Two salts of \([\text{FeL}_2]^2+\) \((L = 2,6\text{-bis}[5\text{-methyl}-1\text{H}-\text{pyrazol-3-yl}]\text{pyridine})\) are isostructural under ambient conditions but show different thermal spin-crossover behaviour, involving a variety of crystallographic phase changes.

While an increasing number of applications for spin-crossover complexes\(^1\)–\(^6\) in devices and nanoscience has been demonstrated,\(^6\) the number of materials showing technologically favourable spin-state switching is still very small.\(^5\) There is therefore continued interest in the structural chemistry of spin-transition materials, which ultimately aims to crystal engineer new spin-crossover compounds with pre-defined functionality.\(^6\)

We recently reported that \([\text{FeL}_2][\text{BF}_4]^2\) \((1; L = 2,6\text{-bis}[5\text{-methyl}-1\text{H}-\text{pyrazol-3-yl}]\text{pyridine})\) adopts different anhydrous forms under slow crystallisation, and upon thermal dehydration of hydrated crystals.\(^7\) The latter material undergoes an abrupt spin-transition around 205 K with wide thermal hysteresis, which is coupled to a sequence of three crystallographic phase changes (see below).\(^7\) This behaviour, which was mostly elucidated by X-ray powder diffraction, makes 1 one of the most structurally complex spin-transition compounds known.\(^6\) We now describe the corresponding perchlorate salt \([\text{FeL}_2][\text{ClO}_4]^2\) \((2)\), which is isostructural with 1 under ambient conditions, but exhibits very different spin-state properties.

As we have previously described, 1 usually crystallises from organic solvents as the brown hydrate \(1\cdot\text{H}_2\text{O}\), which contains two unique iron centres.\(^7\) One of these is high-spin, and donates N–H···F hydrogen bonds to four BF\(_4\)\(^-\) anions. The other is low-spin, and forms N–H···O interactions to four water molecules. An anhydrous phase of the same compound (phase 1\(^a\)) can also be obtained, which is structurally similar to \(1\cdot\text{H}_2\text{O}\) but with the BF\(_4\)\(^-\) ions disordered onto the vacant water sites in the lattice. Exposure of 1\(^a\) to air leads to its rapid hydration to \(1\cdot\text{H}_2\text{O}\).

Heating \(1\cdot\text{H}_2\text{O}\) to 400 K converts it to a different high-spin anhydrous material, 1\(^b\), which is distinct from 1\(^a\) by powder diffraction. Cooling 1\(^b\) \textit{in vacuo} leads to two consecutive phase changes \(1\textcolor{red}{b} \rightarrow 1\textcolor{red}{c} \rightarrow 1\textcolor{red}{p}\) near 303 and 270 K respectively, without changing its high-spin state. Phase 1\(^p\) then undergoes a cooperative transition to a fifth, low-spin phase 1\(^e\). This spin-transition is centred near 205 K with a hysteresis loop of 37–65 K, depending on the history of the sample.

Unlike 1, the structural chemistry of 2 is complicated by pseudopolymorphism. Recrystallisation of 2 from organic solvents often leads to mixtures of unsolvated and solvate phases. However, orange-yellow crystals of unsolvated 2 \((\text{phase 2}\textcolor{red}{a})\) can be obtained in pure form by diffusion of diethyl ether into dilute methanol solutions of the complex at room temperature (more concentrated solutions instead afford the methanol solvate described below, which can be distinguished from \(2\textcolor{red}{a}\) by its brown colouration). Crystalline \(2\textcolor{red}{a}\) is isostructural with anhydrous phase 1\(^a\) although in contrast to 1\(^a\), which is low-spin at 150 K, \(2\textcolor{red}{a}\) contains a residual high-spin fraction at that temperature by X-ray diffraction (ESI). As for 1\(^a\), crystals of \(2\textcolor{red}{a}\)
are hygroscopic and form brown 2·2H₂O over a period of days on exposure to air at room temperature. The resultant crystals afford a similar unit cell to 1·2H₂O at room temperature. Moreover, bulk samples of 1·2H₂O and 2·2H₂O are isostructural at room temperature by X-ray powder diffraction (ESI†).

Despite their isostructural nature, the spin-state behaviour of 1·2H₂O and 2·2H₂O is very different (Fig. 1). Solid 1·2H₂O exhibits an almost invariant 1:1 high : low-spin state population between 5–300 K. In contrast, freshly prepared 2·2H₂O is ca. 85% high-spin at room temperature, according to its 3μT value of 3.1 cm³ mol⁻¹ K⁻¹. This value decreases on cooling, with a small discontinuity around 265 K (Fig. 1). More cooling leads 3μT to decrease further in a gradual but irregular manner until 120 K, when the remaining 25% of the sample undergoes a more abrupt spin-conversion, reaching its fully low-spin state at 110 K. Rewarming the sample shows the transition to exhibit a structured hysteresis below 200 K. The hysteresis loop spans 65 K at its widest point, and involves ca. 40% of the iron centres in the material. Repeated thermal cycling between 300–5–300 K caused some changes to the shape of the 3μT vs. T curve, although the discontinuity at 265 K and the low-temperature hysteresis were retained.

Variable temperature X-ray powder diffraction on 2·2H₂O shed some light on these observations (Fig. 2). The discontinuity in 3μT at 265 K (Fig. 1) is associated with a crystallographic transformation to a new phase, labelled 2·2H₂O* in Fig. 2. This phase change is not exhibited by 1·2H₂O.⁷ The sample retains the 2·2H₂O* structure on cooling between 250–130 K, with only minor changes to the powder pattern being observed (Fig. 2). It is unclear whether the more abrupt part of the transition, that gives rise to the bulk of the hysteresis, involves a further crystallographic phase change at around 110 K.⁶⁻⁸

Heating 2·2H₂O resulted in the loss of 1.5 equiv. of water at 368 K by thermogravimetric analysis (the highest temperature measured on safety grounds). Annealing 2·2H₂O at 370 K leads to its conversion to a new yellow anhydrous phase 2B, which is isostructural with 1B and reverts to brown 2·2H₂O on recoiling in air. This transformation occurred rapidly in the powder diffractometer, where the sample was directly open to the vacuum (Fig. 2), but was more gradual in the magnetometer (ESI†).

As for 1, the anhydrous phases of 2 produced by slow crystallisation (2A) and thermal dehydration of the dihydrate (2B) are distinct from each other by X-ray powder diffraction.

The variable temperature spin-state properties of phases 2B and 1B are again different. While 1B exhibits a highly cooperative spin transition centred near 205 K, 2B remains high-spin upon cooling to 2 K (Fig. 3). In the powder diffractometer, cooling 2B below 295 K caused a transformation to a new phase 2C, which has a very different powder diffraction pattern (Fig. 2). The corresponding material 1B also converts to 1C under these conditions, at the slightly higher temperature of 303 K.⁷ Phases 2B and 2C are isostructural with 1B and 1C (ESI†). However, whereas 1C transforms further to 1D on additional cooling, the phase 2D is retained between 120–250 K (Fig. 2 and 3). Hence, 2C (and presumably 1D) are high-spin structures, and spin-crossover in 1 can only occur owing to the extra 1C → 1D phase change.

In addition to the above, single crystal X-ray analyses were obtained from two solvates of 2. The methanol solvate 2·2CH₃OH
contains one formula unit per asymmetric unit, whose complex cation is low-spin at 150 K. The other solvate 2 xCH₃NO₂ ½(C₂H₅)₂O (x ≈ 0.83) contains three unique molecules in its asymmetric unit, one of which is low-spin at 150 K while the other two have a mixed high/low-spin population. Both structures contain extensive hydrogen bonding between the complex, anions and solvent (ESI†).

The complex cations in 2·2H₂O, 2A, the corresponding phases of 1 and the solvate structures of 2 all associate into four-fold “terpyridine embrace” layers, through interdigitation of the pyrazolyl arms of neighbouring molecules.⁵,¹⁰ These cation layers are separated in the lattice by sheets of anions and, where present, solvent. The cation layers in 2A and 2·2H₂O are homochiral and contain strictly or approximately co-aligned (ESI†)

In conclusion, the complicated structural and spin-state chemistry of the [FeL₂]²⁺ system is even more complex than first reported.⁷ The BF₄⁻ and ClO₄⁻ salts form dihydrate and anhydrous phases which are isostructural, but show contrasting spin-state behaviour. Thus, 2·2H₂O exhibits thermal spin-crossover but 1·2H₂O does not. Conversely, anhydrous 2B is not spin-crossover active, while 1B exhibits a highly cooperative spin-transition below room temperature. X-ray powder diffraction has demonstrated that these results reflect different sequences of phase transitions in the two sets of materials. Calorimetry and Mössbauer spectroscopic studies are in progress to shed more light on this unprecedented structural chemistry.

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Notes and references