The number and shape of lattice solvent molecules controls spin-crossover in an isomorphous series of crystalline solvate salts†‡

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Crystals of \([\text{Fe}_{2}][\text{BF}_4]_2\)–nMeCN (\(L = N-(2,6-\text{di}[\text{pyrazol-1-yl}]\text{pyrid-4-yl})\text{acetamide}; n = 1 \text{ or } 2\) and \(\text{[Fe}_2][\text{ClO}_4]_2\)–MeCN are isomorphous. When \(n = 1\) the compounds exhibit an abrupt, hysteretic spin-transition below 200 K, but when \(n = 2\) the material remains high-spin on cooling. \(\text{[Fe}_2][\text{X}_2]\)–EtCN (\(X = \text{BF}_4^-\) or \(\text{ClO}_4^-\)) are isomorphous with the MeCN solvates and undergo their spin-transition at almost the same temperature. However this now occurs in two-steps via a re-entrant mixed-spin intermediate phase, which correlates with crystallographic ordering of the bent propionitrile molecule.

Crystal engineering of spin-crossover (SCO) molecular materials is of continuing interest, for their development as molecular switches for macro-, micro- and nanoscale device applications. Such compounds also have wider relevance, as models for mechanistic studies of phase transitions in molecular crystals. Isomorphous families of compounds are particularly useful in that regard, in showing how small structure changes can influence the temperature and cooperativity of a thermal spin transition within the same crystal lattice structure. While some groups of isomorphous compounds exhibit very consistent SCO behaviour, in other cases a surprising variation in the cooperativity or occurrence of SCO is observed.

We recently described the solvate crystals \(\text{[Fe}_{2}][\text{X}_2]\)–nMeCN \((L = N-(2,6-\text{di}[\text{pyrazol-1-yl}]\text{pyrid-4-yl})\text{acetamide}; X^- = \text{BF}_4^-\) or \(\text{ClO}_4^-\)). The \(\text{BF}_4^-\) salt undergoes an abrupt spin-transition on cooling which proceeds to ca. 50% completeness, and is accompanied by an unusual crystallographic symmetry breaking involving a twelve-fold expansion of the unit cell. We were therefore keen to investigate other solvate crystals of these complex salts. We now present the acetonitrile and propionitrile solvates of \(\text{[BF}_4]_2\) and \(\text{[ClO}_4]_2\), a family of isomorphous materials where the influence of lattice solvent on their spin state properties is especially clearly defined.

Slow crystallisation of \(\text{[BF}_4]_2\) from MeCN/Et\(_2\)O yielded two different phases, \(\text{[BF}_4]_2\)–nMeCN \((n = 1 \text{ and } 2)\). The pseudopolymorphs adopt the same space group (triclinic, \(P\overline{1}, Z = 2\)) with similar unit cell dimensions, but have different spin-state properties. \(\text{[BF}_4]_2\)–MeCN undergoes an abrupt and hysteretic spin-transition at \(T_{1/2} = 185 \pm 5\) K and \(T_{1/2} = 195 \pm 5\) K from a variable temperature unit cell study (Fig. S7, ESI†). In contrast, \(\text{[BF}_4]_2\)–2MeCN remains high-spin at 120 K. Analogous recrystallisations of \(\text{[ClO}_4]_2\) gave the SCO-active phase \(\text{[ClO}_4]_2\)–MeCN as the only isolable product, which showed \(T_{1/2} = 155 \pm 5\) K and \(T_{1/2} = 165 \pm 5\) K (Fig. S9, ESI†). Both mono-acetonitrile solvates undergo their SCO without a crystallographic phase change.

The molecular geometries in \(\text{[BF}_4]_2\)–2MeCN, \(\text{[BF}_4]_2\)–MeCN and \(\text{[ClO}_4]_2\)–MeCN are very similar (Table S2, ESI†). The high-spin molecules have a twisted coordination geometry with trans-\(N[\text{pyridyl}]-\text{Fe}-N[\text{pyridyl}]\) angles \(\phi\) of 166.04(7)–168.66(14). Published high-spin salts of \(\text{[Fe(bpp)]}_2\) (bpp = 2,6-di[pyrazol-1-yl]-pyridine) derivatives show a range of \(\phi\) values between

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**Scheme 1** The structure of \(\text{[X}_2\text{ solv}} (\text{[X}^- = \text{BF}_4^-\) or \(\text{ClO}_4^-\); solv = MeCN, EtCN, MeNO\(_2\), MeOH or EtOH).
150 ≤ φ ≤ 180°, and are less likely to exhibit SCO as φ decreases.13,14 That reflects the unfavourable activation barrier required to transform a highly distorted high-spin molecule in a solid lattice, to the more regular coordination geometry (φ > 170°) preferred by the low-spin state.13,15 The φ = 167 ± 1° distortion in high-spin 1X2 nMeCN lies on the cusp, where SCO is possible but is rarely observed in practice.16 However, when high-spin [Fe(bpp)]2+ salts with that degree of distortion do undergo SCO, the large structural rearrangement involved imparts cooperativity to the transition.16,17 Thus, the change in φ between the spin states is Δφ = 5.9° in 1[BF4]2 MeCN and 6.6° in 1[ClO4]2 MeCN, which leads to atomic displacements of up to 1.0 Å at the periphery of the molecules during SCO (Fig. S4, ESI†). This structural rearrangement is the most likely source of the abrupt, hysteretic cooperativity in their spin-transitions.

The cations and anions in 1X2 nMeCN form discrete [(FeL2)X2] assemblies by N–H···F or N–H···O hydrogen bonding. The cations associate into chains by translation along the crystallographic a direction, through weak intermolecular π···π overlap of their pyrazolyl rings. The only other close inter-cation contact is a C–H···H=C steric clash involving another pyrazolyl group, in molecules related by the crystallographic inversion centre. That contact only occurs in the high-spin crystals with n = 1, and leads to disorder of that pyrazolyl ring. The basic disposition of the cations, anions and solvent in 1[BF4]2 MeCN is reproduced in 1[BF4]2 2MeCN (Fig. 1).

The extra solvent molecules in 1[BF4]2 2MeCN form centrosymmetric pairs within a new cavity centred at lattice coordinates 1/2, 1/2, 0 (Fig. 1, top). This cavity has a volume of 145 Å3, and is created by the following changes in 1[BF4]2 2MeCN compared to 1[BF4]2 MeCN: a ca. 1.5 Å displacement of nearest neighbour cations within the (100) plane, which also changes the handedness of the triclinic unit cell from α < 90° to α > 90°;18 a ca. 5° rotation of the cation within its lattice site, which is coupled to a small decrease in φ; and 0.5–0.8 Å displacements of each anion. Notably the extensive anion and solvent disorder in high-spin 1[BF4]2 MeCN is mostly quenched in 1[BF4]2 2MeCN. That implies the packing in the latter crystal is generally more compact.

Freshly prepared 1[BF4]2 nMeCN is predominantly the n = 2 phase by microanalysis and TGA (Fig. S11 and S12, ESI†). The material loses 1 equiv. MeCN abruptly at 368 K in the TGA, with the second equivalent being lost more gradually on further heating; the solvent-free material is only achieved above ca. 500 K. Samples of 1[BF4]2 nMeCN lose one equivalent of MeCN on drying in vacuo at room temperature, affording analytically pure 1[BF4]2 MeCN (Fig. 2). In contrast, only the SCO-active phase 1[ClO4]2 MeCN is apparent in that compound by powder diffraction and TGA. Both 1X2 nMeCN materials retain 1 equiv. MeCN upon drying in vacuo at room temperature.

Magnetic susceptibility data from these phases agree well with their crystal structures. Thus 1[BF4]2 2MeCN remains high-spin between 5–300 K, while 1[BF4]2 nMeCN and 1[ClO4]2 MeCN exhibit abrupt, hysteretic spin-transitions at T1/2 = 189 and 165 K respectively (Table 1). Samples of 1[BF4]2 nMeCN transform to the pure 1[BF4]2 MeCN phase inside the vacuum of the magnetometer cavity, unless the sample is protected against solvent loss during measurement (Fig. 2). Magnetic data from 1[ClO4]2 MeCN also contain a small fraction of a...
high-spin phase, although this appears to be solvent-free material generated by *in situ* solvent loss (Fig. S13, ESI†).

The propionitrile solvates 1X2·EtCN (X‘ = BF4− or ClO4−) are isomorphous with the acetonitrile crystals (triclinic, *P*1, *Z* = 2). They are phase-pure by powder diffraction, and are also highly stable to solvent loss by TGA (Fig. S26 and S27, ESI†). These also exhibit abrupt and hysteretic thermal spin-transitions, but now with a clear plateau near 50% conversion (Fig. 3). Interestingly, the average *T*1/2 for the two SCO steps in each 1X2·EtCN material corresponds well with *T*1/2 for the one-step SCO in the corresponding 1X2·MeCN sample (Table 1).

The discontinuous SCO in 1[ClO4]2·EtCN reflects re-entrant crystallographic symmetry-breaking to an intermediate phase (phase 2) near the midpoint temperature of the spin-transition (Fig. S22, ESI†). The intermediate phase (triclinic, *P*1̅, *Z* = 4) retains the same space group as the initial phase, but with a doubled unit cell volume containing 1 : 1 mixture of high- and low-spin molecules. These are segregated into alternating layers within the crystallographic (010) plane (Fig. 4).

The cation molecular structures in phases 1 and 2 resemble those in 1X2·MeCN (Table S6, ESI†). As well as the spin state changes, the phase transformations on cooling 1[ClO4]2·EtCN involve the quenching of disorder in the solvent and ClO4− ions. Most striking is the EtCN molecule, which is equally disordered over “up” and “down” orientations in high-spin (HS) phase 1 (Fig. S17, ESI†). This disorder is mostly quenched in phase 2 where both unique solvent sites adopt the up configuration, but one molecule retains ca. 15% of the down orientation. In low-spin (LS) phase 1, the single EtCN molecule is now fully ordered in the “up” orientation. Hence, the phase 1(LS) → 2 → 1(LS) transformations are accompanied by stepwise crystallographic ordering of the solvent molecules in the lattice.

No crystallographic evidence for phase 2 was found in 1[BF4]2·EtCN, whose SCO plateau spans a narrower temperature range (Fig. 3). However, that does not rule out a symmetry breaking near 190 K in that crystal, which could occur locally but without long-range order in the lattice.20 For comparison, the mixed-anion salt 1[BF4]2[ClO4]2·EtCN (z = 1) was also crystallised. The spin-transition properties of this material lie midway between the pure BF4− and ClO4− salts, and phase 2 was again observed crystallographically in its plateau temperature region. The ordering of the EtCN molecule between the phases of the mixed-anion crystal follows the same sequence as in 1[ClO4]2·EtCN.

Crystal structures of 1X2·2MeNO2 (X‘ = BF4− or ClO4−), 1[BF4]2·MeOH and 1[ClO4]2·1/2EtOH are presented in the ESI.† These materials remain high-spin on cooling which, in some cases, can be related to a strong ϕ distortion in their molecular

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Table 1 Spin-crossover parameters for the isomorphous [Fe(L′)2]X2·MeCN and [Fe(L′)2]X2·EtCN (X‘ = BF4− or ClO4−) materials from magnetic susceptibility data (Fig. 2 and 3 and ESI; scan rate 5 K min−1)

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* This transition proceeds in two equal steps, separated by a plateau at around 50% conversion.
Correlation for pyridyl-substituted [Fe(bpp)₂]²⁺ derivatives, 21‡ (Fig. S33, ESI) exhibit SCO on cooling, with pyridyl substituents with a σₚ⁺ Hammett parameter of ~0.6. 22 This study gives new insight into the importance of lattice solvent for SCO switching in molecular materials, which was recognised in the 1980s 23 but is rarely rationalised in detail. 9, 11, 13-24 SCO in 1X₂â€’MeCN, containing linear MeCN molecules, occurs cooperatively in one step. However, the extra solvent equivalent in [BF₄]⁻MeCN quenches the SCO, without changing its crystal symmetry or the molecular structure of the complex. That could simply reflect more compact crystal packing in the presence of the extra solvent molecule, which would inhibit the structural changes associated with SCO. 25

The same lattice in 1X₂â€’EtCN exhibits two-step SCO via a re-entrant mixed-spin intermediate phase. This correlates with a crystallographic order/disorder transition between two orientations of the bent propionitrile molecule. Discontinuous spin-transitions involving re-entrant intermediate crystal phases are well-known. 19, 20 However the creation of a re-entrant mixed-spin phase during SCO in 1X₂â€’EtCN, by simply changing the shape of the lattice solvent molecule, is a rarer observation. 9 The average T₁/₂ for the two SCO steps in each EtCN solvate is the essentially same as T₁/₂ for the corresponding MeCN solvate salt (Table 1). Hence, the temperature of SCO in 1X₂nsolv (n = 1) is influenced by the X⁻ anion, while the solvent controls the form of the transition.

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Conflicts of interest
There are no conflicts to declare.

Notes and references
18 Triclinic crystals are conventionally indexed with acute or obtuse unit cell angles, depending on whether the cell displays a left- or right-handed helical cantiing when viewed down the shortest a axis (Fig. S6, ESI).
25 There is precedent from some polymorphic SCO materials, where the lower density polymorph exhibits SCO on cooling but the higher density polymorph does not (ref. 3).