Spin Crossover

An Incomplete Spin Transition Associated with a $Z' = 1 \rightarrow Z' = 24$ Crystallographic Symmetry Breaking

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Chem. Eur. J. 2018, 24, 5055 – 5059

DOI: 10.1002/chem.201704896
Abstract: Crystalline [FeL₃][BF₄]₂·Me₆CO (L = N-[2,6-di(pyrazol-1-yl)pyrid-4-yl]acetamide) is high-spin at room temperature, and undergoes an abrupt, hysteretic spin-crossover at $T_{1/2} = 137$ K ($\Delta T_{1/2} = 14$ K) that proceeds to about 50% completeness. This is associated with a crystallographic phase transition, from phase 1 ($P2_1/c$, $Z = 4$) to phase 2 ($P2_1$, $Z = 48$). The cations associate into chains in the crystal through weak intermolecular $\pi-\pi$ interactions. Phase 2 contains a mixture of high-spin and low-spin molecules, which are grouped into triads along these chains. The perchlorate salt [FeL₃][ClO₄]·Me₆CO also adopts phase 1 at room temperature but undergoes a different phase transition near 135 K to phase 3 ($P2_1/c$, $Z = 8$) without a change in spin state.

The structural chemistry of spin-crossover (SCO) compounds$^{[1–3]}$ continues to be heavily studied. The structural relationships underlying SCO functionality$^{[6,7]}$ are fundamental to the de novo design of new SCO materials for device applications or in nanoscience.$^{[8,9]}$ Moreover, SCO crystals have proven especially useful for studying the fundamental physics of crystallographic phase transitions.$^{[6,7]}$

Crystallographic symmetry breaking during SCO is observed in a number of materials.$^{[6,9]}$ Re-entrant symmetry breaking can lead to an intermediate crystal phase during the SCO process, containing a mixture of high-spin and low-spin molecules in its asymmetric unit.$^{[6,9–11]}$ The resultant mixed spin-state population is generally retained over a temperature range, before undergoing another phase change accompanied by full conversion to the low-spin form. Alternatively, irreversible symmetry breaking can occur during SCO to a low-temperature phase which can be either fully low-spin,$^{[12]}$ or contain a mixture of high- and low-spin molecules as before.$^{[13–15]}$ Symmetry-breaking involving a doubling of the crystallographic asymmetric unit is most common in either scenario, with the lower symmetry phase containing distinct high-spin and low-spin molecules arranged in a 0D, 1D, or 2D sublattice.$^{[8–10,12]}$ However, SCO-induced phase changes involving tripling,$^{[10,11,17]}$ quadrupling,$^{[12]}$ six-fold,$^{[13]}$ or 7.5-fold expansion$^{[14]}$ of the asymmetric unit have also been reported, leading to more complicated patterning of spin-states in these low-symmetry phases.

As part of our continuing investigations of complexes derived from [Fe(bpp)]$^{2+}$ (bpp = 2,6-di(pyrazol-1-yl)pyridine),$^{[15,16]}$ we now describe a material exhibiting cooperative but incomplete SCO, whose low-temperature phase shows a 24-fold expansion of the crystallographic asymmetric unit. As well as being the most dramatic example of SCO-induced symmetry breaking yet reported, the low-symmetry phase contains one of the largest numbers of crystallographically independent molecules ($Z$) observed in a molecular compound.$^{[20]}$

The new ligand N-(2,6-di(pyrazol-1-yl)pyrid-4-yl)acetamide (L) was prepared by treatment of 4-amino-2,6-di(pyrazol-1-yl)pyridine$^{[21]}$ with acetyl chloride. The reaction is sluggish, reflecting the de-activated nature of the (pyrid-4-yl)amino group, but proceeds in 67% yield if a 6.5x excess of acetyl chloride is used. The identity of L was confirmed crystallographically, which showed a complicated pattern of acetamido group disorientation upon further cooling to 95 K. Below 95 K the sample remains a mixture of high- and low-spin molecules as before.$^{[13–15]}$ Symmetry-breaking involving a doubling of the crystallographic asymmetric unit is most common in either scenario, with the lower symmetry phase containing distinct high-spin and low-spin molecules arranged in a 0D, 1D, or 2D sublattice.$^{[8–10,12]}$

Solid 1[BF₄]₂·Me₆CO is high-spin at room temperature, but undergoes an incomplete spin transition on cooling according to magnetic susceptibility data (Figure 1). The transition is abrupt and shows a small thermal hysteresis loop, with $T_{1/2} = 130$ and $T_{1/2} = 142$ K (scan rate 5 K min$^{-1}$) immediately below the transition temperature, $X_{M}T = 2.0$ cm$^3$ mol$^{-1}$ K, which corresponds to about a 41% low-spin population at that temperature. This slowly decreases to 1.7 cm$^3$ mol$^{-1}$ K (50% low-spin) upon further cooling to 95 K. Below 95 K the sample remains in a 1:1 high-low-spin form, with an additional decrease in $X_{M}T$ below 50 K reflecting zero-field splitting of the residual high-spin content of the sample.$^{[22]}$

Crystals of 1[BF₄]₂·Me₆CO at 240 K adopt the monoclinic space group $P2_1/c$, with one formula unit in the asymmetric unit (i.e. $Z = 4$). The complex's metric parameters imply it is high-spin at that temperature, as expected from the magnetic data. The compound associates into discrete ([FeL₃][BF₄]₂) as-
seemingly, through N–H···F hydrogen bonds between the acetamido substituents and BF$_4^-$ ions which are all disordered at that temperature; Figure 2). The only significant contact between cations in the lattice is a weak intermolecular π–π overlap between pyrazolyl rings, of nearest neighbors related by translation along the crystallographic a direction.

Cooling the crystal below the SCO transition temperature caused the appearance of new, closely spaced diffraction spots, implying a transition to a lower symmetry phase (phase 2) with a large unit cell. Allowing for the change in spin states, the unit cell transformation to form phase 2 is $a' = 2c$, $b' = b$, $c' = 6a$ and $\beta' = \beta$, giving $V \approx 42800$ Å$^3$, which is 12× larger than for phase 1. Variable temperature unit cell data show the phase 1–phase 2 transition occurs at 135 ± 5 K in cooling mode and 145 ± 5 K in warming mode, which reproduces the thermal hysteresis in the magnetochemical transition.

After several attempts from different crystals and diffractometers, a satisfactory refinement of phase 2 was achieved at 130 K, in the space group P2$_1$ (Z = 48). The loss of the crystallographic c glide and inversion center in phase 2, together with its unit cell volume expansion, generates 24 unique molecules in its asymmetric unit which are labelled ‘A’–‘X’ (Figure 3). The refinement of phase 2 is of moderate precision, reflecting the size of the model and the lower data resolution from the very large unit cell. However the main features of the structure are clear.

Molecules A–J in the refinement are fully or predominantly high-spin according to their metric parameters; molecules O–X are fully or predominantly low-spin; and molecules K–N have a mixed high:low-spin population at the temperature of measurement (Figure 3). That is consistent with the approximate 1:1 high:low-spin ratio expected from the magnetic data (Figure 1). The same pattern of N–H···F hydrogen bonding occurs in phase 2 as in phase 1 although the acetamido substituents, and around half of the anions and solvent molecules, have become crystallographically ordered at the lower temperature.

As before, cations in the lattice associate by weak intermolecular π–π interactions into chains, which run parallel to the unit cell c axis in phase 2. The asymmetric unit contains four unique chains, whose molecules have a HS–HS–HL–HL–HL or HS–HL–HL–HL–HS (HS = high-spin; HL = low-spin; MS = mixed spin state population) spin-state patternning. The four mixed-spin molecules are well-separated from each other in the lattice (Figure 3), and some or all of these might gradually increase their low-spin population upon further cooling. That could explain the small additional decrease in $\chi_M T$ observed between 125 and 95 K (Figure 1). The presence or absence of SCO in solid, high-spin [Fe(bpp)$_2$]$^{3+}$ derivatives often correlates with their coordination geometry. This is conveniently expressed by the parameters $\theta$ (the dihedral angle between the least squares planes of the ligands) and $\phi$ (the trans-N(pyridyl)-Fe-N(pyridyl) bond angle, which is N(2)-Fe(1)-N(22) in Figure 1). An ideal D$_{2d}$ symmet-

Figure 1. Variable temperature magnetic susceptibility data for polycrystaline 1[BF$_4$]$_2$Me$_2$CO (black) and 1[ClO$_4$]$_2$Me$_2$CO (gray), on a temperature ramp of 5 K/min. The inset shows the first derivative of the data for 1[BF$_4$]$_2$Me$_2$CO.

Figure 2. View of the ([FeL]$_2$[BF$_4$])$_2$ hydrogen-bonded assembly in phase 1 of 1[BF$_4$]$_2$Me$_2$CO, showing the atom numbering employed. All orientations of the disordered acetamido substituents and BF$_4^-$ ions are shown. Displacement ellipsoids are at the 50% probability level, and C-bound H atoms are omitted for clarity. Color code: C, white; H, pale gray; B, pink; F, yellow; Fe, green; N, blue; O, red.

Figure 3. The asymmetric unit of the low-temperature phase of 1[BF$_4$]$_2$Me$_2$CO, superimposed on the crystallographic unit cell viewed parallel to the [0 1 0] crystal vector. High-spin cations are colored white, low-spin cations are purple and cations with a mixed high/low-spin population are pink; anions and solvent (yellow) are de-emphasized for clarity. The letter labels for each unique molecule in the model are also shown.
ric complex gives $\theta = 90^\circ$ and $\phi = 180^\circ$. Most low-spin $[\text{Fe(bpp)}]^{2+}$ derivatives approach these values, but high-spin complexes show much more variation. In practice, high-spin complexes deviating more strongly from the ideal values of $\theta$ and $\phi$ are less likely to transform to their low-spin state upon cooling.\[18,29\]

Notably, nine of the ten high-spin cations in phase 2 have a more distorted coordination geometry than the high-spin molecule in phase 1, which could explain why they remain high-spin at low temperatures (Figure 4). Interestingly, these follow a near-linear $\theta$ versus $\phi$ relationship, which is not usual in plots of this type.\[19\] That implies the high-spin molecules all distort along the same structural pathway, which should be a function of the anisotropic plasticity of the crystal lattice. That is reasonable, since the molecules are all approximately co-aligned in the lattice (Figure 3). All the low-spin molecules, and three of the four mixed-spin iron sites, have less distorted geometries than the phase 1 molecule as expected.

Crystalline $[\text{ClO}_4]^-$ also adopts high-spin phase 1 at room temperature, and a full structure refinement at 170 K showed only minor differences to this phase with the BF$_4^-$ salt. However, no SCO was observed upon cooling $[\text{ClO}_4]^-$ to 100 K on the diffractometer. Rather, at 135 $\pm$ 5 K the crystals transform to a new phase (phase 3), which retains the $P2_1/c$ space group but with a doubled unit cell $a$ dimension (as well as small increases in $c$ and $\beta$).\[22\] Both unique molecules in phase 3, labelled ‘A’ and ‘B’, are fully high-spin from their metric parameters, with molecule B showing significantly reduced $\theta$ and $\phi$ values compared to phase 1.\[22\] The $\pi-\pi$ stacked cation chains, which now run parallel to the unit cell $a$ axis, contain alternating A and B cations.

Magnetic susceptibility data confirmed that $[\text{ClO}_4]^-$ indeed remains predominantly high-spin between 5–300 K. However, an abrupt reduction of $\chi_mT$ from 3.3 to 3.0 cm$^3$ mol$^{-1}$ K$^{-1}$ occurs reproducibly near 145 K, close to the crystallographic phase transition temperature (Figure 1). For a phase change to have such an effect on $\chi_mT$, without an associated spin transition, is unusual in a compound of this type.\[26\] However high-spin $[\text{Fe(bpp)}]^{2+}$ derivatives with reduced values of $\theta$ and $\phi$, as in molecule B of phase 3,\[22\] can exhibit magnetic moments up to 10 % lower than their undistorted analogues.\[27\] Hence, rather than indicating a change in spin-state population, the magnetocchemical feature at 145 K might simply reflect the changes in molecular coordination geometry during the high-spin phase 1–phase 3 transition.

In conclusion, thermal SCO in 1 performs a low temperature phase with an approximate 1:1 high:low-spin population, that is distributed between 24 crystallographically unique molecules (i.e. $Z^* = 24$).\[26\] This is the most severe example of symmetry breaking yet observed in an SCO crystal.\[8\] Moreover, notwithstanding one compound with $Z^* = 56$,\[28\] crystals with such high $Z^*$ values as phase 2 are very rare.\[26,29\] High $Z^*$ crystals have been proposed to be kinetic intermediates in the crystallization pathway; or, to arise from frustrated, mutually orthogonal packing interactions in the lattice.\[20\] Either description could apply to phase 2. On one hand, phase 2 may be an intermediate in the SCO of $[\text{BF}_4]^-$, with around half the molecules kinetically trapped in their high-spin form.\[10,30\] On the other, competing ferroelastic and antiferroelastic interactions between molecules over different length scales in the lattice, are also known to stabilize mixed-spin phases in SCO materials.\[31\]

### Experimental Section

Synthetic procedures, crystallographic data, and details of the instrumentation used for the spectroscopic and crystal structure measurements are given in the Supporting Information.\[22\]

### Acknowledgements

This work was funded by the Leverhulme Trust (RPG-2015-095) and by the EPSRC (EP/K012576/1 and EP/K00512X/1). We thank Diamond Light Source for access to beamline I19 (MT15059) that contributed to the results presented here. Support by COST network CM1305 Explicit Control of Spin States in Technology and Biology (ECOSTBio) is also acknowledged.

### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** iron · N ligands · spin-crossover · symmetry-breaking · X-ray crystallography

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parameters; and X-ray powder diffraction data. CCDC 1569541 (4-aminono-2,6-dipyrrozol-1-ylpyridine). 1569542 and 1569543 (\([\text{BF}_4]_2\cdot\text{MeCO}\)). 1569544 and 1569545 (\([\text{ClO}_4]_2\cdot\text{MeCO}\)). See the Supporting Information for more details.

[22] The Supporting Information contains experimental procedures and characterization data; crystallographic experimental details; additional crystallographic Figures and Tables, for the ligands and complexes; crystallographic Figures and Tables, for the ligands and complexes; and X-ray powder diffraction data. CCDC 1569541 (4-aminono-2,6-dipyrrozol-1-ylpyridine). 1569542 and 1569543 (\([\text{BF}_4]_2\cdot\text{MeCO}\)). 1569544 and 1569545 (\([\text{ClO}_4]_2\cdot\text{MeCO}\)). See the Supporting Information for more details.

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