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**Title:** Mononuclear spin-transition materials based on the bapbpy scaffold  
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Synthesis and magnetic properties of bapphen-based mononuclear Fe(II) spin-crossover complexes

Abstract

The new rigid ligand bapphen and its iron(II) complexes [Fe(bapphen)(NCX)2] (X = S, or Se) were synthesized. The complex [Fe(bapphen)(NCS)2] was obtained in two different forms (1a and 1d) via two different preparative methods. The magnetic susceptibility measurement revealed that 1a is HS at room temperature and has a three-step incomplete spin transition, while 1d has no SCO properties and remains HS state over the full temperature range of 5-300 K. The magnetic behaviour of [Fe(bapphen)(NCS)2] (2a) shows an incomplete and gradual spin transition over the full temperature range of 5-350 K, the cooperativity of the transition is lost upon substitution of S by Se.
5.1. Introduction

As discussed in Chapter 1, the spin crossover (SCO) phenomenon in octahedral \( \text{d}^4 - \text{d}^7 \) transition metals represents a prototype of molecular switches,\(^1\text{-}^3\) which might be used for the building of nano-sized gas\(^4\text{-}^5\) or temperature sensors\(^6\) and electronic information processing or data storage devices.\(^7\text{-}^8\) Iron(II)-based SCO compounds have been actively investigated for several decades, as they can switch between a diamagnetic low-spin (LS) state and a paramagnetic high-spin (HS) state upon temperature variation, upon application of high pressures, upon light radiation, or under the influence of strong magnetic or electric fields.\(^9\) However, in order to reach a real technological impact, it is imperative that the SCO transition should occur near room temperature.\(^10\) Furthermore, the occurrence of cooperative SCO with hysteresis loops is critical for information storage application.\(^3\) Cooperativity originates from the combination of short- and long-range interactions in the solid state.\(^11\) These interactions depend on many parameters such as the crystal structure, the inclusion of guest molecules in the crystal lattice, or the size and crystallinity of the crystallites. As a result, it still remains challenging to design molecular compounds combining these two properties. e.g., cooperative SCO with transition temperatures around room temperature.

One approach to tune the transition temperature of a SCO material is to make use of the ligand field strength of the ligand.\(^9\) The SCO properties of a compound depend on the ligand field strength imposed on the metal ion by all surrounding donor atoms. Basically, a higher ligand field splitting (LFS) results in an increase of the temperature \( T_{1/2} \) at which half of the material has gone through SCO.\(^12\) However, in Chapter 2 it was shown that the mere occurrence of SCO, as well as the transition temperatures at which it occurs, seems rather erratic and therefore difficult to predict. Packing effects, for example, play a very important role in solid-state SCO compounds.\(^13\) Structural changes should be kept to a minimum if one hopes to keep the crystal packing of a new compound similar to that of a known SCO compound.

Inspired by earlier investigations on the SCO compounds \([\text{Fe}(\text{bapbpy})(\text{NCS})_2]\)\(^14\) and \([\text{Fe}(\text{phen})_2(\text{NCX})_2] (\text{X}=\text{S, Se}, \text{phen} = 1,10\text{-phenanthroline})\),\(^15\) a new rigid N\(_4\)-donor ligand was designed, namely \( N,N'\text{-bis(pyrid-2-yl)-1,10-phenanthroline-2,9-diamine (bapphen, Scheme 5.1)} \). This tetradentate ligand consists of two amino-pyridines connected by a phenantroline backbone. On the one hand the ligands bapbphen and bapbpy are structurally similar: (i) both must coordinate to the metal centre at the basal
plane of an octahedron, leaving the axial positions for the binding of two trans thiocyanate or selenocyanate ions; (ii) both contain two non-coordinating N–H bridges aimed at forming intermolecular hydrogen bonds with neighbouring molecules. These hydrogen bonds have been shown to play a critical role in the cooperativity of the SCO compounds $\text{[Fe(bapbpy)(NCS)$_2$]}$ and its derivatives, and they must be kept untouched in the design of any new cooperative bapbpy-based SCO compounds.$^{13,16}$ On the other hand, the ligand bapphen is in principle more conjugated and more rigid than bapbpy because of the phenantroline backbone, which might enhance the ligand field strength, and therefore increase the transition temperature of its iron(II) complexes compared to $\text{[Fe(bapbpy)(NCS)$_2$]}$.

In this Chapter, the two new compounds $\text{[Fe(bapphen)(NCX)$_2$]}$ are described with X = S or Se. Their magnetic properties have been investigated and are compared to their bapbpy-based analogues $\text{[Fe(bapbpy)(NCS)$_2$]}$ (3) and $\text{[Fe(bapbpy)(NCSe)$_2$]}$ (4).

![Scheme 5.1](image.png)

**Scheme 5.1** Schematic representations of the ligands bapbpy, bapphen, and $\text{[Fe(bapphen)(NCX)$_2$]}$ (X = S for 1, or X = Se for 2).

### 5.2. Results

#### 5.2.1. Synthesis and characterization

The synthesis of the ligand bapphen was performed by the previously described$^{14}$ palladium-catalyzed Buchward-Hartwig cross-coupling reaction between 2-aminopyridine and 2,9-dibromo-1,10-phenanthroline (see Scheme 5.2), which are commercially available or can be prepared following literature procedures.$^{17,18}$ Coordination of the ligand bapphen to either iron(II) thiocyanate or iron(II)
Scheme 5.2. Synthetic route towards the ligand bapphen, and its complexes $[\text{Fe(bapphen)}(\text{NCX})_2]$ ($X = S$ for 1 or $X = \text{Se}$ for 2). Conditions for i: 2 mol% Pd(dba)$_2$, 4 mol% (S)-BINAP, 4 equivalent KOtBu, 80 $^\circ$C in dry and degassed toluene, 3 d, yield: 68%.

selenocyanate, to prepare compounds 1a-d, or 2a-c, was achieved using the three different synthesis methods a, b, and c that are extensively described in Chapter 4, plus method d that consisted in the slow diffusion of MeOH and Fe(NCS)$_2$ into a DCM solution of the ligand. As described in Chapter 4, different preparative methods with the same molecular building blocks may lead to materials with different SCO properties, and extreme care was taken to fully characterize the materials obtained by the different methods. The new compounds 1a-d and 2a-b were analyzed with IR spectroscopy and mass spectrometry. They all showed the expected $[\text{Fe(bapphen)}(\text{NCX})]^+$ monocationic peak by electron-spray mass spectrometry (calculated at $m/z$ 478.0532 for 1 and 525.9978 for 2, see Table 5.1), which confirms coordination of the ligand bapphen to the Fe(II) ion. Consistently, the IR spectra of all iron compounds show the characteristic stretching vibrations of the coordinated thiocyanate ligands for 1, and of the selenocyanate ligands for 2 in the range of 2080 to 2100 cm$^{-1}$ (See Table 5.1).

Elemental analyses were performed for compounds 1b, 1c, 1d, 2b, and 2c after thorough vacuum drying, and fitted to the formula $[\text{Fe(bapphen)}(\text{NCX})_2] \cdot n\text{DMF}$ with $n = 0, 1, \text{or } 2$ (Table AIII.1, Appendix III), but not for method a as explained in Chapter 4. The analyses of 1b and 1d suggested that no DMF molecules were trapped in the crystal lattice. The samples of both 1c and 1d were crystalline, they had been obtained using liquid-liquid diffusion of MeOH into DMF or DCM respectively. For 1c elemental analysis was not very conclusive on the value of $n$; however, powder X-ray diffraction showed the same phase as 1d (Figure AIII.1, Appendix III). For 2c, the single crystal X-ray structure determination showed two DMF solvent molecules per iron complex, but once the crystals were taken out of the mother liquor they
immediately became a reddish brown powder, which indicates the escape of solvent molecules from the crystal lattice. Elemental analyses for 2b and 2c after drying the crystals under vacuum for two hours, clearly showed that both compounds contained no DMF molecules in their crystal lattices (Table AIII.1). Thus the two lattice DMF molecules in 2c are loosely bound, to form after exposure to air or vacuum a solid of the same composition as 2b.

Table 5.1. Numbering, formulae, yields, m/z ratio for the [Fe(bapphen)(NCX)]⁺ monocationic peak observed by mass spectrometry, and infrared thiocyanate/selenocyanate stretching vibrations for compounds 1 and 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Yield (%)</th>
<th>m/z</th>
<th>NCX⁻ vibrations (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>trans-[Fe(bapphen)(NCS)₂]</td>
<td>67</td>
<td>478.0525</td>
<td>2082</td>
</tr>
<tr>
<td>1b</td>
<td>trans-[Fe(bapphen)(NCS)₂]</td>
<td>52</td>
<td>478.0527</td>
<td>2084</td>
</tr>
<tr>
<td>1c</td>
<td>trans-[Fe(bapphen)(NCS)₂]</td>
<td>64</td>
<td>478.0532</td>
<td>2082</td>
</tr>
<tr>
<td>1d</td>
<td>trans-[Fe(bapphen)(NCS)₂]</td>
<td>42</td>
<td>478.0532</td>
<td>2081</td>
</tr>
<tr>
<td>2a</td>
<td>trans-[Fe(bapphen)(NCSe)₂]</td>
<td>68</td>
<td>525.9975</td>
<td>2086</td>
</tr>
<tr>
<td>2b</td>
<td>trans-[Fe(bapphen)(NCSe)₂]</td>
<td>81</td>
<td>525.9985</td>
<td>2090</td>
</tr>
<tr>
<td>2c</td>
<td>trans-[Fe(bapphen)(NCSe)₂]∙2DMF</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2c</td>
<td>trans-[Fe(bapphen)(NCSe)₂]∙2DMF</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a Single crystals of 2c were analyzed by single crystal X-ray structure determination and elemental analysis only.

5.2.2. Description of X-ray structures

A number of attempts to grow single crystals of 1 using method c were undertaken, with different concentrations and volumes. However, the resultant crystallites were not of an acceptable quality for crystal structure analysis. Changing the solvent from DMF to DCM resulted in red square-shaped single crystals, 1d, suitable for X-ray diffraction techniques. The experimental powder X-ray diffractogram of 1c was found to be identical to the calculated diffractogram from the single crystal X-ray structure of 1d (Figure AIII.1, Appendix III), suggesting that 1c and 1d are the same phase of the same material. Overall, it is worth mentioning that although the ligands bapphen and bapbpy are structurally very similar, the crystallization of their iron complexes are very different: complex [Fe(bapbpy)(NCS)₂] can be easily crystallized using diffusion of
MeOH into DMF in a Corning tube (method c), while 1 only crystallized in more specific conditions using DCM instead of DMF. The X-ray crystal structure of 1d was determined at 100, 240 and 300 K. Remarkably the same X-ray diffraction patterns were obtained at the three temperatures, giving identical cell dimensions from 110 to 300 K. Thus, no phase transitions occurred upon variation of the temperature, suggesting that 1d may not have SCO properties. Therefore, only the crystal structure obtained at 100 K for 1d is presented below. The X-ray crystal structure of 2c was determined both at 110 and 250 K. The molecular geometries of 1d and 2c are shown in Figure 5.1, and selected bond lengths and angles for 1d and 2c are provided in Table 5.2. Both 1d and 2c show a similar coordination environment as for the compound [Fe(bapbpy)(NCS)$_2$];$^{14, 16}$ the tetradentate ligand bapphen is coordinated to iron(II) in the basal plane, leaving the two thiocyanate (1d) or selenocyanate (2c) ligands in trans positions on the octahedron (Figure 5.1). Two independent DMF molecules are present per iron complex in 2c.

Compound 1d crystallized in the triclinic space group P-1. The average Fe–N bond length was found to be 2.15 Å at 100 K, which is typical of a HS Fe(II) complex in an FeN$_6$ octahedral environment. The basal N–Fe–N coordination angles, which vary from 78.31(7)$^\circ$ to 85.53(7)$^\circ$ (Table 5.2), and the torsion angle N1–N3–N4–N6 = 18.98(8)$^\circ$, are indicative of a distorted octahedral geometry. As expected, the phenantroline backbone is flat, and the torsion angle N4–C13–C14–N3 = 6.39(3)$^\circ$ is significantly smaller than the one found for the bipyridine-based complex [Fe(bapbpy)(NCS)$_2$] in the HS phase [N3–C10–C10B–N3B = 12.90(3)$^\circ$]$^{14}$ Furthermore, the angle between the two planes of the two terminal pyridine rings is 34.77$^\circ$ in 1d, which is very similar compared to the one found in HS [Fe(bapbpy)(NCS)$_2$] (33.08$^\circ$),$^{14}$ which thus seems to be the result of the steric clash between facing hydrogen atoms on the terminal pyridines.

Compound 2c crystallizes in the monoclinic space group $P2_1/c$ both at 250 K and 110 K. The average Fe–N bond length for 2c is 2.15 Å at 250 K and 2.08 Å at 110 K, indicating that compound 2c is in the HS state at 250 K while it is most likely in a mixed HS/LS state at 110 K. In the structure of 2c, the two DMF molecules are bound via relatively strong N–H···O [N2···O2S = 2.761(4) Å, N5···O1S = 2.786(4) Å] hydrogen bonding interactions between the two N–H donor groups of the ligand bapphen and the acceptor carbonyl group of DMF. The packing in 2c is built from one-
dimensional chains with the repetitive motif DMF–1⋯DMF along [1 1 0], via the N–H⋯O interactions. The structure is different to that of [Fe(bapbpy)(NCS)$_2$]·2DMF$^{16}$ due to different space group and packing.

Figure 5.1. Displacement ellipsoid plots (50% probability level) for compound 1d (HS) at 100(2) K (top) and for compound 2c (HS) at 250(2) K (bottom). Hydrogen atoms were emitted for clarity.
Table 5.2. Selected bond lengths (Å) and angles (°) for the crystal structures of 1d and 2c.

<table>
<thead>
<tr>
<th></th>
<th>1d</th>
<th></th>
<th>2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>100(2)</td>
<td>110(2)</td>
<td>250(2)</td>
</tr>
<tr>
<td>Spin state</td>
<td>HS</td>
<td>HS+LS</td>
<td>HS</td>
</tr>
<tr>
<td>Fe1–N1</td>
<td>2.144(2)</td>
<td>2.098(3)</td>
<td>2.156(3)</td>
</tr>
<tr>
<td>Fe1–N3</td>
<td>2.126(2)</td>
<td>2.070(3)</td>
<td>2.144(3)</td>
</tr>
<tr>
<td>Fe1–N4</td>
<td>2.137(2)</td>
<td>2.051(3)</td>
<td>2.118(3)</td>
</tr>
<tr>
<td>Fe1–N6</td>
<td>2.142(2)</td>
<td>2.111(3)</td>
<td>2.174(3)</td>
</tr>
<tr>
<td>Fe1–N7</td>
<td>2.184(2)</td>
<td>2.068(4)</td>
<td>2.145(5)</td>
</tr>
<tr>
<td>Fe1–N8</td>
<td>2.155(2)</td>
<td>2.075(4)</td>
<td>2.158(5)</td>
</tr>
<tr>
<td>N2–O2S</td>
<td>–</td>
<td>2.761(4)</td>
<td>2.779(5)</td>
</tr>
<tr>
<td>N5–O1S</td>
<td>–</td>
<td>2.786(4)</td>
<td>2.798(5)</td>
</tr>
<tr>
<td>N6–Fe1–N4</td>
<td>85.29(7)</td>
<td>86.9(1)</td>
<td>85.3(1)</td>
</tr>
<tr>
<td>N4–Fe1–N3</td>
<td>78.31(7)</td>
<td>80.4(1)</td>
<td>78.7(1)</td>
</tr>
<tr>
<td>N3–Fe1–N1</td>
<td>85.53(7)</td>
<td>86.7(1)</td>
<td>85.2(1)</td>
</tr>
<tr>
<td>N8–Fe1–N4</td>
<td>84.99(7)</td>
<td>88.0(1)</td>
<td>88.0(2)</td>
</tr>
<tr>
<td>N7–Fe1–N3</td>
<td>82.43(7)</td>
<td>85.8(1)</td>
<td>86.0(1)</td>
</tr>
<tr>
<td>N7–Fe1–N8</td>
<td>177.19(7)</td>
<td>177.1(1)</td>
<td>175.3(2)</td>
</tr>
<tr>
<td>N4–C13–C14–N3</td>
<td>–6.39(3)</td>
<td>0.57(5)</td>
<td>0.97(6)</td>
</tr>
<tr>
<td>N6–N4–N3–N1</td>
<td>–18.98(8)</td>
<td>–12.1(1)</td>
<td>–13.4(2)</td>
</tr>
<tr>
<td>C1–N1–N6–C22</td>
<td>–42.00(2)</td>
<td>–38.2(3)</td>
<td>–34.1(4)</td>
</tr>
</tbody>
</table>

In the crystal packing of 1d at 100 K, each molecule interacts with two adjacent iron complexes via N–H···S intermolecular interactions along the crystallographic b axis (Figure 5.2a). The intermolecular N···S distance are N2···S2 = 3.370(2) Å and N5···S1 = 3.404(2) Å, indicating strong hydrogen bond interactions that are comparable to the ones found in [Fe(bapbpy)(NCS)$_2$].$^{14}$ Regarding π–π stacking interactions, the Fe1–S1–Fe1 intermolecular angle between the adjacent molecules via sulfur atom on the thiocyanate ligand is 103.89° (Figure 5.2a). The centroid-centroid distance in 1d was found to be Cg1–Cg2 = 7.195 Å at 100 K (Cg1 and Cg2 are defined as the terminal pyridine ring between two neighbouring complexes), i.e., there is no π–π stacking interaction in the direction of the N–H···S hydrogen bonding network. As a
result, the intermolecular distance between the two iron centres of two closest neighbouring molecules in 1d is much longer (Fe−Fe = 9.262(5) Å) (Figure 5.2a) than in [Fe(bapbpy)(NCS)$_2$]. However, two layers of the one dimensional chains of 1d are held together by strong π−π stacking of the phenantroline backbones following the direction [1 0 −1] (Cg3−Cg4 = 3.599 Å, Figure 5.2b). Overall, whereas the N−H···S hydrogen bonding network in 1d seems similar to that found in [Fe(bapbpy)(NCS)$_2$], the π−π stacking interactions are organized in a very different manner, resulting in large iron-to-iron intermolecular distances, which seems to play a role in SCO.

![Figure 5.2](image)

**Figure 5.2.** (a) N−H···S hydrogen bonding network along the crystallographic $b$ axis. (b) A 2D array of two layers of 1d interact via π−π stacking following the direction [1 0 −1] at 100(2) K.

### 5.2.3. Magnetic properties

The temperature dependence of $\chi_M T$ was measured for samples 1a, 1b, 2a and 2b, and crystalline samples 1c and 1d, in both the heating and the cooling modes (Figure 5.3), where $\chi_M$ is the molar magnetic susceptibility and $T$ the temperature. Samples 1c and 1d show room-temperature $\chi_M T$ values of 3.51 and 3.57 cm$^3$ K mol$^{-1}$, respectively, in agreement with a HS iron(II) centre in an octahedral FeN$_6$ environment. However, no significant change in $\chi_M T$ values was observed between 30 K and 300 K for both samples: both 1c and 1d stay in the high-spin (HS) state. This result is consistent with the X-ray single crystal studies of 1d at 110, 240, and 310 K, and confirms that 1c and 1d are identical materials. Unexpectedly, compounds 1a and 1b show complicated SCO behaviour across the same temperature range. The magnetic susceptibility measurement for the powder sample 1a shows two gradual transitions at low temperature and one abrupt transition with hysteresis around 280 K (Figure 5.3). The $\chi_M T$ value of 3.0 cm$^3$ K mol$^{-1}$ remains constant from 300 K to 280 K, where it abruptly
decreases to a value of 2.3 cm$^3$ K mol$^{-1}$ at 260 K. Then the value of $\chi MT$ gradually decreases from 2.3 cm$^3$ K mol$^{-1}$ down to 1.3 cm$^3$ K mol$^{-1}$ at 61 K. The further decrease of $\chi MT$ below 50 K is a typical feature of a kinetically frozen spin transition (see Discussion). The transition temperatures for the first transition of 1a, measured as the maximum of $d(\chi MT)/dT$ vs. $T$ (Figure AIII.2), was found to be 268(4) K in the cooling mode and 280(4) K in the heating mode, which defines a hysteresis width of 12 K (Table 5.3). The second and third transitions occur at 152(8) K and 77(4) K, respectively, and do not show any hysteresis. For compound 1b, the magnetic susceptibility measurements showed similar SCO behaviour compared to 1a, with a less complete first transition and a higher residual HS fraction at low temperatures, i.e., higher $\chi MT$ values across the whole temperature range.

![Figure 5.3](image-url)

**Figure 5.3.** Thermal variation of $\chi MT$ for compounds 1a, 1b, 1c, and 1d (left); 2a, and 2b (right). Scan rate 0.3-1.1 K min$^{-1}$. The cooling and heating curves are identical for 1c and 1d, therefore only the heating curve is shown respectively.

The remarkable difference between the magnetic properties of samples 1a, 1b, and 1d (1c) suggests that packing effects play a critical role in the SCO behaviour of [Fe(bapphen)(NCS)$_2$]. The power X-ray diffractograms of the three materials 1a, 1b, and 1d, was thus measured as it can provide global information on phase/crystal structure in the solid state. Sample 1a clearly shows a diffractogram that is different from 1d, which suggests that both samples have different structures. As shown in
Figure 5.4, the major differences between 1a and 1d are: (i) the intense reflection peaks at $2\theta \approx 19^\circ$ and $21^\circ$ for 1a (circle), which are not present in 1d; (ii) other reflections of 1a, e.g. at $2\theta \approx 24^\circ$ (diamond), and $25^\circ$ (triangle) that are absent in 1d. The powder X-ray diffractogram for 1b, although poorly resolved, however shows some resemblance to the calculated diffractogram for 1d. In combination with the magnetic susceptibility measurement of 1b, these data suggest that 1b is a mixture between 1a and 1d in an amorphous phase. Overall, compound 1 shows at least two forms 1a and 1d with remarkably different magnetic properties, which are obtained depending on the preparation methods.

![Figure 5.4](image)

**Figure 5.4.** Experimental powder X-ray diffractograms for 1a and 1b in the range 10-40° ($2\theta$) measured at room temperature. The calculated powder pattern derived from the crystal structure of 1d at 240 K using program Mercury$^{19}$ is also shown. The symbols in 1a indicate the most significant differences with samples 1b and 1d.

The magnetic susceptibility measurements for 2a and 2b show SCO behaviour for both compounds. The $\chi_M T$ values for both compounds gradually decrease from 350 K to 60 K, and after a short plateau decrease again due to a kinetically frozen spin transition (Figure 5.3). As for compound 1 the $\chi_M T$ values are higher in 2b compared to 2a across the whole temperature range, indicating a higher degree of metallation with method b.
A single transition temperature can be defined for \(2a\) and \(2b\); its value is 101(4) K and 85(4) K for \(2a\), and \(2b\) respectively (see Appendix III). Comparing the magnetic susceptibility measurements for compounds \(1a\), \(1b\) and \(2a\), \(2b\), it appears that the spin crossover in \(2a\) and \(2b\) is more gradual, and that the hysteresis loop is lost with NCSe\(^-\) ligands compared to thiocyanate ligands, in which the SCO was found to be cooperative in \(1a\) and \(1b\) (Figure 5.3).

### Table 5.3. Transition temperatures for compounds \(1a\), \(1b\), \(2a\), and \(2b\) as determined by magnetic susceptibility measurements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_{1/2}^1) (K)(^a)</th>
<th>(T_{1/2}^{1\downarrow}) (K)(^b)</th>
<th>(T_{1/2}^{1\uparrow}) (K)</th>
<th>(\Delta T_{1\text{hys}}^1) (K)</th>
<th>(T_{1/2}^2) (K)</th>
<th>(T_{1/2}^3) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1a)</td>
<td>274(4)</td>
<td>268(4)</td>
<td>280(4)</td>
<td>12(6)</td>
<td>152(8)</td>
<td>77(4)</td>
</tr>
<tr>
<td>(1b)</td>
<td>282(4)</td>
<td>277(4)</td>
<td>286(4)</td>
<td>9(6)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(2a)</td>
<td>101(4)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(2b)</td>
<td>85(4)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) \(T_{1/2}^1\) is defined as \((T_{1/2}^{1\uparrow}+T_{1/2}^{1\downarrow})/2\). \(^b\) \(T_{1/2}^{1\downarrow}\) and \(T_{1/2}^{1\uparrow}\) are defined as the temperatures where \(d(\chi_M T)/dT\) has a maximum in the cooling mode or in the heating mode (Appendix III).

### 5.3. Discussion

The \(\chi_M T\) vs. \(T\) plots for \(1a\) and its analogue [Fe(bapbpy)(NCS)\(_2\)] (3a), as well as for \(2a\) and [Fe(bapbpy)(NCSe)\(_2\)] (4a) (Figure 5.5), show very different SCO behaviours. This is remarkable since bapbpy and bapphen are structurally very similar ligands, thus showing the sensitivity of the SCO phenomenon to small changes in the molecular structure of the metal complex. Upon careful observation, however, the \(\chi_M T\) vs. \(T\) plot for \(1a\) shows multi-step spin transitions, which is rather similar to [Fe(bapbpy)(NCS)\(_2\)] even if three steps are observed instead of two, and even if the residual HS fraction remains high at low temperature for \(1a\) whereas for [Fe(bapbpy)(NCS)\(_2\)] the SCO is complete. Similarly, the \(\chi_M T\) vs. \(T\) plot for \(2a\) shows a gradual transition, which was also found for [Fe(bapbpy)(NCSe)\(_2\)] (see Chapter 4).

The fact that the transitions in \(1a\) and \(2a\) are incomplete might be explained by the interplay between thermal spin-crossover and spin-trapping.\(^{20-22}\) In thermal SCO, for both LS and HS states the electronic energies can be calculated as a function of the
Figure 5.5. Comparison of $\chi M T$ vs. $T$ curves for compounds 1a, 2a, 3a ([Fe(bapbpy)(NCS)$_2$]), and 4a ([Fe(bapbpy)(NCSe)$_2$]). $\Delta T^S$ and $\Delta T^{Se}$ indicate the change in the SCO transition temperature $T_{1/2}$ between X = S and X = Se for [Fe(L)(NCX)$_2$] compounds (L = bapbpy or baphen).

The average metal-to-ligand distance (Figure 5.6a). The difference between the zero-point energies of the two states can be expressed as $\Delta E^0_{HL} = \Delta E^0_{HS} - \Delta E^0_{LS}$ (Figure 5.6a). In general, all complexes will be in the LS state at low temperatures, whereas at elevated temperatures an entropy-driven HS state can be observed. An energy barrier ($\Delta E_{act}$) must be overcome before the HS $\rightarrow$ LS transition can take place (Figure 5.6a). Under normal conditions, the energy needed for overcoming this barrier ($\Delta E_{act}$) is provided by thermal energy ($kT$). Upon lowering the temperature rapidly, however, if the HS $\rightarrow$ LS relaxation is slow, i.e. $kT \ll \Delta E_{act}$, it is possible to ‘freeze’ the metastable HS species. This is typically realized in quench-cooling experiments, where the sample is cooled down to 5 K within seconds, or in a $T_{LIESST}$ (LIESST = Light-Induced Spin-State Trapping) experiment, in which the SCO compound first undergoes a slow and complete spin-crossover to the LS state upon cooling, followed by radiation of the LS state material at low temperatures to photochemically produce the HS state at low temperature (Figure 5.6b). When the laser is switched off, the compound remains HS until it is warmed above the $T_{LIESST}$ temperature where the thermal energy becomes high enough to overcome the activation barrier that is necessary to relax from the HS...
state to the LS state \( (kT \geq \Delta E_{\text{act}}) \). However if \( T_{\text{LIESST}} \) approaches \( T_{1/2} \) as shown in Figure 5.6c, the HS state becomes metastable and may not undergo the complete transition to the LS state, because the thermal relaxation of HS to LS becomes too slow near \( T_{1/2} \), i.e., near \( T_{\text{LIESST}} \). This case is similar to thermal spin trapping. For compounds \([\text{Fe(bapbpy)}(\text{NCX})_2]\) the transition temperatures \( T_{1/2} \) are high compared to \( T_{\text{LIESST}} \) \( (T_{\text{LIESST}} = 56 \text{ K for } [\text{Fe(bapbpy)}(\text{NCS})_2]) \), leading to low residual HS fraction in the LS phase. In contrast, for \([\text{Fe(bapphen)}(\text{NCX})_2]\) the low \( T_{1/2} \) leads to high residual HS fractions even at 5 K.

![Figure 5.6](image)

**Figure 5.6.** (a) Schematic representation of the potential wells for the LS and HS states of an iron(II) SCO compound; (b) and (c) schematic representations of relaxation processes when slow thermal spin-crossover and LIESST are followed by slow warming above \( T_{\text{LIESST}} \), in the case of an abrupt SCO system and with \( T_{\text{LIESST}} < < T_{1/2} \) (b) or when \( T_{\text{LIESST}} \approx T_{1/2} \) (c).

Furthermore, striking differences were observed between the magnetic behaviour of \([\text{Fe}(L)(\text{NCS})_2]\) and \([\text{Fe}(L)(\text{NCSe})_2]\) \((L = \text{bapphen or bapbpy})\). For compound \([\text{Fe(bapphen)}(\text{NCS})_2]\) a higher \( T_{1/2} \) was found for 1a than for \([\text{Fe(bapbpy)}(\text{NCS})_2]\) (3a, \( \Delta T^S > 0 \), see Figure 5.5). This is indeed what was expected since the more conjugated and more rigid phenantroline backbone was thought to give a higher ligand field strength, and therefore increase the transition temperature of its iron(II) complexes compared to 3a. However, for compound \([\text{Fe(bapphen)}(\text{NCSe})_2]\), the transition temperature \( T_{1/2} \) in 2a is more than 90 K lower than that of \([\text{Fe(bapbpy)}(\text{NCSe})_2]\) (4a, \( \Delta T^S < 0 \), see Figure 5.5). Thus, the simple model based on the ligand field strength cannot be used to predict the evolution of transition temperatures in SCO. Indeed, it does not take into account crystal packing effects and supramolecular interactions, which play a critical role in the SCO phenomenon.
This role is best demonstrated by the effect of different preparative methods on the SCO behaviour of compound 1. Previous studies have shown that different polymorphs arising from different preparative methods can have very different SCO properties.26–28 The first form of compound 1, obtained via method a, exhibits cooperative spin crossover. It was obtained from a methanol suspension that was stirred with Fe(NCS)$_2$ overnight leading to impregnation of the ligand suspension by the metal to form the complex. In contrast, the second form, 1d, was obtained from slow crystallization from MeOH–DCM mixtures after three days. This difference in preparation crystallization results in two distinctive crystal structures for compound 1 (Figure 5.4), which strongly affects the FeN$_6$ coordination sphere and decides whether SCO can occur or not.

Comparing the crystal structures of 1c/1d and 3c ([Fe(bapbpy)(NCS)$_2$]) may help understanding why 1d has lost SCO properties (Figure AIII.3, Appendix III). Although the ligand sets with bapphen and bapbpy are almost identical, there are small deviations of the orientation of the thiocyanate ligands, which has been suggested as a possible reason for the absence of SCO (see Chapter 2). Furthermore, the crystal packing in 1d is very different from that of 3c. For example, although the 1D chains of N–H···S intermolecular interactions exist in both crystal structures, the π–π stacking interactions do not occur between dipyridylamine units along the infinite 1D chain in 1d, but rather between phenantroline moieties following the direction [1 0 −1]. The fact that 1d does not have SCO properties may thus either be attributed to the different orientation of the NCS$^-$ ligands or to the absence of π–π stacking interaction along the direction of the N–H···S network.

5.4. Conclusion

The new rigid ligand bapphen was synthesized, and a series of new iron(II) complexes based on bapphen was prepared. The complex [Fe(bapphen)(NCS)$_2$] appears to exist as two different forms, 1a and 1d. In 1a a three-step incomplete SCO is observed with a hysteresis loop occurring near 280 K. Although the intermediate phases in 1a are not fully characterized yet, our hypothesis is that $T_{LIEST}$ might be very close to $T_{1/2}$ for this compound, causing very slow relaxation from the second intermediate phase to the fully LS state. Further characterization of the two intermediate phases is ongoing. The crystal structure of 1d was obtained, but this form of [Fe(bapphen)(NCS)$_2$] has no SCO properties. The magnetic behaviour of [Fe(bapphen)(NCSe)$_2$] (2a) shows that the cooperativity of the transition is lost upon substitution of S by Se, which is consistent
with the trend found for bapbpy. Overall, this case study demonstrates that the mere occurrence of SCO, as well as the transition temperatures, are impossible to predict based on ligand field strength, as packing effects play a critical role in the magnetic properties of solid-state SCO compounds.

5.5. Experimental

5.5.1 General information

All reactions were performed under argon using standard Schlenk line techniques. The applied vacuum was about $10^{-3}$ mbar. Toluene was dried over sodium. Degassed solvents were obtained by bubbling argon through 50 mL solvent in a Schlenk flask for one hour. Degassed solvents were used for all complex syntheses. The reagent 2,9-dibromo-1,10-phenanthroline was synthesized using literature procedures.\(^{17,18}\) All other chemicals were obtained from commercial sources and used without further purification. Filtration of complexes was carried out using Whatman RC60 membrane filters. NMR Spectra were measured on a Bruker DPX-300 spectrometer at room temperature. Chemical shifts are indicated in ppm relative to TMS. Mass spectra were obtained using soft electron-spray from a Thermoquest Finnigan AQA. High resolution mass spectra were measured using direct injection (2 µL of a 2µM solution in DMF and 0.1% formic acid on a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electron-spray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 275 °C) with resolution R=60.000 at m/z=400 (mass range = 150-2000) and dioctylphtalate (m/z=391.28428) as "lock mass". Infrared spectra were acquired on a Perkin Elmer FT-IR spectrometer PARAGON 1000 at room temperature. Elemental analyses (C,H,N,S) were obtained from a Perkin-Elmer 2400 Series II analyzer.

Single crystal X-Ray diffraction data of 1d and 2c were collected by measuring all reflection intensities using a KM4/Xcalibur (detector: Sapphire3) with enhance graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) under the program CrysAlisPro (Version 1.171.35.11 Oxford Diffraction Ltd., 2011). The program CrysAlisPro was used to refine the cell dimensions. Data reduction was done using the program CrysAlisPro. The structure was solved with the program SHELXS-97\(^{29}\) and was refined on $F^2$ with SHELXL-97.\(^{29}\) Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms (except when specified) were placed at calculated positions using the instructions AFIX 43 with isotropic displacement parameters having values 1.2 times $U_{eq}$ of the attached C atoms. The H
atoms attached to N1 and N2 were found from difference Fourier maps, and its coordinates/isotropic factor were refined freely [the N–H distance was restrained to 0.88(3) Å using the DFIX command].

For magnetic susceptibility measurements, each sample was mounted in a plastic straw before introduction in a Quantum Design MPMS–XL SQUID magnetometer. DC magnetization measurements were performed in a field of 0.1 T, from 5 to 350 K (heating mode) and from 350 to 5 K (cooling mode) with a rate of 0.3–1.1 K min⁻¹ for compounds 1b, 1c, 2a, and 2b; from 5 to 300 K (heating mode) and from 300 to 5 K (cooling mode) with a rate of 0.3–1.1 K min⁻¹ for compounds 1a and 1d. For each sample the total measuring time was ~20 h. Corrections for the diamagnetism of the samples were calculated using Pascal’s constants.³⁰

5.5.2 Preparation of N,N’-bis(pyrid-2-yl)-1,10-phenanthroline-2,9-diamine (bapphen):

2-Aminopyridine (280 mg, 2.97 mmol), 2,9-dibromo-1,10-phenanthroline (500 mg, 1.48 mmol), Pd(dba)₂ (20.9 mg, 0.0363 mmol), (S)-BINAP (36.6 mg, 0.0587 mmol) and KOtBu (666 mg, 5.94 mmol) were weighed into a two-neck round-bottom flask, placed under argon atmosphere, and suspended in distilled and degassed toluene (30 mL). The brown suspension was heated to 80 °C and stirred under argon for 40 hours. The red/brown suspension was then cooled to room temperature and demineralized water (30 mL) was added. The mixture was stirred vigorously for 1.5 hours, filtered, and washed three times with water, diethyl ether, and hexanes. The yellow solids were collected, dried in vacuum for two hours, to yield 68% of bapphen (368 mg, 1.01 mmol). ¹H NMR (DMSO-d₆): δ= 10.12 (s, 2 H; 2 NH), 9.26 (d, J = 6 Hz, 2H, pyH³,³'), 8.31 (m, 2H, pyH⁶,⁶'), 8.23 (d, J = 6 Hz, 2H, phenH³,⁸), 7.64 (s, 2H, phenH⁵,⁶), 7.56 (d, J (H,H)= 9 Hz, 2 H, phenH⁴,⁷), 7.49 (m, 2 H, pyH⁴,⁴'), 6.98 ppm (m, 2 H, pyH⁵,⁵'). ¹³C NMR (DMSO-d₆): δ=154.11 (Cq), 153.14 (Cq), 147.76 (pyC⁶,⁶'), 143.26 (phenC¹¹,¹²), 137.98 (pyC⁴,⁴'), 137.46 (phenC³,⁸), 124.06 (phenCq), 122.87 (phenC⁵,⁶), 116.59 (pyC³,³'), 114.62 (phenC⁴,⁷), 111.58 (pyC³,³'). MS (MeOH) m/z (calc): 364.4 (365.0, [M+H]⁺). HR–MS (DMF): m/z (calc): 365.1506 (365.1509, [M+H]⁺). EA calc (%) for C₂₂H₁₆N₆H₂O: C 69.10, H 4.74, N 21.97; found: C 70.54, H 3.61, N 21.53. IR spectroscopy (cm⁻¹): 3012, 1622, 1576, 1560, 1516, 1472, 1452, 1340, 1311, 1230, 1142, 1089, 994, 840, 770, 729, 616, 594, 514, 486, 414.
5.5.3 Preparation of complexes [Fe(bapphen)(NCX)$_2$] (X=S or Se):

**Preparation of 0.1 M [Fe(NCX)$_2$] solution (X=S or Se):** FeSO$_4$ (152 mg, 1.00 mmol), ascorbic acid (5 mg), and KNCS (194 mg, 2.00 mmol) or, respectively, KNCSe (288 mg, 2.00 mmol), were mixed in MeOH (6 mL) and stirred under argon for half an hour. The white, respectively slightly orange, suspension was filtered over Celite on filter paper into a 10 mL volumetric flask. The flask was filled up to 10 mL with MeOH, resulting in a clear solution, which was prepared fresh every time.

Four methods noted a, b, c, or d were used to synthesize the iron(II) complexes [Fe(bapphen)(NCX)$_2$] (X=S or Se). The compounds are designated a, b, c or d, depending on their preparation method.

**Method a:** bapphen (40 mg, 0.11 mmol for 1a; 50 mg, 0.14 mmol for 2a) was suspended in degassed MeOH (3 mL) and stirred under argon to form a yellow suspension. 1.1 equivalent of Fe(NCS)$_2$ or Fe(NCSe)$_2$ (0.12 mmol for 1a; 0.15 mmol for 2a, 0.1 M stock solution) was added to the mixture, and an immediate colour change to red was observed. The suspension was stirred under argon for 18 hours, filtered over a micropore filter, washed with degassed MeOH, and finally dried in vacuo for 3 hours.

**Method b:** bapphen (20 mg, 0.05 mmol for 1b; 51 mg, 0.14 mmol for 2b) was dissolved in degassed DMF (3 mL) under argon. To the clear yellow solution, 1.1 equivalent of Fe(NCS)$_2$ or Fe(NCSe)$_2$ (0.06 mmol for 1b; 0.15 mmol for 2b, 0.1 M stock solution) was added and an immediate colour change to red was observed. The solution was stirred under argon for 18 hours, upon which a dark precipitate appeared. The precipitate was filtered over a micropore filter, washed with MeOH, and finally dried in vacuum for 3 h.

**Method c:** to grow crystals of compound 1 (1c): 10 mg of bapphen was dissolved in 2 mL degassed DMF, affording a clear yellow solution. A small amount of ascorbic acid (5 mg) was added to prevent oxidation. 1 mL aliquots of this solution were pipette-filtered over 1 cm Celite into the vertical compartment of two Y-shaped glass tubes, 1.0 mL of the 0.1 M Fe(NCS)$_2$ solution was carefully added into the other compartment of the glass tube. Then both solutions were frozen by dipping each Y-shaped glass tube into liquid nitrogen. Then an additional layer of pure DMF (1 mL) was added on top of the frozen bapphen solution, and finally degassed MeOH was carefully added to fill the entire glass tube. The glass tubes were then stoppered and kept under argon using balloons at room temperature, and if possible under sun light, to allow slow liquid/liquid diffusion. Single crystals were obtained typically within a week once formed. The crystals of 1c or 1d were not vacuum or air sensitive and therefore could be handled under ambient conditions for several weeks.
To grow crystals of compound 2 (2c), bapphen (25 mg) was dissolved in degassed DMF (5 mL). 1 mL aliquots of this solution were pipette-filtered over 1 cm Celite into five Corning tubes. To each tube 0.15 mL of the Fe(NCSe)_2 solution was carefully added to create a two-layer system. Degassed methanol was then layered on top of these layers. The tubes were then stoppered and left untouched at room temperature, and if possible under sunlight, to allow slow liquid/liquid diffusion. Within 3 days, dark crystals of 2c appeared at the wall of the vials. The tubes were immediately sent for single crystal X-ray structure determination. Once the crystals left the mother liquor they immediately became reddish brown powder.

**Method d:** to grow single crystals of 1d, the procedure of 1c (above) was followed using DCM instead of DMF. The quantities of chemicals were followed with exact same amounts.

[Fe(bapphen)(NCS)_2] (1a): the red solid was obtained with a yield of 67% (40 mg, 0.074 mmol). IR spectroscopy (cm\(^{-1}\)): 3278, 3206, 3080, 3134, 2082 (NCS\(^{-}\)), 1630, 1600, 1581, 1543, 1516, 1472, 1428, 1370, 1244, 1149, 1105, 1009, 847, 773, 731, 647, 592, 500, 418, 316. HR–MS (DMF): \(m/z\) (calc): 478.0525 (478.0532, [M–NCS]\(^+\)).

[Fe(bapphen)(NCS)_2] (1b): the red solid was obtained with a yield of 52% (15 mg, 0.029 mmol). IR spectroscopy (cm\(^{-1}\)): 3278, 3190, 3132, 3040, 2084 (NCS\(^{-}\)), 1630, 1600, 1582, 1542, 1472, 1418, 1369, 1266, 1244, 1147, 1104, 1010, 848, 773, 732, 668, 648, 527, 500, 418, 336, 322. HR–MS (DMF): \(m/z\) (calc): 478.0527 (478.0532, [M–NCS]\(^+\)). EA calc (%) for C\(_{24}\)H\(_{16}\)FeN\(_8\)S\(_2\): C 53.74, H 3.01, N 20.90, S 11.93; found: C 52.57, H 1.97, N 20.49, S 11.05. \(^{1}\)H NMR (DMSO-\(d_6\)): \(\delta\) = 84.43, 78.55, 38.76, 27.67, 12.22, 11.51, 9.76.

[Fe(bapphen)(NCS)_2] (1c): dark red crystallites were obtained with a yield of 64%, however the crystals were not good enough for single crystal X-ray structure determination. IR spectroscopy (cm\(^{-1}\)): 3278, 3192, 3132, 3052, 2082 (NCS\(^{-}\)), 1629, 1600, 1582, 1542, 1472, 1418, 1368, 1244, 1147, 1104, 1009, 848, 722, 730, 668, 648, 500, 470, 418, 321. HR–MS (DMF): \(m/z\) (calc): 478.0532 (478.0532, [M–NCS]\(^+\)). EA calc (%) for C\(_{24}\)H\(_{16}\)FeN\(_8\)S\(_2\): C 53.74, H 3.01, N 20.89, S 11.95; found: C 52.87, H 2.74, N 20.11, S 11.24.

[Fe(bapphen)(NCS)_2] (1d): small red square-shaped blocks were obtained with a yield of 42%. IR spectroscopy (cm\(^{-1}\)): 3276, 3190, 3130, 3055, 2081 (NCS\(^{-}\)), 1629, 1599, 1580, 1542, 1473, 1422, 1368, 1243, 1147, 1103, 1008, 848, 772, 729, 667, 647, 499, 469. HR–MS (DMF): \(m/z\) (calc): 478.0532 (478.0532, [M–NCS]\(^+\)). EA calc (%) for C\(_{24}\)H\(_{16}\)FeN\(_8\)S\(_2\): C 53.74, H 3.01, N 20.89, S 11.95; found: C 53.36, H 2.74, N 20.11, S 11.15. Crystal data: Fw = 536.42, small red block, 0.11 × 0.08 × 0.08 mm\(^3\), triclinic, P\(-1\) (no. 2), \(a = 8.6588(3), b = 9.2618(3), c = 14.2198(4)\) Å, \(\alpha = 101.113(2)°, \beta = 96.671(3)°, \gamma = \)
90.935(3)°, \( V = 1110.54(6) \text{ Å}^3 \), \( Z = 2 \), \( D_\chi = 1.604 \text{ g cm}^{-3} \), \( \mu = 7.472 \text{ mm}^{-1} \), abs. corr. range: 0.541–0.667. 15376 Reflections were measured up to a resolution of \( (\sin \theta \lambda)_{\text{max}} = 0.62 \text{ Å}^{-1} \). 4361 Reflections were unique (\( R_{\text{int}} = 0.0321 \)), of which 4037 were observed \([I > 2\sigma(I)]\). 324 Parameters were refined using 2 restraints. \( R_1/wR_2 \) \([I > 2\sigma(I)]\): 0.0354/0.0938. \( R_1/wR_2 \) [all refl.]: 0.0390/0.0967. \( S = 1.035 \). Residual electron density found between −0.40 and 0.72 e Å\(^{-3}\).

\[ \text{[Fe(bapphen)(NCSe)\(_2\] (2a): the red solids were obtained with a yield of 68\% (59 mg, 0.094 mmol) IR spectroscopy \((\text{cm}^{-1})\): 3277, 3188, 3132, 3040, 2086 (NCSe–), 1628, 1600, 1580, 1542, 1472, 1424, 1368, 1266, 1243, 1148, 1104, 844, 731, 668, 647, 616, 513, 499, 418, 322. HR–MS \((\text{DMF})\): \( m/z \) (calc): 525.9975 (525.9978, [M–NCSe]\(^+\)).} \]

\[ \text{[Fe(bapphen)(NCSe)\(_2\] (2b): the red solids were obtained with a yield of 81\% (57 mg, 0.11 mmol). IR spectroscopy \((\text{cm}^{-1})\): 3277, 3189, 3132, 3056, 2090 (NCSe–), 1629, 1600, 1581, 1542, 1516, 1472, 1423, 1390, 1369, 1351, 1266, 1243, 1148, 1104, 1009, 846. \text{HR-MS \((\text{DMF})\): \( m/z \) (calc): 525.9985 (525.9978, [M–NCSe]\(^+\)).} \]

\[ \text{EA calc \( \% \) for } \text{C\(_{24}\text{H}_{16}\text{FeN}_8\text{Se}_2}: \text{C } 45.72, \text{H } 2.56, \text{N } 17.78; \text{found: C } 45.15, \text{H } 1.76, \text{N } 17.45. \]

\[ \text{\( ^1H \text{NMR (DMSO-\text{d}_6)} \): } \delta = 83.76, 78.09, 44.09, 38.35, 27.27, 12.28, 11.31, 9.44. \]

\[ \text{[Fe(bapphen)(NCSe)\(_2\]·2DMF (2c): crystal data: Phase I (110(2) K): } \text{Fw} = 776.41, \text{black irregular shape crystal, } 0.36 \times 0.15 \times 0.14 \text{ mm}^3, \text{monoclinic, } P2_1/c \text{ (no. 14), } a = 13.8105(4), b = 16.6679(4), c = 14.6516(5) \text{ Å, } \beta = 112.851(4)^\circ, V = 3107.99(18) \text{ Å}^3, \ Z = 4, \ D_\chi = 1.659 \text{ g cm}^{-3}, \mu = 2.874 \text{ mm}^{-1}, \text{abs. corr. range: 0.566–0.755. 16892 Reflections were measured up to a resolution of } (\sin \theta \lambda)_{\text{max}} = 0.59 \text{ Å}^{-1}. 5481 Reflections were unique } (R_{\text{int}} = 0.0321), \text{of which 4446 were observed } [I > 2\sigma(I)]. 448 Parameters were refined using 134 restraints. \( R_1/wR_2 \) \([I > 2\sigma(I)]\): 0.0420/0.0972. \( R_1/wR_2 \) [all refl.]: 0.0566/0.1029. \( S = 1.045 \). Residual electron density found between -1.09 and 1.18 e Å\(^{-3}\). Phase II (250(2) K): \text{Fw} = 776.41, \text{dark red irregular shape crystal, } 0.36 \times 0.15 \times 0.14 \text{ mm}^3, \text{monoclinic, } P2_1/c \text{ (no. 14), } a = 14.0472(7), b = 16.6733(6), c = 14.9392(7) \text{ Å, } \beta = 113.775(6)^\circ, V = 3202.0(2) \text{ Å}^3, \ Z = 4, \ D_\chi = 1.611 \text{ g cm}^{-3}, \mu = 2.790 \text{ mm}^{-1}, \text{abs. corr. range: 0.525–0.743. 14132 Reflections were measured up to a resolution of } (\sin \theta \lambda)_{\text{max}} = 0.58 \text{ Å}^{-1}. 5206 Reflections were unique } (R_{\text{int}} = 0.0346), \text{of which 3900 were observed } [I > 2\sigma(I)]. 446 Parameters were refined using 146 restraints. \( R_1/wR_2 \) \([I > 2\sigma(I)]\): 0.0456/0.1141. \( R_1/wR_2 \) [all refl.]: 0.0656/0.1221. \( S = 1.032 \). Residual electron density found between -0.44 and 0.50 e Å\(^{-3}\). Once the crystals left the mother liquor they immediately became reddish brown powder. \text{EA calc \( \% \) for } \text{C\(_{24}\text{H}_{16}\text{FeN}_8\text{Se}_2}: \text{C } 45.72, \text{H } 2.56, \text{N } 17.78; \text{found: C } 45.73, \text{H } 2.63, \text{N } 17.64. \]
5.6 References: