Unique Spin Crossover Pathways Differentiated by Scan Rate in a New Dinuclear Fe(II) Triple Helicate: Mechanistic Deductions Enabled by Synchrotron Radiation Studies

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Abstract

The achievement of targeted properties in spin crossover (SCO) materials is complicated by often unpredictable cooperative interactions in the solid state. Herein, we report a dinuclear Fe(II) triple helicate 1, which is a rare example of a SCO material possessing two distinct magnetic behaviors that depend upon the thermal scan rate. Desolvated 1 was seen to undergo spin transition (ST) which was complete following slow cooling (1 K min⁻¹), but incomplete ST (corresponding to 50% conversion) on fast cooling (10 K min⁻¹). The incomplete ST observed in the latter case was accompanied by a higher temperature onset of ST, differing from TIESST (Temperature-Induced Excited Spin-State Trapping) materials. The two SCO pathways have been shown to arise from the interconversion between two structural phases (a and b), with both phases having associated high spin (HS) and low spin (LS) states. SCXRD (Single Crystal X-ray Diffraction) experiments using controlled cooling rates and a synchrotron light source enabled short collection times (2-3 minutes per dataset) which has enabled the identification of a mechanism by which the slow-cooled material may fully relax. In contrast, fast-cooled materials exhibit disordered arrangements of multiple structural phases, which has in turn revealed that the [HS-LS] ↔ [LS-HS] equilibria are controllable in the solid by varying the scan rate. Such behavior has been previously observed in solution studies, but its control in solids has not been reported up to now. This study demonstrates how intermolecular cooperativity can allow multiple distinct magnetic behaviors, and provides some insight into how [HS-LS] ↔ [LS-HS] equilibria can be controlled in the solid state, which may assist in the design of next-generation logic and signaling devices.
1. Introduction

Spin crossover (SCO) compounds are an exciting class of materials with a range of potential applications across diverse fields.\textsuperscript{1-3} Such materials most commonly incorporate coordination complexes with $3d^{4-7}$ transition metal centers and intermediate ligand fields, and are thereby able to switch between high spin (HS) and low spin (LS) on application of external stimuli such as temperature, pressure and light irradiation.\textsuperscript{1-12} SCO has been observed in both the solution and solid state, with the latter being markedly affected by the supramolecular environment present in the crystal lattice such as intermolecular contacts and steric factors, which consequently may give rise to cooperative behaviors that include both abrupt and hysteretic spin transitions (ST).\textsuperscript{5} Of the possible $3d$ metal centers available for use in SCO compounds, Fe(II) has been the most extensively employed. The easily distinguishable LS ($S = 0$) and HS ($S = 2$) states, as well as the
manipulation of these two states through variation of the coordination environment can result in large changes in the physical and magnetic properties. Most notably the change of bond lengths of approximately 10% from the LS to HS state typically occurs.\textsuperscript{5-6}

The majority of the SCO studies so far have focused on the synthesis of mononuclear compounds, which simplifies the probing of intermolecular cooperativity.\textsuperscript{9,12-13} Additionally, polymeric metal-organic frameworks (MOFs) have been well studied, wherein direct bonding connectivity may readily enhance cooperative effects in the solid.\textsuperscript{14} On the other hand, discrete multinuclear SCO compounds offer a mixture of inter- and intramolecular cooperativity, which potentially provide multiple avenues for modulating the magnetic properties of SCO solids. Although mononuclear complexes have been widely used to probe intermolecular cooperativity,\textsuperscript{9,12-13} multinuclear complexes displaying various topologies are also being extensively studied.\textsuperscript{7} Within assemblies of multinuclear complexes the cooperative effects between metal centers occurring via their ligand backbone may tune their SCO properties, and ultimately result in switching behavior governed by a complex interplay between inter- and intramolecular cooperativity. Relative to polynuclear SCO complexes, dinuclear systems provide a simpler means for tuning these two sources of cooperative effects. The SCO profile of a given dinuclear complex can be associated with three different magnetic states: [HS-HS], [HS-LS]/[LS-HS] and [LS-LS]. The physical bridging of metal centers by ligand linkers means that in the intermediate [HS-LS]/[LS-HS] state, structural rearrangement at one metal center upon SCO influences the steric environment and ultimately the ligand field of the second metal ion. This may potentially stabilize, or destabilize the HS state, which can result in either abrupt SCO or gradual SCO for which there is little to no cooperativity, or in severe cases, trapping of the [HS-LS]/[LS-HS] at low temperature without the [LS-LS] state being formed. Such a structural rearrangement
with SCO has been associated with crystallographic symmetry breaking in several studies,\textsuperscript{7,15-19} wherein structural rearrangement during SCO is severe enough to result in a change in the crystallographic phase of the material. The appearance of a phase change is, currently, fairly unpredictable. A change of phase can often accompany different packing patterns of structurally equivalent molecules or the formation of molecular isomers, and often lead to drastic effects on the SCO properties. With regards to dinuclear triple helicates, which take the form $[\text{M}_2\text{L}_3]$, the cooperativity is shared across their three separate ligand strands with identical structures. To date, most of the Fe(II) helicate structures exhibiting SCO properties involve an imidazolimine-based coordination environment.\textsuperscript{20-29} Manipulation of the SCO properties in these dinuclear systems relies on the design of ligand structure(s) so as to induce a suitable ligand field. Several distinct dinuclear triple helicates have been shown to exhibit spin switching, with different structures from those conjoining metal cations via ligand bridging.\textsuperscript{14} Up to the present, the observation of two equivalent $[\text{HS-LS}]/[\text{LS-HS}]$ species in equilibrium has been only reported for the solution state,\textsuperscript{19} with no examples of $[\text{HS-LS}] \leftrightarrow [\text{LS-HS}]$ equilibrium being reported for the solid state. Control of $[\text{HS-LS}] \leftrightarrow [\text{LS-HS}]$ equilibria is desirable, as it may allow the generation of class II quantum cellular automata for signal and logic processes.\textsuperscript{30,31}

Many spin-switching materials, particularly those possessing a highly cooperative SCO, have demonstrated magnetic profiles that depend on the scan rate at which magnetic susceptibility measurements are conducted. A thermal hysteresis can result from the magnetic susceptibility in responding to the altered temperature, with larger hysteresis often being produced at faster scan rates.\textsuperscript{6} Another example of rate dependence on SCO is kinetic trapping of the HS state, where the high spin state is trapped by fast cooling.\textsuperscript{32-34} For example Weber et. al. presented an Fe(II) SCO
compound that produced a loss of both the completeness of the ST and hysteresis with increased scan rate.\textsuperscript{34}

In much rarer circumstances, altering the scan-rate may also result in different structural pathways for the spin transition. For example, Real et. al.\textsuperscript{35} presented a mononuclear structure that demonstrated two distinct hysteretic SCO profiles — differing in both $T_{1/2}$ values and hysteresis width — that were found to emerge at different scan rates. A polymeric example with similar behavior was reported by Zhang et. al.\textsuperscript{36} Additionally, Yamasaki and Ishida\textsuperscript{37} presented another mononuclear structure which was shown to have equivalent magnetic profiles on cooling, but heating at different scan rates allowed the differentiation of two distinct profiles. In these studies, differences in magnetic profiles were proposed to be the result of a phase transition, whereby two different LS phases shared the same HS phase. In this way the spin crossover profile was manipulated by a kinetically controlled structural phase change.

Herein, we report a rare example of dinuclear SCO Fe(II) compound that possesses kinetic control of both the forward and reverse spin crossover pathways from [HS-HS] to [LS-LS]. The [Fe$_2$L$_3$](BF$_4$)$_4$ helicate, herein denoted as 1, was formed using ligand L, which features a bridging 4,4’-oxydianiline group, linking two 4-imidazoleimine coordination environments, each of which also bears a terminal pyridyl group. The complex may act as a metalloligand towards further metal ions, similar to our previous work.\textsuperscript{38-43}
In thermal magnetic experiments of the desolvated sample, two distinct magnetic profiles were observed, coming about due to the conformation of the bulk solid to one of two phases, herein denoted a and b, each of which have distinct HS and LS states. That is, one magnetic profile is observed when the solid is in phase a, giving rise to HS-a $\leftrightarrow$ LS-a spin transitions, while distinct behavior arises from the solid conforming to phase b, providing HS-b $\leftrightarrow$ LS-b spin transitions. At the slow scan rate of 1 K min$^{-1}$, cooling enabled a phase transition from HS-b to HS-a, which underwent complete SCO to LS-a. At faster scan rates of 4, 7 and 10 K min$^{-1}$, no interconversion between the HS phases was able to occur, resulting in an incomplete ST from HS-b to LS-b with
2. Results and discussion:

Synthesis and Characterisation

The reaction of 4,4-oxydianiline and 1-(pyridine-4-yl)-1H-imidazole-4-carbaldehyde in ethanol produced the desired ligand L in 79% yield. Scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS), high resolution electrospray ionization mass spectrometry (HR-ESI...
MS) and $^1$H and $^{13}$C NMR confirmed the formation of the proposed L structure (Figure S1-S4). The HR-ESI mass spectrum demonstrated a major peak observed at $m/z$ at 533.1523 [L + Na]$^+$ with the appropriate isotope pattern also observed (Figure S3).

The addition of iron(II) tetrafluoroborate to a suspension of L in acetonitrile (MeCN) followed by a slow vapor diffusion of diethyl ether into the reaction mixture produced orange plate crystals of 1 suitable for analysis. The HR-ESI mass spectrum demonstrated major peaks at $m/z$ 410.5572 and 576.4459 which correspond to [Fe$_2$L$_3$]$^{4+}$ and [Fe$_2$L$_3$(BF$_4$)]$^{3+}$ respectively (Figure S5). The SEM-EDS spectrum confirmed the presence of C, N, F, O and Fe atoms. A mass change of -4.37% was calculated (Figure S7), consistent with the loss of 6 H$_2$O molecules per mole and in accordance with the CHN elemental analysis. SCXRD experiments confirmed the structure of 1 (Figure 1).

**Magnetic Measurements**

The magnetic susceptibility measurements including light-induced spin state trapping (LIESST) studies were undertaken on solvated and desolvated samples. Desolvation is desirable in applied materials as it is easily maintained, as opposed to an optimal degree of solvation. In the 1 K min$^{-1}$ cooling cycle, the onset of SCO occurred at 225 K, reaching $T_{1/2}$ at 169 K, and gradually reaching a local minimum of 0.70 cm$^3$ K mol$^{-1}$ at 71 K. Low temperature fluctuations were observed in the region below 80 K, with the cooling mode reaching an apex of 0.82 cm$^3$ K mol$^{-1}$ at 47 K, and the heating mode locally apexing at 45 K with 0.81 cm$^3$ K mol$^{-1}$, relaxing to a local minimum further along the heating mode. Additionally, the 1 K min$^{-1}$ plots display a small reverse SCO event in the higher temperature range with a hysteresis loop of 54 K width (Figure 2b).

When the experiment is performed at faster scan rates, features associated with the primary SCO event and reverse SCO are drastically modified. In the cooling cycles of 4, 7 and 10 K min$^{-1}$, the
reverse SCO is not observed, with the $\chi M T$ declines consistently with that of the 1 K min$^{-1}$ cooling scan, only until 303 K, where the slowest scan rate exhibited reverse ST (Figure 2b). The faster cooling scans continue to decrease in $\chi M T$, reaching $T_{SCO}$ at 252 K, which was retraced in each heating mode, and reaching approximately 50% conversion to the fully LS state, demonstrated by the gradually declining plateau region below 150 K. This may arise due to the occupation of the HS-LS state in all SCO molecules in the solid, or by conversion of half of the sample to LS-LS while the other half remains in HS-HS. In the 4 K min$^{-1}$ cooling mode, there is a small rise in magnetic susceptibility, featuring a small hump at 50 K (3.60 cm$^3$ K mol$^{-1}$). The 4 K min$^{-1}$ heating mode features a more distinguished hump, reaching a local maximum of 3.98 cm$^3$ K mol$^{-1}$ at 56 K before again declining and retracing the corresponding cooling mode from 170 K (Figure 2c). In the region where reverse SCO is observed for the 1 K min$^{-1}$ scans, the same feature is somewhat apparent, but obfuscated at 4 and 7 K min$^{-1}$, whereby $\chi M T$ rises away from the cooling mode plots above 270 K, reaching a peak of 7.02 cm$^3$ K mol$^{-1}$ at 325 K in the 4 K min$^{-1}$ heating mode and 6.97 cm$^3$ K mol$^{-1}$ at 322 K with 7 K min$^{-1}$ heating. In the region above 350 K, there is little differentiation between any of the scan rates.
Figure 2. a) Magnetic susceptibility curves for desolvated I at sweep rates of 1, 4, 7 and 10 K min\(^{-1}\). b) Close-up of magnetic susceptibility above 230 K. c) Close-up of low-temperature magnetic susceptibility for scan rates of 4, 7 and 10 K min\(^{-1}\).

The magnetic profiles of all scan rates align well only for the temperature region higher than the reverse SCO event. In the cooling modes, all spin transition curves track well with each other until the reverse ST event seen to begin at 302 K for the 1 K min\(^{-1}\). This reverse ST event is indicative of a phase change between two distinct [HS-HS] phases, which we denote HS-a and HS-b. In the slowest scan rate of 1 K min\(^{-1}\), the sample is able to fully convert from HS-b to HS-a, before the bulk of the sample converts from HS-a to the [LS-LS] (LS-a) configuration by the primary ST event. In the fastest cooling rate of 10 K min\(^{-1}\), no interconversion between HS-b to HS-a is able to take place, and the solid then converts via a different spin transition pathway from HS-b to the [HS-LS] state (LS-b). Furthermore, in the 4 and 7 K min\(^{-1}\) scans, the deviation between the heating and cooling modes upper region of the primary ST event may be due to a conversion from HS-b.
to HS-a in the temperature region in which this phase is stable, before the increase in temperature destabilized the HS-a phase and the bulk of the solid returns to the HS-b phase.

In addition, Mössbauer measurements revealed that both 1·6H₂O and desolvated 1 are fully LS at 78 K, and fully HS at 298 K (S2.1). The magnetic susceptibility measurements for the solvated sample showed that 1·6H₂O undergoes complete spin transition at scan rates 1 and 4 K min⁻¹ (S2.2). Further, LIESST studies demonstrated that 1 undergoes a photomagnetic response with exposure to red (800 nm) and green (532 nm) light (S2.3). Raman studies performed on 1·6H₂O with a green laser (514 nm) and controlled cooling of 1 K min⁻¹ revealed marker peaks of the HS and LS states, and increased laser power at 100 K resulted in spectral data consistent with the HS state (S3).

**Magneto-structural correlations - Kinetic control of the SCO mechanism:**

To unambiguously label the crystal structures herein, nomenclature is introduced which specifies the temperature and scan rate of each collection in the form [compound]@temperature/[scan rate], where the scan rates are referred to as relax, 1 K min⁻¹, 2 K min⁻¹, 4 K min⁻¹ and flash. For example, the structure of 1 collected at 150 K after cooling at 4 K min⁻¹ will be labeled 1@150/4. 1 crystallized in the triclinic space group P-1 with four BF₄⁻ counterions, four MeCN, 5.75 H₂O and one diethyl ether (Et₂O) molecule per helicate. A solvent mask was applied in all structures except 1@100/relax, which had no solvent accessible voids. The [Fe₂L₃]⁴⁺ helicate architecture consists of three ditopic imidazoleimine ligands coordinating to two Fe(II) centers, one at each end of the resulting complex. The coordination environment of each Fe(II) center is composed of three imidazole-imine donor groups, with six nitrogens coordinating overall so that both the imine and imidazole donors each adopt facial orientation to give a distorted octahedral arrangement. Distal
non-coordinating pyridyl groups provide H-bonding capacity towards the periphery of the structure. These groups, along with the benzene moieties, engender key intermolecular interactions between helicate molecules that dictate the interhelical spacing and steric interactions in the resulting lattice. The packing and resulting steric interactions in helical SCO molecules have been shown previously to have a marked effect on the nature of the ST.\textsuperscript{22,27} The three ligands used to form the helicate structure (A, B and C) were found to each be involved in a different set of intermolecular interactions (Figure 3). Ligand A forms a continuous 1D chain, stabilized by N\cdots HC hydrogen bonds between pyridyl N atoms and imidazole CH groups, as well as π-π interactions between terminal pyridyl groups of adjacent helicates. The terminal segment of ligand B, proximal to Fe1, also participates in a substantially offset π-π interaction with an equivalent terminal group of a neighboring helicate. On the other hand, the distal segment of ligand B near the Fe2 center does not participate in any π-π stacking, with the neighboring ring systems being heavily offset reflecting the adjacent positions of BF\textsubscript{4} counter ions. With respect to ligand C, the pyridyl group at the Fe1 end of the helicate lies close to the central O atom of ligand A on an adjacent helicate of opposite helicity (Table S3), while the pyridyl group at the Fe2 end makes no close intermolecular contacts to adjacent helicates. For single crystals of 1, SCO may occur at either helicate Fe center in the helicate (see below), but complete transition to the LS-LS state is inhibited at 100 K, unlike the situation occurring for 1\cdot6H\textsubscript{2}O (Supporting Information S2.2) and desolvated 1 (Figure 2). The inhibition may be influenced by the position of the Et\textsubscript{2}O molecule, which lies between the terminal pyridyl of ligand A at the Fe1 end and the terminal pyridyl of ligand B at the Fe2 end.
Figure 3. a) Crystal packing image of 1@250 shown along the cell direction vector (1, 0, 1). b) Crystal packing of 1@250 shown in the b-axis direction. HS Fe centers are orange, ligand A red, ligand B blue, ligand C green.
Two distinct structural pathways were observed for the relaxed and the flash scan rates when cooled to 100 K, while \textbf{1@100/4} showed a structure having undergone both pathways in equal part. At 250 K the average coordinate bond length (\(D\)) of 2.20 and 2.19 Å were found for Fe1 and Fe2, respectively; indicative of the HS state at both metal centers. The respective \(\Sigma\) values\(^5\) of 89.2 and 85.1° for Fe1 and Fe2 are also consistent with the assignment of the HS state. First, when cooled to 100 K allowing for relaxation (\textbf{1@100/relax}), the \(D\) and \(\Sigma\) values measured for Fe1 were 2.20 Å and 83.4°, while those for Fe2 were 2.00 Å and 58.3°. This is indicative of a HS-LS state at 100 K when cooled in this manner. Analysis of the helicate packing shows tighter packing of adjacent 1D chains along the crystallographic \(b\)-axis (Figure 4), concomitant with higher packing density. This is demonstrated by the markedly shorter \(b\)-axis and cell volume, which are 18.2 Å and 5744 Å\(^3\) in the 250 K structure, respectively, and drop to 16.7 Å and 5359 Å\(^3\) in \textbf{1@100/relax} (Table 1). Furthermore, the \textbf{1/100/relax} packing coefficient of 47.3% — compared to 44.4%, 46.2% and 46.05% for \textbf{1@250}, \textbf{1@100/4} and \textbf{1@100/flash} respectively — indicates a more tightly packed helical arrangement (S4). The Fe2 centers that undergo a spin transition are connected along the 1D chains described above by terminal \(\pi\)-\(\pi\) and N\(^-\)HC contacts for ligand \textbf{A}, as well as close packing of the pyridyl groups of ligand \textbf{B} at the Fe2 end of the helicate, as shown in Figure 4.

\textbf{Table 1.} Selected parameters of \(b\)-axis, \(V\), average Fe-N distance (\(D\)), \(\Sigma\) and crystal packing coefficient of \textbf{1}.

<table>
<thead>
<tr>
<th>Structure (1@...)</th>
<th>(b) (Å)</th>
<th>Volume (Å(^3))</th>
<th>Packing (%)</th>
<th>(D) (Å)</th>
<th>(\Sigma) (°)</th>
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<tr>
<td>100/relax</td>
<td>16.73</td>
<td>5359</td>
<td>47.30</td>
<td>Fe1: 2.20, Fe2: 2.00</td>
<td>Fe1: 83.36, Fe2: 58.34</td>
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<tr>
<td></td>
<td>100/flash</td>
<td></td>
<td></td>
<td>Fe1: 2.16, Fe2: 2.08</td>
<td>Fe1: 78.84, Fe2: 70.73</td>
</tr>
<tr>
<td>----------------</td>
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</tr>
<tr>
<td></td>
<td>250</td>
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<td>5744</td>
<td>44.08</td>
<td>Fe1: 2.20, Fe2: 2.20</td>
</tr>
<tr>
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<td>5533</td>
<td>45.64</td>
<td>Fe1: 2.13, Fe2: 2.09</td>
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<tr>
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<td>5586</td>
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<td>17.98</td>
<td>5643</td>
<td>45.05</td>
<td>Fe1: 2.19, Fe2: 2.18</td>
</tr>
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</table>

Flash conditions:

- **Fe1**: 2.16, 78.84
- **Fe2**: 2.08, 70.73
- **Fe1**: 2.20, 89.10
- **Fe2**: 2.20, 84.91
- **Fe1**: 2.13, 79.40
- **Fe2**: 2.09, 71.22
- **Fe1**: 2.16, 83.25
- **Fe2**: 2.11, 74.79
- **Fe1**: 2.19, 87.10
- **Fe2**: 2.19, 84.22
- **Fe1**: 2.13, 76.29
- **Fe2**: 2.08, 71.05
- **Fe1**: 2.15, 78.56
- **Fe2**: 2.10, 73.72
- **Fe1**: 2.19, 86.29
- **Fe2**: 2.18, 83.48
- **Fe1**: 2.18, 81.65
- **Fe2**: 2.01, 61.97
- **Fe1*: 2.14, 77.12
- **Fe2*: 2.15
- **Fe1**: 2.19, 81.21
- **Fe2**: 2.01, 63.54
- **Fe1*: 2.17, 83.94
- **Fe2*: 2.16
- **Fe1**: 81.21
- **Fe2**: 63.54
- **Fe1*: 82.04
Figure 4. Crystal Structures of 1@100/relax (blue), with HS Fe1 (orange) and LS Fe2 (purple) overlaid with 1@250 (red) with both Fe centers in HS state (orange). Molecules pack closer together along the b-axis in 1@100/relax than 1@250.

On the other hand, when the sample was flash cooled to 100 K (1@100/flash), the observed values of D and Σ for Fe1 were 2.16 Å and 78.8°, and 2.08 Å and 70.7° for Fe2. This may be interpreted as a superposition of HS and LS Fe centers at both crystallographically distinct Fe centers, and will be referred to as the MS-MS state from here on (where MS refers to a mixed population of HS and LS states). This suggests that, in contrast to the 1@100/relax structure above, flash cooling promotes the transition of the Fe1 or Fe2 centers of different helicates, with around half of the helicates having undergone a transition to the HS-LS, and a small population transitioning to the LS-HS state at 100 K, rather than solely selective transition of Fe2 throughout the material. Interestingly, the b-axis (17.7 Å) and cell volume (5495 Å³) are larger than that of 1@100/relax which, along with a packing coefficient of 46.0%, suggests more space is present between adjacent helicates (Figure 5).
Figure 5. Overlay of 1@100/flash (blue) with MS Fe centers (gray), and 1@250 (red) with HS Fe centers (orange). Contraction along the $b$-axis in 1@100/flash is minor relative to that of the 1@100/relax structure.

Finally, cooling at 4 K min$^{-1}$ caused symmetry breaking in the lattice, whereby $P-1$ symmetry persisted with a doubled $c$ axis, observed between 150 and 100 K, leading to an additional helicate being resolved per asymmetric unit. The same analysis of each distinct helicate in 1@100/4 showed that one helicate adopted the HS-LS state (Fe1, $D = 2.18$ Å, $\Sigma = 81.6^\circ$; Fe2, $D = 2.01$ Å, $\Sigma = 62.0^\circ$) similar to 1@100/relax, while the additional symmetrically inequivalent helicate was found to be MS-MS (Fe1, $D = 2.14$ Å, $\Sigma = 77.2^\circ$; Fe2, $D = 2.15$ Å, $\Sigma = 81.7^\circ$) similar to the situation in 1@100/flash. That is, the 1@100/4 showed a pathway combining that of the relaxed and flash cooled samples, where both pathways to SCO are observed simultaneously. The HS-LS helicates pack in 2D sheets parallel to the $ab$ plane, interspaced with parallel 2D sheets of MS-MS helicates (Figure 6).
Figure 6. a) Crystal packing image of 1@100/4 shown along the cell direction vector (2, 0, 1).
b) Crystal packing of 1@100/4 shown in the b-axis direction. Helicates (HS-LS) are shown with
blue ligands, HS Fe1 and LS Fe2 centers in these helicates are orange and purple, respectively.
Helicates trapped in MS-MS are shown in red with gray Fe centers.
The supramolecular arrangement of the helicates for different cooling rates provides an interesting comparison. In this regard, the packing of adjacent 1D chains along the $b$-axis of the 1@100/relax is distinct from the other scan rates, with a markedly shorter $b$-axis and cell volume, which are 18.2 Å and 5744 Å$^3$, respectively in 1@250, but drop to 16.7 Å and 5359 Å$^3$ in 1@100/relax (Figure 7). On the other hand, the flash-cooled material (1@100/flash) gave values for $b$ and $V$ of 17.7 Å and 5495 Å$^3$, and the 100 K structures at cooling rates of 1, 2 and 4 K min$^{-1}$ showed similarly expanded lattices (compared to 1@100/relax). As described above, the $b$-axis direction corresponds to important intermolecular interactions along this axis which link Fe1 centers along the 1D chain formed by ligand A linkages, as well as close packing of ligand B terminal groups, which is tightest in 1@100/relax and looser in 1@100/flash. These results suggest that there may be some slow rearrangement of the structure that prohibits 1D chains from approaching each other at faster scan rates.
The helical packing, intermolecular interactions and changes in ligand conformation were compared for the above three pathways as a function of temperature. This was undertaken in an attempt to pinpoint any structural features that may be responsible for promoting the different pathways for SCO observed in structures cooled at different scan rates. First, in order to attempt to quantify the steric effects which may participate in the spin transition dynamics, the molecular volume of the helicates and the crystal packing coefficients (the percentage value of crystal volume occupied by the helical structures) were calculated (Figure 8). At 250 K, a packing coefficient of 44.1% was determined, while 1@100/relax was found to have a value of 47.3% and 1@100/4 and 1@100/flash presented values of 46.2% and 46.0% respectively. This represents a significant difference between the HS-LS structure obtained after slow relaxation and both the intermediate and flash-cooled structures. The molecular volume of the helicate measured at 250 K before cooling was 1271.6 Å³, which reduced rather insignificantly — to 1267.8 Å³ in 1@100/relax for example — a difference of -0.3%. This suggests that the higher crystal packing coefficient of the HS-LS structure is related to tighter packing of the helicate molecules in the lattice, as opposed to changes in the molecular volume of individual helicates.
Reorientations of the coordination environment upon spin transition in either Fe center of the helicate induce different reconfigurations within each ligand. These reorientations impose varying degrees of both intramolecular strain within the helicate and steric strain on adjacent helicates, which, in turn, may allow or inhibit the different pathways of spin transition. The steric effects influencing the crystal lattice may be related to the dynamics of molecular reorientation of individual helicate molecules. Reconfigurations of ligand molecules in neighboring helices are often seen to have a drastic effect on the cooperative or anticooperative effects observed in a transitioning solid. As such, several parameters were calculated from the crystal structural data to describe the behavior of each ligand throughout the respective variable temperature (VT) experiments. As the coordinating sections of the ligand are less able to reorient, the terminal pyridyl and internal benzene groups are the moieties that are most likely to provide the greatest reorientation to relieve the intramolecular strain required for the structure to undergo SCO.

The helicate can be divided into components, with the orientation of each component used to provide insight into the overall conformation achieved by different parts of each ligand. The linker moieties were modeled using linker torsion (S5.1), which indicates the degree of twist of each of the benzene rings, relative to a reference plane describing the linker segment overall. The angle between the intermetallic axis and the axis defined by the two coordinating N atoms in each chelate ring was taken, and this was further deconstructed into pitch and yaw angles to more specifically indicate the direction of the reorientations in the chelate groups (S5.2-S5.3). By a similar methodology, angles between the intermetallic axis and the secondary bond axes were calculated. Here, the secondary bond axis refers to the interval between N atoms in terminal pyridines, and
the C atoms opposite in the ring (N1 - C3 or N8 - C28), which reflects the direction in which a coordinate bond from the secondary donor sites may form, similar to methods employed in our previous work (S5.2).43 This allows for quantification of the degree of spreading of the terminal pyridyl groups. Since the coordinating imidazoleimine and the terminal pyridine are both rigid groups, the spread of the secondary bond axes is closely linked to the orientation of the internal chelating section of the ligand. All of these parameters are defined such that they refer to an internal structural feature for consistent comparison; either the intermetallic axis, or in the case of linker ring torsions, a reference plane describing the linker orientation.

Following analysis of the structural measurements (Table 2) we are able to suggest a mechanism by which slow cooling allows the lattice of 1 to undergo a transition to [HS-LS] in the full population of helicate molecules in the solid, while faster cooling inhibits this transformation. Several ligand reconformations are demonstrated in the 1@100/relax structure, which differ significantly from the 250 K structure (Table 2). One key feature is that the linker segment of ligand A repositions with a transition of Fe2 to LS. This occurs due to the rearrangement of the chelate group of A at Fe2, which changes the pitch to negative, and causes the benzene rings in A to exchange torsion values (Table 2). This, along with motion towards the terminal C pyridyl at Fe1 of an adjacent helicate, may induce a transition of the adjacent Fe1 to LS, due to the semi-rigid connection between the terminal pyridine and chelating imidazoleimine. This is demonstrated in the kinetically trapped 1@100/4 structure through the low Fe1 octahedral distortion parameters. Additionally, the rearrangement of the C imidazole group skews the orientation of the CH group associated with the terminal N···HC hydrogen bond, weakening the contact between Fe1 centers along the 1D chains, which may contribute to the loss of inversion symmetry across these sites (S6). Further reorientation in ligand groups puts into effect an overall supramolecular
rearrangement. Transitioning the bulk of helicates in the solid to the [HS-LS] state instigates a significant decrease in B yaw at both ends of the helicate which allows terminal pyridyl groups of B to draw inwards and lower the secondary bond axis values of B. This in turn leads to the compression of 1D chains towards each other, as shown above.

Table 2. Selected geometric parameters describing the orientations of helicate components (See S5). 1 K min\(^{-1}\) values are shown to compare with those obtained at the extreme ends of the temperature range.

<table>
<thead>
<tr>
<th>Structure (1@...)</th>
<th>(^*)A torsion(^a) (°)</th>
<th>A Pitch(^b) (°)</th>
<th>A Yaw(^c) (°)</th>
<th>B Yaw(^c) (°)</th>
<th>(^*)A Secondary bond axis(^d) (°)</th>
<th>(^*)B Secondary bond axis(^d) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/relax</td>
<td>Fe1: 61.20, Fe2: 32.83</td>
<td>Fe1: 6.99, Fe2: -2.87</td>
<td>Fe1: 33.30, Fe2: 33.12</td>
<td>Fe1: 34.17, Fe2: 37.93</td>
<td>Fe1: 43.95, Fe2: 44.15</td>
<td>Fe1: 32.08, Fe2: 46.12</td>
</tr>
<tr>
<td>100/flash</td>
<td>Fe1: 45.83, Fe2: 50.53</td>
<td>Fe1: 3.34, Fe2: 1.26</td>
<td>Fe1: 32.55, Fe2: 34.42</td>
<td>Fe1: 33.08, Fe2: 35.39</td>
<td>Fe1: 42.52, Fe2: 51.93</td>
<td>Fe1: 42.08, Fe2: 48.24</td>
</tr>
<tr>
<td>100/1</td>
<td>Fe1: 40.88, Fe2: 56.02</td>
<td>Fe1: 2.29, Fe2: 1.08</td>
<td>Fe1: 32.81, Fe2: 35.65</td>
<td>Fe1: 33.45, Fe2: 35.34</td>
<td>Fe1: 42.78, Fe2: 51.11</td>
<td>Fe1: 43.15, Fe2: 47.33</td>
</tr>
<tr>
<td>150/1</td>
<td>Fe1: 35.53, Fe2: 56.57</td>
<td>Fe1: 1.95, Fe2: 1.67</td>
<td>Fe1: 32.24, Fe2: 35.01</td>
<td>Fe1: 33.39, Fe2: 34.96</td>
<td>Fe1: 42.50, Fe2: 51.52</td>
<td>Fe1: 43.24, Fe2: 47.63</td>
</tr>
<tr>
<td>200/1</td>
<td>Fe1: 31.71, Fe2: 59.99</td>
<td>Fe1: 2.13, Fe2: 2.54</td>
<td>Fe1: 31.55, Fe2: 35.46</td>
<td>Fe1: 33.25, Fe2: 34.08</td>
<td>Fe1: 43.23, Fe2: 53.78</td>
<td>Fe1: 43.49, Fe2: 52.66</td>
</tr>
<tr>
<td>250</td>
<td>Fe1: 31.07, Fe2: 59.95</td>
<td>Fe1: 2.28, Fe2: 2.56</td>
<td>Fe1: 31.71, Fe2: 35.60</td>
<td>Fe1: 33.39, Fe2: 33.99</td>
<td>Fe1: 43.46, Fe2: 54.28</td>
<td>Fe1: 43.59, Fe2: 52.36</td>
</tr>
</tbody>
</table>

\(^a\) The linker torsion angle measured from planes of each benzene group linked to a reference plane, identifying the degree of twist the linker region adopts at each end of the helicate.

\(^b\) Pitch specifies the back and forth rocking orientation of the chelate groups in relation to the intermetallic axis.

\(^c\) Yaw specifies the side-to-side twisting orientation of the chelate rings relative to the intermetallic axis.
d The secondary bonding axis measures the orientation of the terminal pyridine groups with respect to the intermetallic axis.

* In structures exhibiting orientational disorder, the parameter value was calculated for each part, and those values were scaled by the occupancy of the respective part and summed to provide the stated value.

The trends in unit cell shrinkage and contraction along the b-axis were confirmed in 1·6H₂O and desolvated 1 using VT-PXRD with controlled ramping rates of 1 and 4 K min⁻¹ (Figure 9a and b). In 1·6H₂O, the higher values of b and V are consistent with the population of the lattice in the fully HS state. Cooling modes of both 1 and 4 K min⁻¹ showed a marked decrease in b and V upon cooling to 150 K, with b reaching 16.4 Å at both scan rates, and V reaching 5186 Å³ and 5224 Å³ with 1 and 4 K min⁻¹ cooling, respectively. As cooling cycles progress down to 40 K, the cell continues to shrink in terms of b and V, with b reaching a minimum of 16.3 Å and V reaching a minimum of 5056 Å³ with 1 K min⁻¹ cooling, versus 5043 Å³ with 4 K min⁻¹ cooling. In the heating mode of 1 K min⁻¹, the b-axis length tracked with that observed in the cooling mode, with some deviations while more significant deviations were observed in the V plot. Heating at 4 K min⁻¹ provided an interesting result at 60 K, where the cell was seen to expand, with b and V measured at 16.6 Å and 5342 Å³, respectively. This is consistent with the magnetic susceptibility curve of 1·6H₂O measured at 4 K min⁻¹, which displayed a peak in \( \chi_M T \) of 1.04 cm³ K mol⁻¹ at 59 K (Figure S9). The nature of these low temperature dynamics is difficult to qualify, but they may arise due to interconversion between LS-a and LS-b phases at low temperatures, facilitated by an intermediate spin transition, which is also suggested by magnetic susceptibility measurements (Supporting information, S2.2). As the heating cycle continued at 4 K min⁻¹, b and V continued to grow, reaching HS values at 200 K and above.
Figure 9. Selected lattice parameters for 1 from VT-PXRD experiments in the heating and cooling modes corresponding to the scan rates 1 and 4 K min$^{-1}$. Sweeps were performed in the order: 1 K min$^{-1}$ cooling (▽), 1 K min$^{-1}$ heating (▲), 4 K min$^{-1}$ cooling (▽), 4 K min$^{-1}$ heating (▲). a) Plot of 1.6H$_2$O $b$-axis length. b) Plot of 1.6H$_2$O cell volume $V$. c) Plot of desolvated 1 $b$-axis length. d) Plot of desolvated 1 cell volume $V$.

More distinct variation between the two chosen scan rates was observed in the PXRD experiments of desolvated 1 (Figure 9c and d). In the 1 K min$^{-1}$ cooling cycle, the 298 K structure provided $b$ and $V$ values of 16.8 Å and 5237 Å$^3$, respectively, indicative of the bulk desolvated sample being fully HS. These values remained fairly constant, until they began to drop sharply at 190 K and below. The cell continued to shrink to a minimum $b$-axis length of 16.3 Å and a volume
of 4988 Å³ at 70 K, indicating that all or most of the sample was in the [LS-LS] state. The heating mode of 1 K min⁻¹ varied slightly from the cooling mode, but overall reproduced the same general plot shape, reaching \(b\) and \(V\) values of 16.8 Å and 5246 Å³ at 300 K. The 4 K min⁻¹ cooling mode, which was performed immediately after the 1 K min⁻¹ heating mode, showed an increase in cell size at 250 K, with the \(b\)-axis reaching 16.9 Å and \(V\) reaching 5265 Å. The onset of cell shrinkage occurred at higher temperatures using the faster scan rate, reflected by the cell volume of 5165 Å³ at 200 K — contrasting with 5198 Å³ measured at 190 K using the 1 K min⁻¹ cooling rate. The cell parameters continued to shrink along the 4 K min⁻¹ cooling mode, reaching minimum values for \(b\) and \(V\) of 16.5 Å and 5065 Å³ at 50 K, with the heating mode approximating the same trend in the reverse direction. The low-temperature values found using the faster scan rate of 4 K min⁻¹ are larger than those found when cooling at 1 K min⁻¹, and support the finding that cooling desolvated 1 at faster scan rates causes the lattice to transition with only about 50% completion (Figure 2). Additionally, the trends in unit cell parameters \(b\) and \(V\) which were established by SCXRD experiments were reproduced by PXRD, suggesting that the spin transition in the bulk material is governed by the same or a similar mechanism to that observed in single crystals and the above magnetic susceptibility.

3. Conclusion

In summary, we present a new Fe(II) dinuclear helicate 1 which undergoes SCO that is incomplete in single crystals of 1 but complete in 1·6H₂O. Desolvated 1 may achieve complete SCO at slow scan rates (1 K min⁻¹) and incomplete SCO at faster scan rates (4, 7 and 10 K min⁻¹). The manipulation of the SCO profile by the temperature scan rate is shown to be associated with occupation of structurally distinct phases in the solid, denoted \(a\) and \(b\). Both phases have their own corresponding HS and LS states, allowing the material to conform to one of four states: HS-\(a\), LS-
a, HS-b and LS-b. This allows for kinetic control of the SCO profile exhibited by the solid, as different scan rates can alter the resultant SCO behavior. Interconversion between distinct HS or LS phases was demonstrated by the deviation that was observed between the cooling and heating modes in the magnetic susceptibility study. VT-SCXRD studies, corroborated with VT-PXRD, showed that the full relaxation pathway to LS-a was facilitated by contraction along the b-axis, while this contraction was inhibited by fast cooling, causing a transition to LS-b.

Our study demonstrates the degree of multifunctionality which can be manifested in SCO materials, facilitated by the supramolecular environment. Steric influences between SCO molecules can be used to convert between distinct structural phases, and when controlled by scan rate, diverse magnetic behavior can occur. This work may forge avenues by which the control of dinuclear [HS-LS] ↔ [LS-HS] equilibria can be investigated and manipulated in the solid state, potentially aiding the design of next-generation signaling and logic materials.

4. Materials and Methods

4.1. Synthetic Procedures

1-(Pyridine-4-yl)-1H-imidazole-4-carbaldehyde was synthesized from the procedure that was previously reported.43

Synthesis of ligand L: 4,4’-oxydianiline (1140 mg, 5.7 mmol, 1 equiv) was dissolved in 30 mL of ethanol (EtOH) and added dropwise to 1-(pyridine-4-yl)-1H-imidazole-4-carbaldehyde (2027 mg, 10.6 mmol, 2 equiv) in 70 mL of EtOH. The reaction mixture was heated at reflux with stirring for 4 h, after which pale white precipitate formed, and was collected by filtration. The product was washed with cold EtOH to give L as a white powder. Yield: 2301 mg, 79.2%. 1H NMR (DMSO-
d6, 400 MHz) δ (ppm); 8.725 (s, 1H), 8.709 (d, 2H), 8.629 (s, 1H), 8.530 (s, 1H), 7.901 (d, 2H), 7.329 (d, 2H), 7.078 (d, 2H); 13C NMR (DMSO-d6, 100 MHz) δ (ppm); 155.47, 153.85, 151.93, 147.43, 143.06, 142.15, 137.35, 122.98, 119.79, 119.63, 114.53; HR-ESI MS (positive ion detection, EtOH): m/z (calcd, exp) = [L+H]+; 511.1195, 511.2010; [L+Na]+; 533.1815, 533.1523.

Synthesis of 1·6H2O: Iron(II) tetrafluoroborate hexahydrate (747 mg, 2.2 mmol) was dissolved in 75 mL of MeCN and added dropwise in a 2:3 ratio to a suspension of L (1754 mg, 3.4 mmol) in 125 mL of MeCN. The reaction mixture was heated at reflux for 1 h with stirring, resulting in a clear orange solution. After filtration, slow vapor diffusion of diethyl ether into the reaction mixture over two weeks led to the formation of orange plate crystals. These were collected by gravity filtration and air dried before analysis. Yield: 554 mg, 23.6%; Elemental analysis (%) (calcd, exp) for C90H66N24O3Fe2B4F16.6H2O): C (51.48, 51.51), H (3.75, 4.08), N (16.02, 16.16); HR-ESI MS (positive ion detection, MeCN): m/z (calcd, exp) = [Fe2L3(BF4)2]4+, 410.6124, 410.5679; [Fe2L3(BF4)3]3+; 576.4847, 576.4833; [Fe2L3]2+; 906.2300, 906.1909.

2.2. Physical Measurements

High resolution ESI-MS experiments were performed using a Waters Xevo QToF mass spectrometer (Waters, Milford, MA, USA), operating in positive ion mode. The ligand was dissolved in EtOH and the metal complex was dissolved in MeCN. The samples were infused directly into the ESI source via a syringe. Nuclear magnetic resonance (NMR) data was acquired at the Biomedical Magnetic Resonance Facility (Western Sydney University) using a Bruker Avance 400 MHz NMR spectrometer. CHN analysis was carried out at Kumamoto University, Japan. Simultaneous thermal analysis (STA) was conducted on a NETZSCH STA449 Jupiter instrument using aluminium crucible. STA measurements were acquired using Argon for both the
purge and protective gases; the temperature range of 303-863 K was cycled at a rate of 10 K per
minute.

Raman spectroscopic measurements were carried out with a Renishaw inVia Qontor Raman
microscope, operating with a 514 nm diode laser. The polycrystalline powder sample \( \text{I} \cdot 6\text{H}_2\text{O} \) was
deposited directly into a low-temperature stage, and controlled cooling at 1 K min\(^{-1} \) was used to
sequentially ramp from 301 K to each temperature in the series. 1% laser power (0.89 mW) was
used to acquire most spectra, and 10% power (8.9 mW) was used to cause a LIESST excitation at
100 K.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) spot analysis
were acquired using a Phenom XL in low vacuum with a chamber pressure of 10 Pa and an
accelerating voltage of 15 kV. All samples were mounted on an aluminium stub with double-sided
conductive carbon tape and then imaged uncoated. Spot EDS analysis was carried out using
Phenom EDS software with a silicon drift detector (SDD).

To collect \( \text{I}@100/\text{relax} \), a suitable single crystal of \( \text{I} \) was selected under a polarizing microscope
(Leica M165Z) and mounted on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip
with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker D8
Quest Single Crystal diffractometer with Photon II detector using a \( \mu \text{S} \) 3.0 Microfocus source
with Mo-K\( \alpha \) radiation (\( \lambda = 0.710723 \) Å). The single crystal, mounted on the goniometer using cryo
loops for intensity measurements, was coated with paraffin oil and quickly transferred to the cold
stream using an Oxford Cryo stream 800 attachment. The crystal was mounted at 250 K for
screening, and after 1 h was cooled at 2 K min\(^{-1} \) to 100 K for collection of the full dataset.
Symmetry related absorption correction using the program SADABS\(^{45} \) were applied and the data
were corrected for Lorentz and polarization effects using Bruker APEX 3 software.\textsuperscript{46} The structure was solved by ShelXT using intrinsic phasing\textsuperscript{47} and full matrix least-square refinements were carried out using ShelXL\textsuperscript{48,49} and olex2 graphical user interface.\textsuperscript{50}

All other single crystal data was collected employing the MX1 beamline at the Australian Synchrotron using silicon double crystal monochromated radiation ($\lambda = 0.71073$ Å).\textsuperscript{51} For 1@100/flash, a crystal of 1 was mounted at 100 K and scanned after instrument setup. For each scan rate-dependent experiment a crystal of 1 was selected and mounted at 250 K. After collecting a full dataset, the temperature was reduced at the specified scan rate to the next specified temperature, followed by data collection, down to the minimum temperature of 100 K. For each structure, two collections were taken, each consisting of a sweep through $\theta$ of 360°, but differing by the setting of $\kappa$ to 0 or 180°. XDS software\textsuperscript{52} was used for data integration, processing, scaling and the merging of raw datasets. The empirical absorption correction was then applied at the synchrotron using SADABS.\textsuperscript{45} The structure was solved with ShelXT\textsuperscript{47} using the intrinsic phasing method and the full-matrix least-squares refinements were carried out using a suite of SHELX programs\textsuperscript{48,49} via the Olex2 interface.\textsuperscript{50} Refinement details can be found in the ESI (S7). The crystallographic data in CIF format has been deposited at the Cambridge Crystallographic Data Centre with CCDC nos. ____________. It is available free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

PXRD measurements were carried out in Empyrean X-Ray Diffractometer (Supplier: PANalytical BV) fitted with a Copper tube ($\lambda = 1.5406$ Å) and a PIXcel detector. In order to enable data collection at low temperature and at controlled temperature variation rate, the sample stage was configured with Oxford PheniX cryostat. Raw data collection was performed over the 2θ range
5° to 40° with step size 0.013° and 995s measurement time per step. A full pattern Pawley fit using HighScore Plus software (Supplier: PANalytical BV) was performed on the PXRD scans using the cif obtained from SCXRD to extract unit cell parameters at each temperature. More details available in Supplementary Information section.

Magnetic susceptibility measurements were conducted using a Quantum Design SQUID magnetometer calibrated against a standard palladium sample. The solvated sample was collected from diffusion vials before air drying. Magnetic susceptibility measurements were collected at scan rates of 1 and 4 K min⁻¹ in the heating and cooling modes. Desolvation was achieved by holding samples at an isotherm of 400 K for 30 minutes, and cooling and heating runs were collected for this desolvated sample at scan rates of 1, 4, 7 and 10 K min⁻¹. LIESST studies were conducted on solvated and desolvated samples under red (800 nm) and green (532 nm) laser irradiation. For each measurement, the sample was irradiated with the selected light source at 5 K until saturation of the magnetic signal, after which the sample was heated at 1 K min⁻¹. Measurements were taken under an applied field of 0.5 T at a scan rate of 1, 4, 7 and 10 K min⁻¹.

Mössbauer experiments were performed using a Wissel MVT-1000 Mössbauer spectrometer with a ⁵⁷Co/Rh source in a constant-acceleration transmission spectrometer (Topologic Systems) equipped with a closed-cycle helium refrigerator cryostat (Iwatani Co., Ltd.). All isomer shifts are given relative to α-Fe at room temperature.

ASSOCIATED CONTENT
The Supporting Information is available free of charge at __________

CIF files (.cif)

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NOTES

There is no conflict of interest to report.

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