	104.60(3)
β [°]	99.29(3)	99.25(3)	98.53(3)	98.50(3)	99.12(3)
γ [°]	105.44(3)	105.39(3)	106.26(3)	106.36(3)	105.47(12)
V [Å <sup>3</sup> ]	2604.1(13)	2588.7(13)	2578.0(13)	2560.5(13)	2574.4(12)
μ [mm <sup>-1</sup> ]	0.520	0.522	0.524	0.528	0.525
reflns	9823	9952	9955	9720	10009
$R_1$ (all data)	0.0407	0.0506	0.0537	0.0495	0.0642
$wR_2$	0.1178	0.1403	0.1555	0.1404	0.1779
S	1.064	1.071	1.044	1.020	1.035
octahedral volume [Å <sup>3</sup> ]	12.48(5)	12.43(5)	9.77(4)	9.76(4)	12.42(5)
$\Sigma$ [°]	145.85	144.72	100.13	100.52	144.26
av. Fe-N <sub>pv</sub> [Å]	2.125	2.123	1.932	1.929	2.123
av. Fe-N <sub>pz</sub> [Å]	2.187	2.182	1.985	1.984	2.181
FeFe (ac) [Å]	9.743(3)	9.730(3)	9.850(3)	9.829(3)	9.723(3)
[O3–H3…O8] [Å]	2.747(3)	2.751(4)	2.908(3)	2.939(3)	2.758(5)
[N10–H10A…O6] [Å]	2.934(3)	2.921(3)	2.834(3)	2.856(3)	2.910(4)
[O1–H1…O10] [Å]	2.876(3)	2.867(3)	2.818(3)	2.818(3)	2.818(3)
[N5–H5B…O9] [Å]	2.893(2)	2.882(3)	2.934(3)	2.938(3)	2.938(3)
py…py <b>A</b> [Å] <sup>[a]</sup>	4.802(2)	4.794(2)	4.748(2)	4.730(2)	4.786(2)
ру…ру <b>В</b> [Å] <sup>[a]</sup>	4.566(2)	4.570(2)	4.628(2)	4.607(2)	4.562(2)
phen…pz C [Å] <sup>[a]</sup>	4.465(2)	4.453(2)	4.269(2)	4.251(2)	4.439(2)
phen…pz <b>D</b> [Å] <sup>[a]</sup>	4.733(2)	4.702(2)	4.464(2)	4.448(2)	4.679(2)
phen…pz E [Å] <sup>[a]</sup>	4.113(2)	4.095(2)	3.786(2)	3.767(2)	4.075(2)
phen…pz <b>F</b> [Å] <sup>[a]</sup>	3.598(2)	3.592(2)	3.558(2)	3.547(2)	3.590(2)
C–H…pz <b>a</b> [Å] <sup>[b]</sup>	3.722(3)	3.711(3)	-	-	3.699(5)
C–H…pz <b>b</b> [Å] <sup>[b]</sup>	3.412(3)	3.392(3)	3.356(3)	3.336(3)	3.377(4)
C–H…pz <i>c</i> [Å] <sup>[b]</sup>	-	_	3.712(3)	3.691(3)	-
ClO <sub>4</sub> <sup>-</sup> occupancy (O5,O8:O55,O88)	0.8:0.2	0.8:0.2	1:0	1:0	0.8:0.2
acetone 1 occupancy (C2S:C3S)	0.4:0.6	0.4:0.6	1:0	1:0	0.4:0.6
acetone 2 occupancy (C7S:C8S)	0.3:0.7	0.3:0.7	1:0	1:0	0.3:0.7

[a] Centroid-to-centroid distance. [b] Distance from H to centroid.



Figure 1. Representation of the cation of 1:  $[Fe(H_4L)_2]^{2+}$ . Grey non-labelled atoms are C, and lighter grey atoms are H. For clarity, only H atoms on non-C atoms are shown.

fragments from adjacent molecules. Each connection is reinforced by two complementary C–H··· $\pi$  interactions (Figure 3). Stacking  $\pi$ ··· $\pi$  interactions between phenol/pyrazolyl fragments, or between phenol rings serve to connect the zig-zag chains to each other forming sheets (Figure 4). In this structure, one  $\text{ClO}_4^-$  and the acetone molecules ex-

hibit crystallographic disorder (Figure 2) over two positions with various occupancy ratios (see Table 1).

Magnetic properties: The bulk magnetization of a polycrystalline sample of 1 was measured in the 5-300 K temperature range under the influence of a constant magnetic field of 5 kG (Figure 5). At 300 K, the product  $\chi T$  is 3.45 cm<sup>3</sup> K mol<sup>-1</sup> ( $\chi$  is the molar magnetic susceptibility), which indicates the presence of  $Fe^{II}$  ions in the HS (S= 2) state ( $\chi T = 3.0 \text{ cm}^3 \text{ K mol}^{-1}$  is expected for g=2). The value of  $\chi T$  stays almost constant upon cooling the system at 1 K min<sup>-1</sup> until it initiates a sudden decline near 150 K, which takes place in various (reproducible) small steps and more gradually towards the end, down to  $0.19 \,\mathrm{cm}^3 \mathrm{K} \,\mathrm{mol}^{-1}$ at 100 K. This value is consistent with an almost complete conversion of the Fe<sup>II</sup> centres to the LS state, and remains practically constant until the lowest measured temperature. Upon re-heating, the  $\chi T$  versus T data are superimposable on the values obtained as T was decreased until about 90 K, at

which the former diverge by describing a small decline down to a plateau at 0.10 cm<sup>3</sup> K mol<sup>-1</sup> (corresponding to virtually 100% of LS centres). When T reaches  $\approx 170$  K there is a very abrupt, one-step symmetric increase in  $\chi T$  up to  $3.39 \text{ cm}^3 \text{Kmol}^{-1}$ , at which it again joins the curve seen in the cooling mode, up to 300 K. These results show that complex 1 experiences a process of almost complete thermal SCO and describes a large hysteresis loop ( $\Delta T_{0.5} \approx 40 \text{ K}$ wide), which implies the existence of bistability of the system over a significant temperature range. The shape of this loop is markedly asymmetrical; the cooling branch (with  $T_{0.5}\downarrow = 133$  K) exhibits several small steps resulting in various slope maxima (Figure 6, left) whereas the warming branch shows a very sudden jump  $(T_{0.5}\uparrow = 173 \text{ K})$ , and only one maximum of the first derivative of  $\chi T$  with respect to T. The residual amount of HS centres still present after cooling below 90 K presumably corresponds to marginal portions of the sample that have remained thermally trapped in that state. The small decline in  $\gamma T$  observed near that temperature upon warming of the sample is attributed to the relaxation of some of these trapped residual centres to the LS



Figure 2. Representation of two cations of **1** (at 200 K) interacting through two py rings (thick dashed line A) and hydrogen bonds (thin dashed lines) through  $ClO_4^-$  anions. The crystallographic disorder of  $ClO_4^-$  (two equivalent anions shown) and two acetone molecules (also hydrogen-bonded to the cations) is emphasized; second positions are shown as lighter grey. Selected atoms are labelled and hydrogen atoms are not shown.



Figure 3. Representation of a zig-zag chain formed along the *ab* direction by the cations of **1** (at 200 K), by means of two types of  $\pi \cdots \pi$  stacking interactions (dashed lines C and D) and two types of C–H $\cdots \pi$  interactions (ellipses a and b). The cell directions are indicated.

state. Clearly, the spin transition is coupled to other changes that influence the dynamics of the process. On the one hand, the kinetics of the direct process (cooling mode) differs significantly from that of the inverse transit. On the other hand, the transformations are highly affected by cooperative phenomena. The latter is certainly a consequence of the extensive network of intermolecular interactions in 1 (vide supra). The asymmetry of the hysteresis must be related to some sort of crystallographic phase transition that in-



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Figure 4. Representation of the connection (at 200 K) between two zigzag chains of **1** (one darker than the other) that results from two types of  $\pi$ ··· $\pi$  stacking interactions (dashed lines E and F) and one C–H··· $\pi$  interaction (ellipses c). In fact, the latter is only operative in the LS state (see main text and Table 1). The cell directions are indicated.



Figure 5.  $\chi T$  vs. *T* curve per mol of **1** in the cooling (blue) and warming mode (red) and after quenching the compound at 10 K and increasing the temperature (black) (Tr.=trapped). The ClO<sub>4</sub><sup>-</sup> anions in the boxes represent the species with order–disorder transitions and the temperatures and spin state at several crucial points (see main text).

fluences differently in one sense than in the other. In view of this behaviour, the possibility of fully thermally trapping this system in a metastable state was explored. A polycrystalline sample of **1** was cooled rapidly to 10 K under a field of 5 kG, and its susceptibility was measured while the system was warmed (Figure 5). At 10 K, the value of  $\chi T$  is 2.70 cm<sup>3</sup>K mol<sup>-1</sup> and slowly increases upon warming at 1 K min<sup>-1</sup> to a constant value of 3.29 cm<sup>3</sup>K mol<sup>-1</sup> near 50 K. When the temperature reaches about 99 K, an abrupt decrease to a constant value of 0.79 cm<sup>3</sup>K mol<sup>-1</sup> takes place in the curve, which then suddenly jumps to 3.39 cm<sup>3</sup>K mol<sup>-1</sup> at around 173 K. This behaviour is clear evidence that the

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Figure 6. Left: The first derivative of  $\chi T$  vs. *T* for **1** in the cooling and warming mode. Middle: Thermal hysteresis of the cell angles of **1** from single-crystal X-ray diffraction. Right: Excess heat capacity of **1** with decreasing and increasing temperature. Blue is the cooling mode, red is the warming mode and black is the thermal trapping.

compound may be fully trapped into a metastable HS state through a process of thermally induced excited spin state trapping (TIESST),<sup>[23]</sup> remaining in this state until the temperature approaches  $T_{\text{TIESST}}$  ( $\approx 104$  K, see Figure S2), at which the system exhibits 75% thermal relaxation. Restoration of the HS state occurs upon further warming, in the same conditions as seen before. The value of  $T_{\text{TIESST}}$  measured for **1** is among the highest ever observed<sup>[24,25]</sup> and could reflect the fact that the SCO is coupled to another phase transition.

**Thermal properties**: Variations in the thermal properties of **1** associated with these magnetic and structural transitions were investigated by using differential scanning calorimetry (DSC) using polycrystalline material. The raw DSC traces (Figure 7) are consistent with the asymmetric nature of the SCO of **1**, exhibiting a very broad hump in the 145–120 K region upon cooling and a very sharp and more energetic anomaly at 172 K detected upon warming. These features



Figure 7. DSC trace for crystals of compound **1** upon cooling (light gray line) and warming (dark grey line,  $10 \text{ Kmin}^{-1}$ ). Similar results were observed for repeated cycles and for several batches. Note that cooling was performed at  $2 \text{ Kmin}^{-1}$  to obtain a satisfactory evaluation of the LT lattice baseline, which resulted in an apparently even broader anomaly.

were reproducible over various temperature cycles. The excess heat capacity  $(\Delta C_p)$  due to the phase transitions occurring in 1 is shown in Figure 6, right, and coincide with the maxima of the derivative of  $\chi T$  (Figure 6, left). The corresponding excess enthalpy and entropy of the transition (i.e.,  $\Delta_{trans}H/\Delta_{trans}S$ ) amount to 9.29 kJ mol<sup>-1</sup>/54.1 J mol<sup>-1</sup>K<sup>-1</sup> and 3.53 kJ mol<sup>-1</sup>/26.7 J mol<sup>-1</sup>K<sup>-1</sup> for cooling and warming, respectively, also reproducing the difference in sharpness of the SCO process. The values of both  $\Delta_{\text{trans}}H$  and  $\Delta_{\text{trans}}S$  for the warming branch are typical of cooperative SCO systems.<sup>[26]</sup> Remarkably, even in the cooling regime the excess entropy is much higher than the value expected solely from the spin-state change ( $R\ln 5 = 13.4 \text{ Jmol}^{-1}\text{K}^{-1}$ ), which indicates an additional vibrational component that can be ascribed to intermolecular interactions in 1. Because DSC is a dynamic technique, the smaller values obtained in the cooling regime may be a consequence of the slower dynamics of one of the processes that shows up because the transition occurs at a lower temperature upon cooling.

Correlation of the SCO with the structure: To understand the details of the structural phase transition(s) accompanying the SCO, an extensive variable-temperature crystallographic investigation of complex 1 was undertaken. Single crystal X-ray diffraction data were collected at 100 K. The basic structure is the same as that observed at 200 K, although with significant differences. At 100 K, the Fe-N bond lengths in complex 1 now range from 1.928(2) to 1.985(2) Å (av. 1.967 Å), which represents approximately a 9% reduction with respect to the structure at 200 K. This is consistent with the thermal process of spin transition from HS to LS observed for 1, which leads to a volume reduction in the coordination polyhedron from 12.48(5) to 9.76(4)  $Å^3$ (a 21.8% reduction) as calculated with IVTON.<sup>[27]</sup> The distortion of this polyhedron from octahedral, as characterised by the parameter  $\Sigma$ <sup>[28]</sup> is reduced from 145.85 to 100.52° on lowering the temperature. The large values of  $\Sigma$  are in line with these observed in Fe<sup>II</sup>/bpp complexes, which is attributed to both the narrow bite angle of the chelating ligands and the peculiar Jahn-Teller distortions experienced by these chromophores.<sup>[15]</sup> The significant reduction is consistent with the HS to LS transition, which also causes a change in the  $\theta$  and  $\phi$  angles to 86.43 and 178.53(7)°, respectively. Comparison of both datasets reveals anisotropic changes to the unit cell parameters (Tables 1 and S2) attributed to a combination of thermal contraction and the effects of the crystallographic phase transitions accompanying the SCO. Thus, the HS to LS transformation results in the following changes:  $\Delta a = +0.016$ ,  $\Delta b = +0.071$ ,  $\Delta c = -0.13$  Å;  $\Delta a = +2.06, \ \Delta \beta = -0.79, \ \Delta \gamma = +0.92^{\circ}$ . The peculiar fact that the various cell dimensions evolve in different directions<sup>[29]</sup> causes an overall volume change of only  $\Delta V = -43.6 \text{ Å}^3$ (1.6%). It is hard to establish a correlation between the expansion tensors and the directions of the various types of intermolecular interactions because the latter constitute a complex network (Figures 2-4 and S1) and, therefore, project on the three cell dimensions. In fact, the spin and crystallographic transitions involve changes to the structural parameters in all the intermolecular interactions, which leads to a reinforcement of most of them. A complete list of parameters describing these interactions at the various temperatures is collected in Table 1. These variations notwithstanding, the most remarkable structural changes of the crystallographic phase transition concern those species that exhibit disorder at 200 K, which become perfectly ordered at 100 K. Examples in which the spin state of  $Fe^{II}$  has been correlated with the crystallographic disorder of spin-inactive<sup>[9-11]</sup> or -active<sup>[12]</sup> components of the system have been reported. To shed light on the relationship between the dynamics of the SCO of complex 1 and its structure, single-crystal X-ray diffraction data were collected under conditions that led to the various metastable magnetic states identified in this system. Thus, the structure of 1 trapped into its metastable HS state was determined after rapidly cooling the sample from room temperature to 100 K (100 K Tr. HS; C). The structure was also obtained in the magnetic bistability region, that is, after slowly cooling the sample from room temperature down to 150 K (150 K $\downarrow$ , HS; **D**) and after slowly warming the system up to 150 K (150 K<sup> $\uparrow$ </sup>, LS; E) from its low-temperature LS state. The expected magnetic state and temperature of the system for these structural determinations are indicated in Figure 5. The main observation from these experiments is that for the cases in which the system is expected to be in its HS metastable magnetic state (C and D), all the structural parameters distinctive of this magnetic state are maintained, including the crystallographic disorder of one ClO<sub>4</sub><sup>-</sup> anion and two acetone molecules (Table 1). Likewise, the structure of the LS compound at the bistability temperature (E) exhibits the features determined for the system in its stable LS state (D). It is thus interesting to note that complex 1 is found to exhibit crystallographic disorder when trapped at 100 K, whereas it might be perfectly ordered when prepared at a higher temperature (150 K) if this state is reached after warming the LS system from 100 K. To the best of our knowledge, complex 1 is the first system in which bistability of the crystallographic order-disorder coupled to a spin transition has been experimentally demonstrated. This aspect of the crystallographic phase transition could help to explain the asymmetry of the magnetic hysteresis. Indeed, the transition taking place during the cooling process occurs from a disordered initial crystallographic state. Therefore, this process is marked by the coexistence of different dynamics of the transformation reflected by a complicated curve for the magnetic HS to LS transition. By contrast, the changes occurring on warming the system occur from an ordered state and, therefore, lead to a much more simple magnetic response of the transformation. Further details of the thermal transition were gathered by determining the cell parameters of 1 at various temperatures for both branches of the hysteresis loop. The evolution of these parameters reflects the structural changes expected from the SCO (Table S2), and also exhibit hysteretic behaviour (Figure 6, middle).

# **FULL PAPER**

Simulating the SCO of 1: Although a number of phenomenological models have been used successfully to describe the phenomenon of SCO, only the Ising-like model was recently used to introduce the coupling of SCO and the ordering of spin-inactive components, such as solvent molecules or anions.<sup>[8]</sup> In addition to the usual term describing the coupling between spin-active centres (denoted J), the model includes terms for the coupling between disordered spin-inactive species (denoted K) and between the spin-active and spin-inactive moieties (denoted I). It successfully reproduced the peculiar transition curves of two SCO complexes that exhibit such disorder: [Fe{2,6-bis(3-methylpyrazol-1-yl)pyrazine]<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> with an asymmetric SCO curve that shows a small abrupt hysteresis for HS fractions above 0.5 and a gradual tail for fractions below 0.5,<sup>[8,9]</sup> and [Fe(2-picolylamine)<sub>3</sub>]Cl<sub>2</sub>•EtOH that has a two-step SCO curve with an intermediate ordered phase.<sup>[8,11]</sup> Therefore, we attempted to use the model with one spin-active and one disordered spininactive sub-lattice [Eqs (5a) and (5b) in reference [8]] to reproduce at least qualitatively the peculiar SCO of compound 1. As pointed out by the authors of the model, we found that the coupling between the disordered spin-inactive species and the SCO centres results in asymmetric SCO curves, the low-temperature (low HS fractions) part being more gradual. Although this allows reasonable simulation of the gradual and asymmetric cooling mode for compound 1 (Figure 8, black line) with parameters I=200, J=20, K=-250, no hysteresis is predicted and the warming curve is identical to the cooling curve. On the other hand, reproducing the hysteresis width and its abrupt warming branch requires a completely different set of parameters (I=370, J=20, K = -250; Figure 8, red and blue lines). In addition, the resulting warming branch remains less abrupt than the experimental findings, due to the coupling between spin-active species and the disorder of the spin-inactive ones, whereas the cooling branch is more abrupt than the warming branch. We have indeed found that no set of parameters allows pre-



Figure 8. Fraction of HS molecules as a function of temperature calculated by using Equations (5a) and (5b) from ref. [8]. Black line (warming and cooling identical): I=200, J=20, K=-250; light and dark grey lines: I=370, J=20, K=-250. *I* is the coupling between the spin-active and spin-inactive moieties, *J* is the coupling between spin-active centres and *K* is the coupling between disordered spin-inactive species.<sup>[8]</sup>

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diction of hysteresis behaviour with a sharper warming branch than the cooling one, such as that exhibited by compound **1**. Because using two sets of parameters to reproduce the experimental behaviour of one same compound is senseless, modelling the comparatively more gradual cooling branch of the hysteresis in the SCO curve of **1** necessitates additional parameters not included in the model. The most likely explanation is related to the influence of temperature on the ordering of the spin-inactive species (not included in the model in reference [8]), which would result in slower dynamics in the cooling branch.

Further development of the theoretical model will be required so as to include the dynamics of the order–disorder process and ascertain how its coupling with the SCO causes the asymmetric nature of the cooperativity and hysteresis associated with these phase transitions in **1** or related complexes.

### Conclusion

The functional groups built into the new 3-bpp ligand H<sub>4</sub>L are at the origin of the intricate network of packing forces in 1 and are, therefore, responsible for the large hysteresis and the dynamic behaviour of the SCO in this compound. The latter is indeed coupled to a complex crystallographic phase transition that involves a process of order-disorder, which results in the asymmetric nature and rich structure of these thermal transformations. The bistability of the spin state of 1 is fully correlated with the crystallographic ordering of some of its components. This situation is shown here experimentally for the first time in both states of the bistable region, as well as in the thermally trapped metastable state. This system represents a promising window for the study of the dynamics of SCO in relation to its coupling with crystallographic phase transitions. For example, work is currently in progress to investigate the dynamics of the HS state of 1 and its structure within both the bistability range and the thermally trapped state.

#### **Experimental Section**

#### Synthesis

2,6-Bis{5-(2-hydroxyphenyl)-pyrazol-3-yl}pyridine ( $H_4L$ ): This ligand was prepared as previously described by our group.<sup>[20]</sup>

[*Fe*(*H*<sub>4</sub>*L*)<sub>2</sub>][*ClO*<sub>4</sub>]<sub>2</sub> (*I*): A suspension of H<sub>4</sub>L (0.0504 g, 0.128 mmol) in acetone (10 mL) was added dropwise with continuous stirring to a solution of Fe(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (0.0165 g, 0.065 mmol) in acetone (5 mL) in the presence of ascorbic acid (0.003 g, 0.017 mmol). The orange solution that formed was stirred for 1 h at RT before being filtered to remove excess ascorbic acid. The filtrate was used to prepare layers with ether (volume 1:1). Large, dark orange, polycrystalline aggregates were obtained after a week, which gave crystals suitable for single-crystal X-ray diffraction (yield: 12.3 mg, 16%). IR (KBr pellet)  $\tilde{\nu}$ =3414 (s), 3319 (s), 1690 (w), 1613 (s), 1486 (m), 1467 (s), 1355 (w), 1290 (m), 1114 (s), 1087 (s), 755 cm<sup>-1</sup> (s); elemental analysis calcd (%) for C<sub>52</sub>H<sub>48</sub>FeN<sub>10</sub>O<sub>15</sub>Cl<sub>2</sub>: C 52.94, H 4.10, N 11.87; found: C 52.79, H 4.08, N 11.87.

**X-ray crystallography**: Data were collected at  $\lambda = 0.7515$  Å by using a single-axis HUBER diffractometer on station BM16 of the European Synchrotron Radiation Facility (Grenoble, France). The crystal habit was a block that was either orange or purple depending on the temperature. Measurements were performed at 200 K (orange), 150 K (orange), 100 K (purple) cooled from 200 K at 5 K min<sup>-1</sup>, 150 K (purple) warmed from 100 K at 5 K min<sup>-1</sup> and 100 K (orange) by mounting the crystal directly at 100 K from RT. Cell refinement, data reduction and absorption corrections were done by using the HKL-2000 suite.<sup>[30]</sup> The structure was solved by using SIR92<sup>[31]</sup> and the refinement and all further calculations were carried out by using the SHELX-TL suite.<sup>[32,33]</sup> All non-hydrogen atoms were refined anisotropically. At 200, 150 (cooling) and 100 K (trapping), one of the perchlorate ions presents disorder of two of its oxygen atoms (O5, O8) over two positions with an occupancy of 0.8:0.2. Both acetone lattice molecules also present disorder of one of their methyl carbons over two positions (C2S:C3S and C7S:C8S) with occupancy factors 0.4:0.6 and 0.3:0.7, respectively. At 100 and 150 K (warming), this disorder is not present. Hydrogen atoms were found by using difference Fourier maps, except for those of the disordered methyl groups. Water and phenol hydrogen atoms were refined with thermal parameters of ×1.5 that of their carrier oxygen and distance restraints. The rest of the hydrogen atoms were placed geometrically on their carrier atom and refined by using a riding model. Monitoring of the cell parameters variation with temperature was done on a block crystal of 1 by using a Bruker APEX II CCD diffractometer on station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, with  $\lambda = 0.7749$  Å from a silicon 111 monochromator. Datasets were also acquired at both 200 and 100 K to confirm the similarity of the structure. Crystallographic data for the various structures and several local and lattice parameters of 1 in the different states studied are given in Table 1. A selection of bond lengths and angles for the Fe<sup>II</sup> coordination sphere is given in Table S1. Table S2 gathers the cell parameters at various temperatures in the range 85-200 K both upon cooling and warming.

CCDC-793027 (200 K HS), -793028 (150 K HS), -793029 (100 K LS), -793030 (150 K LS) and -793031 (100 K Tr.) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Physical measurements: Infrared spectra were recorded as Nujol mulls by using a Perkin-Elmer FT-IR instrument. Microanalyses were carried by using a Perkin-Elmer Series II CHNS/O Analyzer 2400 at the Servei de Microanàlisi of CSIC (Barcelona, Spain). Magnetic measurements (5-300 K) were performed by using a Quantum Design MPMS-XL SQUID magnetometer. Background corrections for the sample holder assembly were applied and diamagnetic corrections of the complexes were performed by using Pascal's constants. Differential scanning calorimetry (DSC) was performed by using a Q1000 differential scanning calorimeter with the LNCS accessory from TA Instruments. The temperature and enthalpy scales were calibrated with a standard sample of indium by using its melting transition (156.6°C, 3296 J mol<sup>-1</sup>). The measurements were carried out at scanning rates of 10 or 2 Kmin<sup>-1</sup> for several batches of 3 to 8 mg of undamaged crystals taken directly out of the mother liquor and sealed in aluminium pans with a mechanical crimp, with an empty pan as reference. To determine the heat capacity, the zero-heat flow procedure described by TA Instruments was followed, with a synthetic sapphire of similar mass to the samples used as the reference compound. An overall accuracy of  $\approx 0.2$  K for temperature and  $\approx 10\%$  for the heat capacity was thus estimated over the whole temperature range. The excess heat capacity,  $\Delta C_{\rm p}$ , associated with the phase transitions, was obtained by estimating a normal heat capacity curve with the high- and low-temperature data, and subtracting it from the total heat capacity. In this estimation no heat capacity step at the transition temperature was considered. The deduced calorimetric figures associated with the SCO/order-disorder transition  $\Delta_{\text{trans}}H$  (integration of  $\Delta C_p$  over T) and  $\Delta_{\text{trans}}S$  (integration of  $\Delta C_{\rm p}$  over lnT) feature the observed difference in sharpness between the warming and cooling modes. Note, however, that the figures corresponding to the cooling mode are subject to higher error due to the difficulty of correctly separating the normal heat capacity from the anomaly for this broader and less energetic peak. Moreover, the low-temperature part

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used for the determination of the normal heat capacity for the cooling mode covers a very limited temperature range due to its closeness to the low-temperature limit of the apparatus.

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