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COMMUNICATION

Abrupt two-step and symmetry breaking spin crossover in an iron(III) complex: an exceptionally wide [LS-HS] plateau

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[Fe(qsal-Br)₂]NO₃·2MeOH is reported which undergoes abrupt two step symmetry breaking spin crossover, T_{1/2}(1st step) = 136 K and T_{1/2}(2nd step) = 232 K with a hysteresis of 16 K and 5 K, respectively and an unprecedented [HS-LS] plateau of 96 K

Spin crossover (SCO) refers to the switching between two states termed high spin (HS) and low spin (LS).^{1,2} It is most often reported in Fe^{II} systems³ but is also known for Fe^{III},^{4,5} and Co^{II} complexes.^{6,7} The interest in SCO materials is driven by the potential application of spin crossover compounds in a wide range of molecular devices as well as a desire to better understand the phenomenon.^{8–10} While the basis for SCO is well understood, the types of transition are remarkably varied ranging from gradual to abrupt either with or without hysteresis.¹ Particularly interesting and still comparatively rare is stepped SCO in which the SCO occurs in two or more steps.^{11–18} As there are more steps, more spin states are accessible potentially resulting in devices of increased complexity and broader applicability.

In addition to greater potential functionality the nature of stepped SCO is also of interest as understanding how this occurs aids in the design of better systems. Thus, in mononuclear systems stepped SCO is generally due to the presence of independent metal centres which undergo SCO at different temperatures.¹⁸ More recently, it has been discovered that stepped SCO may occur as a result of symmetry breaking within the structure. In the case of Fe^{III} only four examples of symmetry breaking SCO have ever been reported.^{14–17} The first was [Fe(3,5-OMe₂-sal₂-baepd)]ClO₄ {3,5-OMe₂-sal₂-baepd = N,N'-bis(3,5-dimethoxysalicylidene)-1,5,8,12-tetraazado-decane} where reversible conversion from a 100% HS → 67% HS → 33% HS state was observed.¹⁴ In 2013 [Fe(nsal₂trien)]NCS (nsal₂trien = 2,5,8,11-tetraazadodeca-1,11-diene-1,12-diyl-dinaphthalen-2-olate) was reported in which complete SCO occurred in two steps via an intermediate phase containing two independent Fe^{III}

centres.¹⁵ More recently, [Fe(salpm)₂]ClO₄·0.5EtOH (Hsalpm = 2-((pyridin-2-ylmethylimino)methyl)phenolate) was proved to undergo SCO via a 75% HS intermediate.¹⁶ In all cases, SCO is rather gradual (except for the 1st step in [Fe(nsal₂trien)]NCS) and none undergo SCO with hysteresis. In contrast, Sato *et al.* reported [Fe^{III}(H-5-Br-thsa)(5-Br-thsa)]·H₂O (H₂-5-Br-thsa = 5-bromo-2-hydroxy(benzylidene)-hydrazinecarbothioamide) which exhibits a five-step SCO with hysteresis in the 1st and last step.¹⁷ In this case, symmetry breaking occurs via a change in space group from P₂/n (full HS or LS) to P_n (intermediate HS-LS states). In our continuing studies on the [Fe(qsal-X)₂]Y {qsal-X = (N-8-quinolyl)-5-X-salicylaldiminate} SCO system^{19–21} in which we are attempting to prepare designed SCO materials we now report [Fe(qsal-Br)₂]NO₃·2MeOH, **1** which exhibits abrupt hysteretic symmetry breaking SCO and an *unprecedented* intermediate [HS-LS] plateau of 96 K.

Complex **1** was isolated as black crystals by layering a solution of Fe(NO₃)₃ in MeOH over a solution of Hqsal-Br²² in CH₂Cl₂ in which NEt₃ had been added (see ESI for full details).

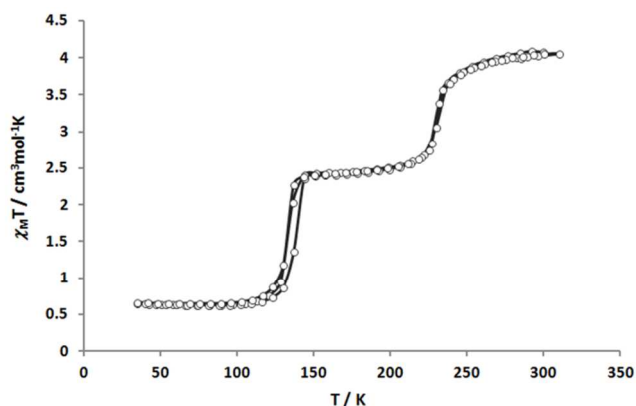


Fig. 1 Thermal variation of $\chi_M T$ versus T plot for **1**.

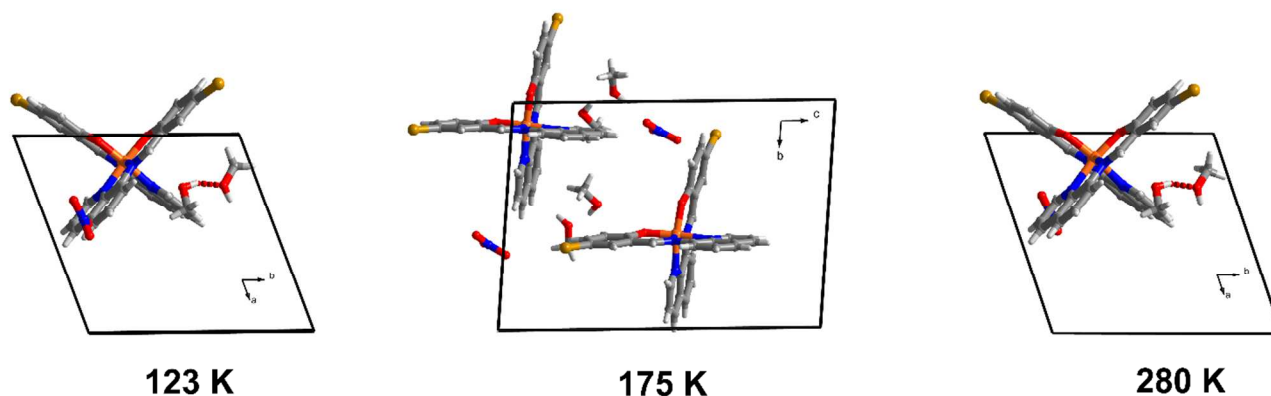


Fig. 2 Unit cell components of **1** at 123, 175 and 280 K (C atoms = grey, N atoms = blue, O atoms = red, Fe atoms = orange).

Magnetic susceptibility studies of **1** between 2 and 300 K in heating and cooling modes at a scan rate of 10 Kmin⁻¹ reveal that **1** undergoes complete and abrupt two step SCO with an exceptionally broad plateau between the two steps (Fig. 1). At 300 K, $\chi_{\text{M}}T$ is 4.07 cm³Kmol⁻¹ consistent with HS Fe^{III}.^{19,21,23} Upon cooling there is a rapid decrease in $\chi_{\text{M}}T$ to ca. 2.45 cm³Kmol⁻¹ with the spin transition occurring at T_{1/2}↓(1st step) = 229 K and indicative of 50% of the Fe centres crossing over. This $\chi_{\text{M}}T$ value persists for almost 100 K before a second abrupt transition occurs at T_{1/2}↓(2nd step) = 128 K with $\chi_{\text{M}}T$ reaching 0.64 cm³Kmol⁻¹ and indicative of LS Fe^{III}. In the warming mode the transitions are centred at T_{1/2}↑(2nd step) = 144 K and T_{1/2}↑(1st step) = 234 K resulting in a hysteresis of 16 and 5 K, respectively. Repeated cycles are unchanged confirming the reproducibility of the SCO.

Following recent work by Brooker *et al.* in which the magnitude of hysteresis was found to be dependent upon scan rate we have also undertaken studies at different scan rates.²⁴ Although there is a slight alteration in the magnetic profile in the plateau region (probably due to sample defects that impact crystallinity),^{15,17} at 1, 2, and 5 K·min⁻¹ the hysteresis is unaffected confirming that the hysteresis loops reported here are real (Fig. S1). To the best of our knowledge, **1** is unique in undergoing abrupt two step SCO with hysteresis in both steps and moreover, possesses the widest single state plateau in Fe^{III} SCO chemistry.

To better understand the magnetic behaviour of **1** the structure was determined at 123, 175, 220 and 280 K. At all temperatures **1** crystallizes in a triclinic $P\bar{1}$ space group. At 280 K the asymmetric unit consists of a single [Fe(qsal-Br)₂]⁺ cation, a NO₃ anion and two MeOH molecules (Fig. 2). The Fe centre is *pseudo*-octahedral with an N₄O₂ donor set. The Fe-N/O bond lengths are on average 2.120(3) and 1.905(2) Å, respectively and characteristic of HS Fe^{III} (Table S1).^{19,21,25} Below 230 K the unit cell doubles in size and there are now two independent Fe^{III} centres at 175 and 220 K, a clear indication of symmetry breaking (Table S2). The Fe1-N/O bond lengths are essentially indistinguishable from those found at 280 K indicating that this centre is HS. However, the Fe2-N/O bond lengths are 1.958(3) and 1.874(3) Å, respectively and consistent with a LS Fe^{III}

centre.^{19,21,25} It follows that in the plateau region a [LS-HS] spin state exists agreeing excellently with the 50% SCO observed in the magnetic data. Further cooling results in a dramatic shrinkage of the unit cell with a single Fe^{III} centre again present and indicative of 're-entrant' behaviour.¹⁵ As expected, the Fe-N/O bond lengths are now typical of LS Fe^{III}. It is important to note that the *a*-axis in the LS and HS structures is equivalent to the *c*-axis of the intermediate [LS-HS] phase while the *b*- and *c*-axes of the [LS-HS] phase are equal to *a*-*b* and *a*+*b*, respectively of the HS and LS structures. A packing diagram clearly showing the doubling of the unit cell in the intermediate phase is shown in Figure S2. The octahedral distortion parameters, Σ and Θ ,^{26,27} also support the spin state assignments from the Fe-L bond lengths. Interestingly while $\Delta\Sigma = 19^\circ$, $\Delta\Theta$ is much larger at 118° suggesting that SCO results in trigonal prismatic distortion along its *pseudo*-threefold axes. Similar results are found in other [Fe(qsal-X)₂]⁺ complexes^{21,23,25} and are most likely the result of the rigidity of the qsal-X ligand which favours such trigonal distortion.

The packing motifs within the crystal structures are remarkably similar at all temperatures. The Fe cations tightly pack into 1D chains via two orthogonal π - π interactions (3.205 and 3.302 Å at 100 K), which are longer in the HS state (3.286 and 3.391 Å at 280 K, Fig. S3, Tables S3 and S4). Although similar changes are found in [Fe(qsal-I)₂]OTf·MeOH the π - π interactions are ca. 0.1 Å shorter in **1**.²¹ This very tight packing might prohibit conversion to the HS state in a single step in **1**. Consequently, an ordered [LS-HS] state is formed instead with symmetry breaking. Such transitions have been successfully modeled using Landau theory where the change in spin state is coupled to the structural phase change.²⁸⁻³⁰ It is noteworthy that in the [HS-LS] state the π - π interactions link the same type of Fe centres together forming distinct HS and LS chains with weaker interactions in the HS chain. The 1D chains are further supported by C-H...O interactions from aromatic C-H groups to coordinated O atoms and alternately MeOH molecules and nitrate anions (Fig. S4-S5). As with the π - π interactions these interactions generally become weaker upon spin crossover. At the same time there is a concomitant strengthening of one of the N-O bonds of the nitrate anion and the C-O bonds of both MeOH molecules

consistent with the weakening of the hydrogen bonds to these molecules (Tables S5 and S6).

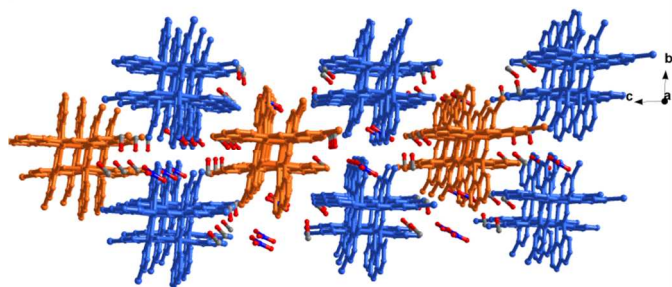


Fig. 3 The checkerboard packing pattern in **1** at 175 K, blue (LS chains) and orange (HS chains).

The 1D chains are linked by parallel four-fold aryl embraces (P4AE) forming 2D sheets (Fig. S6). Interestingly, identical supramolecular motifs are used to form 2D sheets in a range of $[\text{Fe}(\text{qsal-X})_2]^+$ complexes and appear to be sufficient to achieve abrupt SCO.^{19,21} In **1** these 2D sheets are further linked by strong $\text{Br}\cdots\text{O}$ halogen bonds involving one of the MeOH molecules and weaker $\text{C-H}\cdots\text{Br}$ interactions forming a 3D network (see Fig. S7) which viewed down the 1D π - π chains is strongly reminiscent of the 'terpy embraces' found in $[\text{Fe}(\text{bpzpy})_2]^{2+}$ (bpzpy = 2,6-bis(pyrazolyl)pyridine).³¹ In the case of the [HS-LS] structure the HS and LS chains form a checkerboard pattern (Fig. 3).

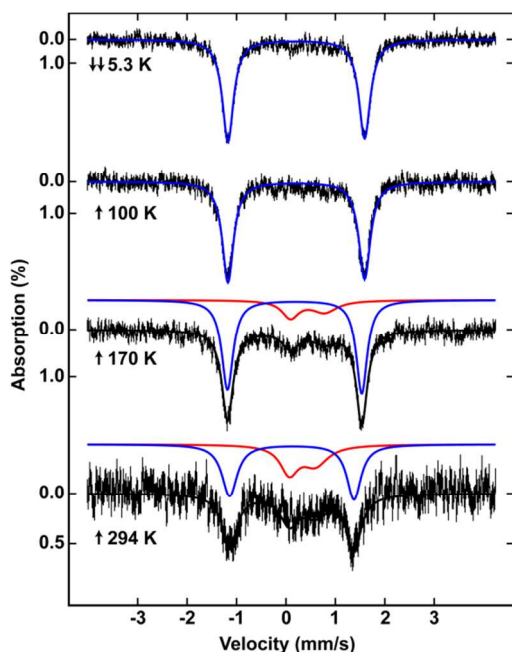


Fig. 4 ^{57}Fe Mössbauer spectra of $[\text{Fe}(\text{qsal-Br})_2]\text{NO}_3$ measured at the temperatures shown. The fits to the data are given as blue lines (LS) and red lines (HS). The sample was rapidly quenched (\Downarrow) to 5.3 K and then slowly warmed (\Uparrow) to each temperature measured.

^{57}Fe Mössbauer spectra were recorded at 5.3, 100, 170 and 294 K and reveal that the sample is LS from 5.3 to 100 K as evidenced by the presence of a sharp quadrupole doublet with a wide quadrupole splitting and low isomer shift (Fig. 4 and Table

S11). By 170 K both HS and LS Fe^{III} are visible as two overlapping quadrupole doublets with ca. 80% of the sample LS. At 293 K the HS fraction increases to 40%. The discrepancy between the Mössbauer spectroscopic and SQUID magnetometric data suggested to us that the sample had lost solvent. We therefore undertook a magnetic susceptibility study of $[\text{Fe}(\text{qsal-Br})_2]\text{NO}_3$ which revealed 50% SCO with $T_{1/2\downarrow} = 125$ K and $T_{1/2\uparrow} = 185$ K and thus a hysteresis of 60 K, one of the largest reported for any SCO compound (Fig. S8). Moreover, the SQUID magnetometric and Mössbauer spectroscopic data are now consistent with each other confirming that solvent loss has occurred. We should mention that despite repeated attempts we have been unable to obtain ^{57}Fe Mössbauer spectra of **1**.

DSC measurements were recorded in heating and cooling modes at rates of $5 \text{ K}\cdot\text{min}^{-1}$ showing two phase transitions at $T_{1/2\downarrow}(\text{1st step}) = 227$ K, $T_{1/2\downarrow}(\text{2nd step}) = 132$ K, $T_{1/2\uparrow}(\text{2nd step}) = 142$ K and $T_{1/2\uparrow}(\text{1st step}) = 231$ K and consistent with the magnetic results (Fig. S9). The enthalpy changes, ΔH are 0.86 and $0.69 \text{ kJ}\cdot\text{mol}^{-1}$ while the entropy changes, ΔS are 3.75 and $5.06 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the 1st and 2nd step, respectively. Although these values are lower than is typical for Fe^{III} they are similar to that reported for $\text{H}[\text{Fe}(5\text{-Clthsa})_2]$ ($\Delta H = 0.54 \text{ kJ}\cdot\text{mol}^{-1}$)³² and agree very well with the expected electronic entropy gain for a spin transition from 2T_2 to 6A_1 ($\{R\ln(6/2) = 9.13 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\}$). Such small changes are consistent with the relatively minor changes in the structural packing noted above. Moreover, VT-IR spectroscopic studies confirm that there is little change in the vibrations upon SCO (Fig. S10).

In summary, we have prepared the first $[\text{Fe}(\text{qsal-X})_2]^+$ complex to undergo symmetry breaking SCO with hysteresis in both steps and an exceptionally broad intermediate plateau. Structural studies indicate that unusually tight packing of the cations may be responsible for the symmetry breaking in this system. Solvent is also found to significantly impact the magnetic performance of the material and future studies will focus on the introduction of other solvents to improve the SCO properties of $[\text{Fe}(\text{qsal-Br})_2]\text{NO}_3$.

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