**Introduction**

Spin crossover in molecular compounds was first observed in the 1930s.1 Despite having been extensively studied it still attracts significant research interest partly due to its potential for industrial applications,2-4 for example in data storage devices,5-6 molecular magnets7 and molecular switches.8, 9 For a spin crossover compound changes in the physical environment,10 including temperature,11 pressure,12, 13 magnetic field or light irradiation,14, 15 can result in a reversible change in the spin state. Many of the spin crossover complexes that have been identified and studied are octahedral Fe(II) species10, 16 but spin crossover is also relatively common for other octahedral 3d4-3d7 metal centres such as Fe(III)15, 17 or Co(II).18, 19 In the solid state, spin crossover is a complex phenomenon and the abrupt or gradual nature, completeness and temperature at which it occurs has been linked to the presence of intermolecular interactions within the crystal lattice. Indeed different polymorphs of the same compound can show different spin crossover behaviour.20-23 Spin crossover complexes with limited cooperative communication between metal centres display very gradual changes in spin state, while species with significant molecular cooperativity show abrupt changes in spin state often with hysteresis. In addition, spin crossovers can be complete, partial or stepped.24, 25 Insights into spin crossover materials and their behaviour are coming from a range of techniques including magnetic data,13, 26 X-ray crystallography,11, 27 spectroscopic techniques including UV-Vis,26, 28 Resonant Ultrasound,29 Mossbauer30, 31 and X-ray photoelectron spectroscopy.32 Given the complexity of spin crossover behaviour,26, 31 it is important to study such systems in detail to further our understanding and allow the customised design of spin crossover materials for desired applications. Spin crossover behaviour has been identified in various Fe(II) complexes containing 3,5-bis(pyridin-2-yl)-1,2,4-triazole derivatives with trans NCs or NCSe ligands: for example, trans-[Fe(MBPT)2(NCS)]52 (MBPT = 4-p-methylphenyl-3,5-

[Fe(abpt)2(NCSe)]2 polymorph A: Structural studies into the spin crossover behaviour

Helen E. Mason,a Michelle L. Hamilton,b Judith A. K. Howarda and Hazel A. Sparkes*a

The spin crossover behaviour of [Fe(abpt)2(NCSe)]2 (abpt = 4-aminopyridine-2-yl)-1,2,4-triazole polymorph A has been examined using single crystal X-ray diffraction and variable temperature UV-Vis transmission spectroscopy. The crystal structure of A is reported at sixteen temperatures between 30 and 375 K, all of which are in the monoclinic space group P21/n with Z = 0.5. Changes in the crystallographic cell parameters, bond lengths, distortion parameters and intra and intermolecular interactions between 375 K and 30 K are discussed. Continuous irradiation with a 670 nm, 5 mW CW laser at 30 K enabled a light induced excited spin state trapping (LIESST) metastable high spin structure, HS+, to be obtained.
structure of A is known, however LS and LIESST HS* structures have not been previously characterised and are reported herein along with a detailed crystallographic study of structural changes occurring during the spin crossover. Single crystal variable temperature UV-Vis transmission spectroscopy, which has been used to monitor spectral changes across the thermal spin crossover temperature range, supports the crystallographic evidence and helps to provide further insight into the spin crossover behaviour of A.

**Experimental**

**Synthetic procedures**

X-ray diffraction quality single crystals of [Fe(abpt)₂(NCSe)₂] polymorph A were produced using the slow diffusion method previously reported for the synthesis of [Fe(abpt)₂(NCS)₂]\(^{29}\). All precursor materials are commercially available and were used as received, solvents were degassed and manipulations carried out under a nitrogen atmosphere. FeSO\(_4\).7H\(_2\)O (0.5 mmol, 0.139 g) and KNCSe (1 mmol, 0.144 g) were stirred in MeOH (8 ml) for 15 min, the resulting pale yellow K\(_2\)SO\(_4\) precipitate removed by filtration and deionised H\(_2\)O (8 ml) added to the remaining clear solution. abpt [4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole] (1 mmol, 0.238 g) dissolved in MeOH (10 ml) was transferred to a narrow (<5 cm) Schlenk tube and the Fe\(^{2+}\)/2(NCSe)\(^{-}\) solution carefully injected into the bottom of the Schlenk to form a layer underneath the abpt solution. A red coloured band immediately formed at the interface between the two layers. Single crystals of polymorph A suitable for X-ray diffraction studies were formed within 1-4 weeks but no crystals of polymorph B were produced.\(^{40}\)

**X-ray Crystallography - Variable temperature and LIESST measurements**

A Bruker Smart 1K CCD diffractometer was used to collect single crystal X-ray diffraction data using graphite monochromised...
MoKα (λ = 0.71073 Å) X-ray radiation. Cooling was achieved using either an Oxford Instruments open flow nitrogen Cryostream or an Oxford Cryosystems Helix for datasets collected at temperatures >105 K or <105 K respectively. Data collection was carried out using SMART software, integration performed using SAINT and face indexed numerical absorption corrections applied using SADABS/2012. The structures were solved by direct methods in SHELXS and refined by full matrix least squares on F² in SHELXL. Non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located geometrically and refined using a riding model except for the N6 hydrogen atoms which were refined anisotropically and all hydrogen atoms were included in geometrically calculated positions with isotropic displacement parameters.

Variable temperature UV-Vis transmission spectroscopy

Variable temperature single crystal UV-Vis transmission spectroscopy was carried out using a custom built setup (Figure 1) based on a cassegrain system (Bruker). Radiation from a Hamamatsu high power UV VIS fiber broadband light source (L10290) was transferred via fibre optic cables to the cassegrain optics and into an Andor Shamrock SR-303i imaging spectrograph coupled with a Newton EMCCD camera (150 lines/mm grating groove density; specifications quote a resolution of 0.88 nm at a centre wavelength of 500 nm). The spot size at the focus of the cassegrain optics is determined by the input fibre optic cable core size; this was chosen such that a

Table 2 - Crystal data and refinement results for A at 375 K, 30 K and 30 K after irradiation.

<table>
<thead>
<tr>
<th>Spin state (temperature)</th>
<th>HS [375(2) K]</th>
<th>LS [30(2) K]</th>
<th>LIESST HS* [30(2) K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₆H₂₆FeN₆Se₂</td>
<td>C₂₆H₂₆FeN₆Se₂</td>
<td>C₂₆H₂₆FeN₆Se₂</td>
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<tr>
<td>Formula weight</td>
<td>742.33</td>
<td>742.33</td>
<td>742.33</td>
</tr>
<tr>
<td>Temperature / K</td>
<td>375(2)</td>
<td>30(2)</td>
<td>30(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>α / Å</td>
<td>8.6568(4)</td>
<td>8.4320(6)</td>
<td>8.5189(7)</td>
</tr>
<tr>
<td>β / Å</td>
<td>10.2722(5)</td>
<td>9.9499(7)</td>
<td>10.0940(8)</td>
</tr>
<tr>
<td>γ / Å</td>
<td>16.6275(8)</td>
<td>16.3484(12)</td>
<td>16.4616(13)</td>
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<tr>
<td>β / °</td>
<td>93.5349(9)</td>
<td>93.1202(14)</td>
<td>93.1989(15)</td>
</tr>
<tr>
<td>Volume / Å³</td>
<td>1475.78(12)</td>
<td>1369.62(2)</td>
<td>1413.3(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>pcalc / (g/cm³)</td>
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<td>1.800</td>
<td>1.744</td>
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<td>μ / mm⁻¹</td>
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<td>3.256</td>
<td>3.155</td>
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<tr>
<td>f(000)</td>
<td>736.0</td>
<td>736.0</td>
<td>736.0</td>
</tr>
<tr>
<td>Radiation</td>
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<td>MoKα (λ = 0.71073 Å)</td>
<td>MoKα (λ = 0.71073 Å)</td>
</tr>
<tr>
<td>2θ range for data collection / °</td>
<td>4.66 to 52.738</td>
<td>4.79 to 56.554</td>
<td>4.73 to 55.756</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10 ≤ h ≤ 10,</td>
<td>-11 ≤ h ≤ 11,</td>
<td>-11 ≤ h ≤ 11,</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>14338</td>
<td>9605</td>
<td>11585</td>
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<td>Rint</td>
<td>0.0396</td>
<td>0.0353</td>
<td>0.0428</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3018/0/202</td>
<td>3381/0/202</td>
<td>3362/0/202</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.076</td>
<td>1.035</td>
<td>1.092</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ(I)]</td>
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<td>R₁ = 0.0362,</td>
<td>R₁ = 0.0452,</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.0953,</td>
<td>wR₂ = 0.0726,</td>
<td>wR₂ = 0.0922</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0716,</td>
<td>R₁ = 0.0459,</td>
<td>R₁ = 0.0523,</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.1094,</td>
<td>wR₂ = 0.0754,</td>
<td>wR₂ = 0.0949</td>
</tr>
<tr>
<td>Largest diff. peak/hole / (e Å⁻³)</td>
<td>0.85/-0.70</td>
<td>0.90/-0.74</td>
<td>2.14/-1.21</td>
</tr>
</tbody>
</table>

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~50 µm diameter region of the crystal was sampled by UV-Vis radiation. A single crystal fragment (<100×100×25 µm), mounted using perfluoropolyether oil onto a 100 µm aperture UV-Vis MicroLoop (MiTeGen, LLC) fixed on an XRD goniometer head, was positioned at the focus of the cassegrain system in the orientation giving the cleanest spectroscopic signal. The crystal was observed using a high-magnification zoom lens system mounted on a Thorlabs CMOS camera. An Oxford Cryosystems non-liquid nitrogen Cobra Cryostream was used to control the sample temperature.

To monitor spectral changes with temperature, Andor’s Solis software was used to collect spectra in kinetic series mode (100 ms exposure, 30 s kinetic cycle time) while cooling from 290 K to 83 K at 150 K/hr. Spectra were presented by the Solis software in absorbance mode by collecting background (no light source) and reference (light source on a MicroLoop without sample) spectra. All data were normalised for comparison because the % transmission, but not the spectral shape, is dependent on the crystal orientation within the light beam. A Savitzky-Golay smoothing filter (polynomial order 2, frame size 13) was applied to the normalised data using MATLAB. MATLAB functions “polyfit” and “polyval” were used to give an estimate of the standard error in the Savitzky-Golay fitted value at a chosen wavelength of interest.

Figure 2 - Cell parameters for A measured as a function of temperature: (◊) and (Δ) data collected using the Cryostream (Crystal 2) and Helix (Crystal 1) respectively; (■) cell parameters for the LIESST HS* state (Crystal 1). Error bars are included but obscured by the data point markers.
Results and discussion

Thermal spin crossover and cell parameter changes

The reported magnetic data for [Fe(abpt)₂(NCSe)₃] polymorph A shows a gradual thermal spin crossover without hysteresis between ~265 – 175 K with Тₓ/ₜ = 224 K. The occurrence of this spin crossover was also clearly indicated, over the expected region, through changes in the crystallographic cell parameters of A upon cooling from 375 to 30 K, with an ~0.3 Å decrease in the length of all of the cell axes and an ~0.4° decrease in the β angle (Figure 2, Table 2 and ESI Table S1). This resulted in an ~8% decrease in the unit cell volume over the full temperature range investigated.

The HS structure of A described in this paper is consistent with the previously reported structure of A at 293 K, since all of the structures determined herein have significant similarities. The 125 K structure is used for the following discussion of the key structural features (Figure 3). A crystallises in the monoclinic space group P2₁/n with half a molecule in the asymmetric unit (Ζ = 0.5, Ζ = 2); the full molecule consists of a 6-coordinate iron metal centre bound to two abpt (each coordinated through both a pyridyl and a triazole nitrogen) and two NCSe ligands. The two NCSe ligands are coordinated to each other and are approximately linear with an Ν₁-C₁-Se₁ bond angle of 177.8(2)°, however the NCSe is slightly bent with respect to the iron metal centre with an Fe₁-N₁-C₁ bond angle of 171.4(2)°. The N-Fe-N angles between the NCSe and abpt ligands range from 87.96(8) - 92.03(8)°. The abpt ligands are slightly distorted from planarity; there is an angle of 10.8(1)° between planes calculated through the two 6-membered pyridyl rings and angles of 9.0(1)° and 11.4(1)° between the 5-membered triazole ring and either of the pyridyl (Ν7, C9-C13) or (Ν2, C2-C6) rings respectively. An intramolecular hydrogen bond is present between N6-H6B···Ν7 for which D-H = 0.94(3) Å, H···A = 2.09(3) Å, D···A = 2.853(3) Å, <DHA = 138(2)°, along with a weak intramolecular C2-H2···Ν4#1 (Ν1 = 1-х, 1-у, 1-ц) interaction with D-H = 0.95 Å, H···A = 2.35 Å, D···A = 3.132(3) Å, <DHA = 140°. In addition, a short intermolecular N6-H6A···Se142 (Ν2 = 1/2+х, 3/2-у, 1/2+ц) interaction for which D-H = 0.96(3) Å, H···A = 2.65(3) Å, D···A = 3.476(2) Å, <DHA = 145(2)° was identified. The structure also contains Π-Π contacts with a centroid (N2, C2-C6) to centroid (N7#3, C9#3-C13#3, #3 = 1-х, 2-у, 1-ц) distance of 3.684(1) Å and an off-set of 1.432(4) Å. These Π-Π contacts create a 1-dimensional chain through the lattice in the approximate direction of the b-axis (Figure 4).

The structure determined at temperatures between 375 - 30 K (ESI Table S1,S3-S5) show that, although the key structural...
features of A discussed above are not significantly altered as a result of the spin crossover, there are changes in some of the geometric parameters which are worth noting. As is commonly observed for spin crossover compounds, all the Fe-N bond distances decrease by ~0.2 Å as the structure goes from HS to LS. In this case the range of Fe-N bond lengths in A decreases from 2.127(3) - 2.218(3) Å at 375 K to 1.955(2) - 2.014(2) Å at 30 K with the change in each unique Fe-N bond length through the spin crossover temperature range (Figure 5) following the trend observed in the magnetic data.35, 36 The thermal HS to LS crossover for A is accompanied by a decrease in the distortion parameter (Σ) and volume of the Fe octahedron (Vp), see Table 3 and ESI Table S3. There is no significant change in unit cell parameters, Σ and Vp between crystal structures of A collected at 225 K (≈ TM) during cooling (↓) and warming (↑) cycles through the spin crossover (ramp rate 120 K/hr) (ESI Table S2). This is consistent with the magnetic data,36 and indicates that thermal hysteresis is not observed for A. A gradual reduction in the diffraction quality occurs as a result of the spin crossover and after prolonged irradiation fracturing of the crystal was visible to the eye. The spin crossover in 2A caused no apparent reduction in crystallinity29 so it is unclear why the structural integrity of the crystal lattice of A, which is isostructural to 2A, is more sensitive to the spin crossover.

In both A and the isostructural sulfur complex, [Fe(abpt)2(NCS)2] polymorph A (2A), the HS to LS spin crossover results in a shortening of the intramolecular C2-H2···N4 (1#1 = 1-x, 1-y, 1-z) interaction distance.29 As indicated by the reduction in Σ, all the N-Fe-N bond angles get closer to 90° upon cooling through the HS to LS spin crossover. The N2-Fe1-N3 angle increases from 74.8(1)° at 375 K to 79.9(1)° at 30 K and there is a concomitant decrease in the N2-Fe1-N3#1 (1#1 = 1-x, 1-y, 1-z) angle from 105.2(1)° at 375 K to 100.1(1)° at 30 K. Similar changes in the N-Fe-N bond angles with temperature are observed for 2A.29 The π-π contacts between symmetry related pyridyl rings (N2, C2-C6) and (N7#3, C9#3-C13#3, #3 = 1-x, 2-y, 1-z), the intramolecular N6-H6B···N7 hydrogen bond and intermolecular N6-H6A···Se1#2 (2#2 = 1/2+x, 3/2-y, 1/2+z) interaction all show either limited or no change across the investigated temperature range (ESI Table S4 and S5).

As a result of the spin crossover significant shifting of adjacent molecules is observed. This can be illustrated nicely by looking at the change in the centroid-centroid distance between two of the adpt ligands pyridyl rings (N2, C2-C6) and (N2#4, C2#4-C6#4, #4 = 2-x, 1-y, 1-z) in neighbouring molecules. Clearly, the separation and offset of these rings are beyond those typically associated with π-π interactions and hence no inference of a significant interaction is intended (Figure 6, Figure 7), however, it is worth noting that a similar change is also observed for 2A as a result of the spin crossover.29

Figure 5 - Change in Fe-N bond lengths as a function of temperature, LIESST HS* values are contained within the dashed oval. Error bars are included but obscured by the data point markers.

Figure 6 - Change in centroid-centroid separation between (N2, C2-C6) and (N2#4, C2#4-C6#4, #4 = 2-x, 1-y, 1-z) pyridyl rings: (o) distances and (◊) offsets as a function of temperature; (●) distance and (♦) offset for the LIESST HS* structure. Note: The values for these interaction parameters lie beyond those typically associated with a π-π interaction. Error bars are included but obscured by the data point markers.

Table 3 - Fe-N bond lengths for all structures, along with the distortion parameter, Σ, and the volume of the Fe octahedron, Vp.

<table>
<thead>
<tr>
<th></th>
<th>30(2) K</th>
<th>30(2) K</th>
<th>125(2) K</th>
<th>150(2) K</th>
<th>175(2) K</th>
<th>225(2) K</th>
<th>275(2) K</th>
<th>325(2) K</th>
<th>375(2) K</th>
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</thead>
<tbody>
<tr>
<td>Fe1-N1 / Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2.115(3)</td>
<td>1.955(2)</td>
<td>1.951(2)</td>
<td>1.950(2)</td>
<td>1.958(2)</td>
<td>2.032(3)</td>
<td>2.120(3)</td>
<td>2.137(4)</td>
<td>2.149(4)</td>
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<td>Fe1-N2 / Å</td>
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<tr>
<td>2.135(3)</td>
<td>2.014(2)</td>
<td>2.014(2)</td>
<td>2.013(2)</td>
<td>2.021(2)</td>
<td>2.096(2)</td>
<td>2.193(2)</td>
<td>2.215(3)</td>
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<td>Fe1-N3 / Å</td>
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<tr>
<td>2.100(3)</td>
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<td>1.957(2)</td>
<td>1.955(2)</td>
<td>1.961(2)</td>
<td>2.027(2)</td>
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<td>2.124(3)</td>
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<tr>
<td>Σ / °</td>
<td>67.4(8)</td>
<td>49.5(6)</td>
<td>50.0(5)</td>
<td>49.8(6)</td>
<td>51.0(6)</td>
<td>59.0(6)</td>
<td>68.3(6)</td>
<td>69.4(8)</td>
<td>70.2(8)</td>
</tr>
</tbody>
</table>

* Σ, the angle distortion parameter, is the sum of the absolute value of the deviation of all 12 cis Fe-N Fe angles from 90°. a Vp is the volume of the Fe octahedron calculated in Olex2.47
A critical LIESST temperature, $T_{\text{LIESST}}$, of $\approx 32$ K has been reported for Fe from magnetic measurements on a microcrystal sample.\cite{36} The sulfur analogue, 2A, which displays $T_{\text{LIESST}} \sim 40$ K, relaxes from the HS* state back to the LS state within $\sim 4000$ s\cite{29,36} at 30 K whereas A relaxes on a much quicker timescale. At 10 K, less than 20% of the HS* state of A exists beyond 500 - 1000 s and complete conversion back to the LS state is observed within $<4000$ s.\cite{36} As the $T_{\text{LIESST}}$ is only just above the minimum temperature of 30 K achievable on the in-house Helix and given the rapid relaxation times in order to try and maintain a photostationary LIESST HS* structure throughout the data collection, the sample was subjected to continuous in-situ laser irradiation (670 nm, 5 mW CW laser). The structural changes observed in the resultant structure were consistent with those expected for a LS to HS* state spin crossover, i.e. the geometric parameters were similar to those seen in the HS structures collected around room temperature, indicating the successful formation of the LIESST metastable HS* state of A. Since the key structural features of the HS* structure are very similar to those of the 275 K HS structure (Table 3) only a few key points are highlighted here. The HS* structure maintains the same monoclinic space group, $P2_1/n$, found in the HS and LS structures, with an $\sim 3\%$ increase in the unit cell volume relative to the 30 K LS structure. As expected the Fe-N bond lengths in the 30 K HS* structure [2.100(3) - 2.185(3) Å] are almost 0.2 Å longer than those in the 30 K LS structure [1.955(2) - 2.014(2) Å]. In addition, the distortion parameter and Fe octahedron volume also increase as a result of the LS to HS* spin crossover: from $\Delta = 49.5(6)$° and $V_p = 10.105(8)$ Å$^3$ (LS, 30 K) to $\Delta = 67.4(8)$° and $V_p = 12.524(11)$ Å$^3$ (HS*, 30 K). It is worth noting that it is unknown whether the crystals used in this study retained a residual ground state, LS, fraction even during continuous irradiation at 30 K and the potential for any resulting bias in the HS* structural parameters was not investigated.\cite{50}

### Variable temperature UV-Vis transmission spectroscopy

Single crystals of A are an intense red colour in the HS state and gradually change to darker red upon cooling and, similar to 2A,\cite{29,36} a residual HS fraction may remain in the predominantly LS state at low temperature. It is therefore challenging to collect good quality transmission spectra, particularly at low temperature, and assignment of the UV-Vis absorption bands to particular transitions is beyond the scope of this study. Figure 8 shows normalised UV-Vis transmission spectra obtained from a single crystal fragment of A at 290 K (HS state), 190 K and 110 K (LS state) collected as part of a kinetic series slow cooling through the spin crossover. At 290 K, where A is purely in the HS state, the spectrum shows one main band at $\sim 524$ nm and an absorbance edge $\sim 580$ nm. Below 190 K the spin crossover is virtually complete, A is essentially in the LS state and there is very little further spectral change. The one featureless band shown in the 190 K and 110 K spectra sits at a slightly longer wavelength than that observed at 290 K, resulting in movement of the absorption edge to longer wavelengths, $\sim 610$ nm and is consistent with the darker red colour of the crystal. Magnetic studies on A have shown a residual yHS at low temperature of 16% for a precipitated polycrystalline sample\cite{35} and 0% for a sample consisting of single crystals.\cite{36} The crystal preparation method used in this study differs from previous reports\cite{35,36} and it is unknown whether there is any residual HS contribution to the low temperature LS spectra. The crystal mount contracts during cooling and the crystal was repositioned in the beam several times during the experiment to maintain consistent illumination, therefore calculation of the percentage HS to LS conversion is not possible from the UV-Vis spectra. Figure 9 shows that, in the wavelength region investigated, the largest change in absorbance with temperature occurs in the $\sim 530$ - 710 nm region with a maximum at 594 nm. It is difficult to distinguish any other small systematic changes with

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**Figure 7** - Illustration of (red dashed lines) the n-n contact between (N2, C2-C6) and (N7, C9-C13) and (red solid arrow) the centroid-centroid separation distance between (N2, C2-C6) and (N7, C9-C13) that decreases as a function of temperature. Symmetry codes: 1 $-x$, 2 $-y$, 1; 2 $-x$, 1; 1 $-y$, 1, 2; 1 $-y$, 1, 2; 1 $-x$, 1+y, 1+z; 1 $-x$, 1+y, 1+z.  

**Figure 8** - Normalised UV-Vis absorbance spectra for [Fe(abpt)2(NCSe)$_2$] polymorph A at 290 K, 190 K and 110 K collected as part of a kinetic series cooling at 150 K/hr.
temperature from the noise, although there is a suggestion of a second transition centred around ~460 nm.

The transition shape and $T_{1/2}$ value reported from magnetic data for the thermal spin crossover in single crystals of A, are closely mirrored in both the profile of the absorbance change with temperature at 594 nm (Figure 10) and the variable temperature crystallographic studies in this paper.

![Graph showing absorbance change](image)

Figure 10 - Normalised absorbance spectrum for A showing the change in absorbance at 594 nm upon cooling at 150 K/hr through the thermal spin crossover temperature range. Note: Lower transmission intensity was observed between 154 - 132 K due to contraction of the crystal mount; at 132 K the mount was adjusted and spectra obtained between 132 - 83 K are consistent with those at 154 K, hence only data above 154 are presented.

### Structural comparison of polymorphs A and B

Unlike A, polymorph B does not undergo a thermal spin crossover at ambient pressure. The previously published structure of polymorph B is used for the following discussions and comparison with polymorph A presented in this paper. Polymorph B, for which data were collected at 300 K, also crystallised in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit ($Z' = 0.5, Z = 2$). There are a number of similarities between the two polymorphs and in B the NCSe ligands are also approximately linear with an Fe-N-C angle of ~179°, the NCSe ligands are also slightly bent with respect to the metal centre with an Fe-N-C angle of ~170°.

In addition, the N-Fe-N angles between the NCSe and adpt ligands are in line with those seen for A ranging from ~87-93°. However, in B the adpt ligands are significantly distorted from planarity and there is an angle of ~36° between planes calculated through the two pyridyl ligands and ~7° and 31° between the 5 membered triazole ring and the two 6 membered rings respectively. This compares to values in A at 300(2) K of 9.4(2)° between the two pyridyl rings and 7.9(2)° and 7.5(2)° between the 5 membered and each of the pyridyl rings. This difference in configuration of the adpt ligands may explain significant differences in the packing of the two polymorphs. In A, the three rings of the adpt ligands of adjacent molecules are aligned above each other with $\pi-\pi$ interactions at each end between the pyridyl rings (at 300(2) K centroid to centroid distance 3.688(2), offset 1.339(6) Å) creating a 1-dimensional chain in approximately the $b$-axis direction. In B, each of the pyridyl rings on an adpt ligand forms $\pi-\pi$ interactions (centroid to centroid distance ~3.73 Å, offset ~1.26 Å) with the pyridyl ring of adpt ligands that are on different molecules, creating a 2-dimensional network approximately parallel to the $ac$ plane.

Given the relatively gradual nature of the spin crossover in A it seems reasonable to suggest that there is limited communication between the molecules. The influence of intermolecular interactions and communication between the metal centres on the spin crossover behaviour of a compound is well documented. In this case it would appear reasonable to suggest that the lack of spin crossover in B is as a result of the 2-dimensional nature of the $\pi-\pi$ interactions in B having affected communication between the metal centres as compared to A which forms a 1-dimensional chain as result of the pi-pi interactions involving the two pyridyl rings of both adpt ligands.

### Conclusions

Structural and spectral changes associated with the spin crossover behaviour of [Fe(adpt)$_2$(NCSe)$_2$] polymorph A have been successfully characterised. A clear shift is observed between the absorbance spectra obtained for the high and low spin complexes, monitoring the spectral changes in this region as a function of temperature shows a change consistent with the spin crossover observed in the previously published magnetic data. Likewise, the unit cell parameters change as a function of temperature with a profile that matches those observed in the magnetic data and supports the occurrence of spin crossover. The Fe-N bond lengths, distortion parameter ($\Xi$) and volume of the Fe octahedron ($V_{\text{oct}}$) all decrease as a result of the HS to LS spin crossover and follow the trends commonly associated with spin crossover complexes. It is interesting to note that for both A (NCSe) and 2A (NCS), the HS to LS spin crossover causes a shifting of adjacent molecules towards each other. This change was apparent in A through a change in distance between two of the adpt ligands pyridyl rings (N2, C2-
C6) and (N2#4, C2#4-C6#4, #4 = 2-x, 1-y, 1-z) in neighbouring molecules, although it should be noted that the separation distance between pyridyl rings remains beyond that associated with significant π-π interactions. A LIEST H5* structure for [Fe(abpt)(NCSe2)] polymorph A at 30 K is also reported and shown to have similar features to the HS structure at approximately room temperature. Comparing the structures of polymorphs A to B (which had been previously published and does not show a thermal spin transition at ambient pressure), shows clear differences in the relative orientations of the pyridyl rings on the same adpt ligand with twist angles of 9.4(2)* and ~36° respectively. The packing was found to be quite different for the two polymorphs with A having 1-dimensional chains created by π-π interactions between pairs of adpt ligands on adjacent molecules in which both pyridyl groups were involved while in B the π-π interactions formed a 2-dimensional network as a result of each pyridyl ring on an adpt ligand forming an interaction to the pyridyl ring on an adpt ligand in different molecules. Given the importance of intermolecular interactions on the spin crossover behaviour of compounds it seems reasonable to suggest that the nature of the interactions in B have affected the communication between metal centres and thus accounts for the lack of spin crossover for this polymorph.

Conflicts of interest
There are no conflicts to declare.

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