# Dalton Transactions



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**Cite this:** *Dalton Trans.*, 2021, **50**, 1434

Received 23rd November 2020, Accepted 4th January 2021 DOI: 10.1039/d0dt04007j

rsc.li/dalton

### Introduction

The conversion between low-spin diamagnetic  $(t_{2g}^{6}e_{g}^{0}; LS)$  and high-spin paramagnetic  $(t_{2g}^{4}e_{g}^{2}; HS)$  states in Fe<sup>II</sup>-based systems has attracted interest over a wide range of scientific fields for fundamental and application-driven considerations.<sup>1–3</sup> Such materials display an assortment of thermal behaviours encompassing gradual transitions, firstorder switching with hysteretic effects and multi-stepped profiles. Central to communication in spin transitions are elastic interactions due to structural changes between HS and LS phases. First-order hysteretic transitions can be described by elastic models<sup>4–7</sup> or Ising-like models,<sup>8</sup> which can be shown to

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# Dual-supramolecular contacts induce extreme Hofmann framework distortion and multi-stepped spin-crossover<sup>†</sup>

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An extended nitro-functionalised 1,2,4-triazole ligand has been used to induce considerable lattice distortion in a 2-D Hofmann framework material *via* competing supramolecular interactions. Single crystal X-ray diffraction analyses on  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3] \cdot 6H_2O$  (N-cintrz: (*E*)-3-(2-nitrophenyl)acrylaldehyde) reveal a substantial deviation from a regular Hofmann structure, in particular as the intra- and interlayer contacts are dominated by hydrogen-bonding interactions rather than the typical  $\pi$ -stacking arrays. Also, the 2-D Hofmann layers show an assortment of ligand conformations and local Fe<sup>II</sup> coordination environments driven by the optimisation of competing supramolecular contacts. Temperature-dependent magnetic susceptibility measurements reveal a two-step spin crossover (SCO) transition. Variable temperature structural analyses show that the two crystallographically distinct Fe<sup>II</sup> centres, which are arranged in stripes (2 : 1 ratio) within each Hofmann layer, undergo a cooperative HS  $\leftrightarrow$  HS/LS  $\leftrightarrow$  LS (HS = high spin, LS = low spin) transition without periodic spin-state ordering. The mismatch between crystallographic (2 : 1) and spin-state (1 : 1) periodicity at the HS : LS step provides key insight into the competition (frustration) between elastic interactions and crystallographically driven order.

be equivalent.<sup>9</sup> Comprehensively describing multi-stepped transitions is a substantial challenge<sup>10,11</sup> as it must encompass both ferro- and anti-ferro-elastic interactions. In complex material structures not all interactions can be simultaneously minimised – this results in elastic frustration,<sup>10</sup> and multistep transitions.<sup>10,11</sup> Further, it has been shown that strong through-bond (covalent) interactions lead to anti-ferro-elastic interactions, whereas weak through-space interactions often result in ferro-elastic interactions.<sup>11,12</sup>

To this end, many studies utilise the intrinsic long-range connectivity of coordination networks to both enhance and disrupt spin-state conversion communication.13-16 Recent reports have shown that Hofmann-type frameworks provide an excellent platform to design, synthesise and develop a deeper understanding of elastic frustration.11,17-28 Since these frameworks are constructed by a modular (metal + ligand) approach, supramolecular interaction networks which act to induce and stabilise elastic frustration<sup>10</sup> can be readily included via ligand functionalisation. Furthermore, as these systems often encapsulate guest molecules in the interlayer spacing, antagonistic host-guest interactions can also be utilised to subtly modify the magnitude of directionality of frustration effects. The 2-D Hofmann framework  $[Fe(bztrz)_2Pd(CN)_4]$ ·guest (bztrz = (E)-1phenyl-N-(1,2,4-triazol-4-yl)-methanimine)<sup>21</sup> exemplifies this approach, whereby utilising a functionalised 1,2,4-triazole



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<sup>†</sup>Electronic supplementary information (ESI) available: Additional structural and magnetic data. CCDC 2045470–2045472. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt04007j



Fig. 1 (a) (E)-3-(2-Nitrophenyl) acrylaldehyde (N-cintrz) and (b) (E)-2-(((4H-1,2,4-triazol-4-yl)imino)methyl)phenol (saltrz). The secondary hydrogen bonding functional groups are coloured red.

ligand results in Hofmann layer distortion and the low temperature stabilisation of a mixed spin-state species (HS:LS). Guest variation in this framework allows a range of multistepped transitions to emerge (half-, two- and three-stepped) through changes to supramolecular interactions and steric effects. This concept opens a huge number of possibilities to produce and develop a deeper understanding the origins of multi-stepped transitions.

Judicious ligand functionalisation has been shown to be a key tool in tailoring multi-stepped SCO behaviour. In particular, ligands with hydrogen bonding and/or aromatic interaction capability have been extensively utilised to drive a competition between long-range ferro- and anti-ferro-elastic interactions. While there are a range of conceivable synthetic methods available to induce such features, we and others have been focused on utilising the unique metal ion binding mode of 1,2,4-triazole ligands (Fig. 1) in Hofmann frameworks, and facile functionalisation of such ligands as an effective approach to generate competition between elastic interactions.17-22,26,28 Here, alongside utilising a functionalised 1,2,4-triazole ligand to construct a 2-D Hofmann framework, we have appended a nitro-group to the periphery of the ligand to supply supramolecular interaction capacity beyond the established 1,2,4-triazole interactions (Fig. 1a). This approach was applied to the related 2-D Hofmann framework  $[Fe_3(saltrz)_6(Pd(CN)_4)_3]$ ·8H<sub>2</sub>O (Fig. 1b),<sup>22</sup> where by ligand the hydroxyl-function groups induced a wide array of competing host-host and host-guest interactions resulting in substantial structural distortion and a four-stepped spin-state transition pathway. Therefore, here our overall aim is to examine the distortive influence of a combination of 1,2,4-triazole and nitrogroup supramolecular contacts on the structure and SCO properties in this new 2-D Hofmann framework material.

### **Results and discussion**

#### Synthesis and characterisation

The N-cintrz ligand (Fig. 1a) is readily prepared by a condensation reaction between 2-nitrocinnamaldehyde and 4-amino4*H*-1,2,4-triazole. The 2-D Hofmann framework [Fe(N-cintrz)<sub>2</sub>Pd(CN)<sub>4</sub>]·3H<sub>2</sub>O was formed as single crystals by slow diffusion of Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, N-cintrz ligand and K<sub>2</sub>[Pd(CN)<sub>4</sub>] in ethanol and water (50:50). Red plate-shaped single crystals were produced over a period of 8 weeks. IR spectroscopy shows a strong CN stretching band (2113 cm<sup>-1</sup>) from the Pd(CN)<sub>4</sub> ligand and an azomethine (C=N) stretching band from the N-cintrz ligand. The bulk phase purity was confirmed by powder X-ray diffraction (Fig. S9†) and elemental (CHN) analysis. Thermogravimetric analysis (RT-600 °C; 1 °C min<sup>-1</sup>) shows a mass loss of *ca*. 2.25% up to 180 °C associated with the loss of 3 water molecules per Fe<sup>II</sup> site; above 180 °C framework decomposition occurs (Fig. S1†).

#### **Overall structure description**

The single crystal structure shows the material is composed of two crystallographic distinct  $\text{Fe}^{II}$  sites in a  $\frac{1}{2}$ **Fe1**:1 **Fe2** ratio (due to **Fe1** residing on an inversion centre), one and a half  $[\text{Pd}(\text{CN})_4]^{2-}$  groups, three N-cintrz ligands (L1, L2 and L3) and three water molecules (2 × A type with hydrogen bonds and 1 × B type with van der Waals interactions; the later are disordered over two positions at a 50:50 occupancy). Thus, the overall formula is  $[\text{Fe}_3(\text{N-cintrz})_6(\text{Pd}(\text{CN})_4)_3]$ ·6H<sub>2</sub>O. The asymmetric unit at 100 and 150 K are the same (Fig. S2 and 3†).

Each  $\text{Fe}^{II}$  centre (**Fe1** and **Fe2**) adopts a distorted octahedral geometry with six N-donor atoms, consisting of four [Pd  $(\text{CN})_4$ ]<sup>2-</sup> anions at the equatorial positions and two N-cintrz ligands in the axial positions. The **Fe1** and **Fe2** sites differ crystallographically due to their N-cintrz ligand connectivity, with **Fe1** coordinated to **L3** and the inversion centre equivalent (**L3**') and **Fe2** coordinated to **L1** and **L2**. The N-cintrz ligands are coordinated through N1 of the 1,2,4-triazole group (Fig. 2).

The three crystallographically distinct N-cintrz ligands (L1, L2 & L3) differ significantly in their geometry and relative arrangement in the interlayer spacing (Fig. 2). Notably, a *trans*orientation is observed for L1 and L2 with respect to the relative position of the unbound N2 of the triazole group and the peripheral NO<sub>2</sub> group, whereas a *cis*-arrangement is present in L3 (Fig. 2). Furthermore, L1 and L2 show greater torsion between the triazole and nitro-benzene rings compared to L3 (Table S2†). The Fe–N–N(trz) 'bite' angle differs for each ligand and Fe<sup>II</sup> site (Table S2†).

The framework structure is formed by the bridging of  $Fe^{II}$  sites by  $[Pd(CN)_4]^{2-}$  anions to produce neutral 2D Hofmann grid-type layers,  $[Fe^{II}Pd(CN)_4]$  (Fig. 3(a)), which lie approximately in the *ac*-plane. Within each layer, the **Fe1** and **Fe2** sites are arranged in stripes along the *a*-axis, with the **Fe1** arrays spaced by pairs of **Fe2** stripes (Fig. 3(b and c)). The **Fe1** and **Fe2** sites show different degrees of octahedral tilting with respect to an idealised planar layer (Fig. 3(b); Table S2†), resulting in layer undulation. Further highlighting the layer distortion, the Fe-N=C angles deviate significantly from 180° (Table S2†).

The interlayer spacing is derived from the head-to-tail interdigitation of N-cintrz ligands from neighbouring layers (Fig. 4). Adjacent Hofmann layers are stacked along the crystal-





Fig. 2 Thermal ellipsoid plot (50% probability) of the asymmetric unit of  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3]$ -6H<sub>2</sub>O at 250 K showing the two Fe<sup>II</sup> sites (Fe1 and Fe2), the three distinct N-cintrz ligands (L1, L2 and L3), the Pd (CN)<sub>4</sub> ligands and the water molecules (2 × type A hydrogen bonded and type B with van der Waals interactions and disordered over two sites).

Fig. 4 Structural view of two adjacent 2-D layers (red & blue) highlighting the head-to-tail ligand interdigitation and array of nitro-group placements within the interlayer spacing (the  $NO_2$  groups are coloured green for clarity).

lographic *b*-axis, with a relatively large interlayer spacing of *ca*. 15 Å (Fig. 4; Table S2†). The nitro-groups from the N-cintrz ligands are directed into the interlayer spacing between adjacent ligands as depicted in Fig. 4. Despite the substantial layer distortion, the layers are efficiently packed with a near-complete head-to-tail overlap of N-cintrz ligands from layers above and below (Fig. 4).

Unlike the majority of 2-D Hofmann frameworks, the intraand inter-molecular interactions are dominated by host-host hydrogen bonding interactions (Fig. 5).<sup>22</sup> The nitro-groups from L1 and L2 form various intra-layer C(H) contacts with neighbouring ligands, as shown in Fig. 5(a). There are also various intra-layer N····C(H) interactions involving L2 and L3 (Fig. 5(a)). The nitro-group from L3 forms the only inter-layer contact (O···N<sup>trz</sup>; Table S3†). The water molecules are engaged in an array of host-guest interactions, as depicted in Fig. 5(b).



**Fig. 3** Structural representation of  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3] \cdot 6H_2O$  at 100 K. (a) A single 2-D Hofmann layer, highlighting the **Fe1** (red) and **Fe2** (orange) distribution in stripes along the *a*-direction. (b)–(c) One 2-D layer illustrating the subtle layer undulation and respective N-cintrz ligands protruding above and below the layers and array of ligand geometries.



**Fig. 5** Structural representation of  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3] \cdot 6H_2O$  (100 K) showing the array of (a) host–host (green) and (b) host–guest (purple) hydrogen bonding interactions present within a single Hofmann layer. The ligands (L1, L2 & L3) are labelled, and hydrogen atoms have been omitted for clarity.

#### Spin crossover properties

Temperature-depended magnetic susceptibility data were collected on a bulk crystalline sample of  $[Fe_3(N-cintrz)_6(Pd (CN)_4)_3]\cdot 6H_2O$  over the range of 300–50–300 K (Fig. 6(a)). At 300 K, the observed  $\chi_M T$  values are ~3.5 cm<sup>3</sup> K mol<sup>-1</sup>, consistent with HS Fe<sup>II</sup> sites. With cooling, the  $\chi_M T$  values remain constant and then gradually decrease between 210 and 100 K, with the  $\chi_M T$  values below 100 K (~0.07 cm<sup>3</sup> K mol<sup>-1</sup>) consistent with LS Fe<sup>II</sup> sites. A subtle two-step character is evident in the SCO profile as can be seen in the  $\delta \chi_M T/\delta T$  plot (Fig. 6(a): inset). Data were collected at a variety of thermal scan rates (0.5, 1, 2 and 4 K min<sup>-1</sup>; Fig. S5†) to determine the nature of the thermal SCO transition without kinetic effects. Differential scanning measurements were also conducted and show *endo*-and *exo*-thermic peaks at temperatures consistent with those obtained by magnetic susceptibility (Fig. S6†).

#### Variable temperature structural analysis

Variable temperature powder X-ray diffraction data were collected using synchrotron radiation to monitor the structural evolution over the SCO temperature range (280–100–280 K). The thermal dependence of the peak positions shows a clear two-step SCO behaviour (Fig. 6(b): inset; Fig. S13†). A plot of the peak position *versus* temperature maps the thermal dependence of the magnetic susceptibility trace in SCO character and temperature (Fig. 6(b)). Fine analysis of the individual patterns did not reveal a phase transition over the entire SCO temperature range.

Single crystal data were collected for the HS (250 K), intermediate plateau (150 K), and LS (100 K) states, respectively. The average Fe–N bond distance at 250 K, for both **Fe1** and **Fe2** are consistent with HS Fe<sup>II</sup> sites (Table 1), as anticipated from the magnetic susceptibility data. The degree of octahedral distortion ( $\Sigma$ ) at **Fe1** is slightly reduced compared to that of **Fe2** (Table 1). Similarly, the average Fe–N bond lengths at 100 K for



**Fig. 6** (a) Temperature-dependent magnetic susceptibility plot ( $\chi_M T vs. T$ ). Data recorded at a scan rate of 2 K min<sup>-1</sup> over the range 300–50–300 K in continuous mode. Other scan rates (4, 1, 0.5 K min<sup>-1</sup>) are provided in the ESI.† (b) Variable temperature (280–100–280 K) synchrotron powder diffraction peak position evolution (2 0 –1 reflection;  $\lambda$  = 0.5903 Å).

both **Fe1** and **Fe2** are consistent with LS  $\text{Fe}^{\text{II}}$  sites (Table 1). The  $\Sigma$  parameter at **Fe1** is seen to increase with transition from HS to LS, whereas the  $\Sigma$  parameter at **Fe2** reduces slightly (Table 1). Despite the **Fe1** and **Fe2** sites being in quite different

Table 1 Selected variable temperature structural parameters

Temperature/K	250	150	100
$\begin{array}{c} d_{\langle \mathrm{Fe1-N}\rangle} & {}^{a}/\mathring{\mathrm{A}} \\ d_{\langle \mathrm{Fe2-N}\rangle} & {}^{a}/\mathring{\mathrm{A}} \\ \mathscr{E}^{\mathbb{O}^{\mathrm{Fe1}}} & {}^{/\circ} \\ \mathscr{E}^{\mathbb{O}^{\mathrm{Fe2}}} & {}^{/\circ} \end{array}$	2.161(2) 2.162(2) 17.6 21.3	2.050(2) 2.031(3) 18.0 19.9	1.959(5) 1.953(5) 19.3 20.6

<sup>*a*</sup> Average bond length of the Fe<sup>II</sup> octahedron. <sup>*b*</sup> Octahedral distortion parameter (sum of  $\mid$  90 –  $\theta \mid$  for the 12 *cis* angles of the Fe<sup>II</sup> octahedron).

local coordination environments, and the presence of a twostep feature in the SCO transition profile, the average Fe–N bonds at 150 K for both **Fe1** and **Fe2** are intermediate between HS and LS (Table 1). This suggests that at the intermediate plateau region there is no three-dimensional long-range ordering of HS and LS sites. Careful inspection of precession images at 150 K did not uncover any diffuse features consistent with site ordering at a shorter length scale or at a lower dimension (Fig. S4†).

Aside from the spin-state variation to the  $Fe^{II}$  sites, the Hofmann framework structure remains relatively unchanged over the SCO temperature range. There is a *ca*. 4.5% overall decrease in unit cell volume, consistent with a complete HS to LS transition. Hirshfeld surface analysis (fingerprint decomposition),<sup>30,31</sup> highlights the domination of NO…HC and N…HO interactions irrespective of temperature (Fig. S7†), and the fingerprint plots (Fig. S8†) indicate that temperature (and hence spin-state) do not drastically affect the intermolecular interactions.

### Discussion

A series of targeted 2-D Hofmann materials incorporating systematically functionalized 1,2,4-triazole ligands exist;<sup>17-22,26,28</sup> these have provided unique insight into the structural and spin-state switching effect of ferro- and anti-ferro-elasticity generated by competing supramolecular interactions.<sup>10-12</sup> All of the  $[Fe(R-trz)_2M(CN)_4]$  guest examples thus far reported show SCO properties dictated by elastic frustration arising from the unique monodentate 1,2,4-triazole binding mode which intrinsically supports antagonistic supramolecular interactions (host-host and host-guest). An important facet of this ligand design is that supplementary supramolecular interaction capacity can be readily integrated into the host network via the inclusion of ligand functional groups with specific hydrogen-bonding interaction capacity and guest molecules. The effectiveness of this approach is illustrated in the example  $[Fe_3(saltrz)_6(Pd(CN)_4)_3]$ ·8H<sub>2</sub>O (Fig. 1b),<sup>22</sup> which shows substantial Hofmann layer distortion and a four-stepped SCO transition driven by ligand hydroxyl group interactions. A further important feature of this 2-D structural platform is that the intermolecular communication pathways, which are important for the long-range transmission of spin-state change, can be tailored by other factors such as ligand length and aromaticity.

To probe these ligand design features further, we investigate here the coexistence of tailored hydrogen-bonding capacity (*i.e.*, the nitro-group) which should provide enhanced antiferro-elastic character when combined with the known propensity of the 1,2,4-triazole group to form various antagonistic host–host and host–guest contacts<sup>17–22,26,28</sup> and that of guest molecules.

From a structural perspective, the 2-D Hofmann framework  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3] \cdot 6H_2O$  closely resembles that of [Fe<sub>3</sub>(saltrz)<sub>6</sub>(Pd(CN)<sub>4</sub>)<sub>3</sub>]·8H<sub>2</sub>O.<sup>22</sup> In particular, the two distinct  $Fe^{II}$  sites (Fe1 and Fe2, Fig. 2), their relative ratio (1:2) and their distribution within the Hofmann layers (i.e., in 1:2 stripes, Fig. 3a and b) is equivalent in both materials. Furthermore, even with the distinction in ligand length and hydrogen bond donor group (i.e., NO2 vs. OH) in N-cintrz and saltrz (Fig. 1), the range of ligand conformations (i.e., cis vs. trans and planar vs. twisted, see Fig. 2) are identical. Moreover, whilst there is a ~2 Å difference in layer separation between the two due to the longer N-cintrz ligand (N-cintrz: 14.8 Å; saltrz: 12.4 Å in HS state), the 2-D layer packings achieved in these structures are each dominated by hydrogen-bonding rather than aromatic contacts typical in Hofmann frameworks. Given the irregularity of this overall structure, it is somewhat surprising that the same Hofmann distortions are observed in both and suggests that it is an energetically preferred structural arrangement. Together, these two structural studies clearly illustrate the fruitful strategy of including secondary hydrogen bonding capacity to drive substantially distorted Hofmann structures.

The primary motivation for introducing lattice distortion into 2-D Hofmann frameworks was to further probe and develop a deeper understanding of elastic competition and the relationship to multi-stepped SCO transitions.<sup>10,11</sup> Broadly speaking the lattice distortive effects of  $[Fe_3(N-cintr2)_6(Pd(CN)_4)_3]\cdot 6H_2O$  and  $[Fe_3(saltr2)_6(Pd(CN)_4)_3]\cdot 8H_2O^{22}$  in the HS state are equivalent. This equivalent distortive effect at the Fe<sup>II</sup> sites is readily quantified by comparing the  $\Sigma$  parameter at each of the HS Fe<sup>II</sup> sites, whereby  $\Sigma$  values of ~18° and ~21° are observed for **Fe1** and **Fe2**, respectively, in both materials. Despite this seemingly equivalent inherent frustration of the HS lattices, with temperature perturbation very different SCO traces are observed:  $[Fe_3(N-cintr2)_6(Pd(CN)_4)_3]\cdot 6H_2O$  shows a gradual two-step SCO and  $[Fe_3(saltr2)_6(Pd(CN)_4)_3]\cdot 8H_2O^{22}$ shows a cooperative four-step SCO.

One of the primary distinctions between  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3]\cdot 6H_2O$  and  $[Fe_3(saltrz)_6(Pd(CN)_4)_3]\cdot 8H_2O^{22}$  is the interlayer communication pathways. There are two interlayer communication pathways *via* hydrogen bonding in  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3]\cdot 6H_2O$ ,  $NO_2\cdots N^{trz}$  and  $NO_2\cdots C(H)$ , as depicted in Fig. 7. These interactions act as direct connections between **Fe1** and **Fe2** on distinct layers (Fig. 7). There are also various interlayer aromatic contacts between head-to-tail overlapped N-cintrz ligands (Fig. 4). On the other hand, for  $[Fe_3(saltrz)_6(Pd(CN)_4)_3]\cdot 8H_2O$ ,<sup>22</sup> there are no direct interlayer hydrogen bonding interactions, but longer communication pathways do exist *via* the water molecules (host…water…host).



Fig. 7 The intermolecular contacts (red dashes) between adjacent layers (red and blue). Fe1 and Fe2 sites noted.

The primary mode of interlayer communication is *via* aromatic contacts between head-to-tail overlapped saltrz ligands. There is clear theoretical evidence that frustrated elastic interactions can lead to disordered states in both two-<sup>12</sup> and three-dimensional<sup>31</sup> models. Therefore, the enhanced intermolecular interactions in  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3]\cdot 6H_2O$  may mean that this framework is more strongly frustrated than  $[Fe_3(saltrz)_6(Pd(CN)_4)_3]\cdot 8H_2O$ .<sup>22</sup> Rather than leading to additional spin-transition steps, this probable enhanced frustration and emerges in  $[Fe_3(N-cintrz)_6(Pd(CN)_4)_3]\cdot 6H_2O$  as short-range spin-state order at the HS : LS intermediate plateau. This picture is supported by recent calculations that suggest that long-range interactions are important for the spin-state ordering arrays observed in  $[Fe_3(saltrz)_6(Pd(CN)_4)_3]\cdot 8H_2O$ .<sup>11,22</sup>

The observation of a 50:50 HS:LS plateau in a parent system that contains a 2:1 ratio of inequivalent Fe<sup>II</sup> sites raises a number of interesting scenarios regarding the local stabilisation of this mixed spin-state.32 Both elastic interactions and crystallographically distinct metal sites have been proposes as driving forces for antiferro-elastic order.<sup>33</sup> Firstly, we note that this 50% plateau is incompatible with the parent symmetry of the structure, and that any 50% ordering necessarily requires reduction in the local symmetry; this is consistent with the crystallographic observation of intermediate Fe-N distances, with site-averaging of local HS and LS states at each of the inequivalent Fe<sup>II</sup> sites at the plateau temperature, 150 K. The absence of any discernible evidence for symmetry reduction in the X-ray diffraction data at the SCO plateau, either in the form of Bragg modulation peaks or diffuse scattering features, suggests two possible scenarios regarding the 50% spin state stabilisation. Firstly, it may be that the length scale of any spin-state ordering is below the observable limit, leading to extreme smearing of X-ray scattering associated with these features; given the stoichiometry mismatch between HS:LS fraction and inequivalent Fe<sup>II</sup> sites (requiring, for example, ABAB-type ordering to impose itself upon an AABAAB lattice) there appears a strong possibility that long-range ordering of any 50:50 HS:LS patterning is disrupted by low energy defects (for example, of type ABAABAB). Such defects could

prevent long-range spin-state ordering from occurring - in which case the two peaks observed in  $\delta \chi_M T / \delta T$  must indicate spin-state transitions rather than true thermodynamic phase transitions.<sup>11,34</sup> Alternatively, the peaks in  $\delta \chi_{\rm M} T / \delta T$  could signal true phase transition with long-range order, but the defects could prevent this from being detectable crystallographically. Secondly, it may be that long-range ordering of HS:LS sites occurs in less than three-dimensions, vielding diffuse scattering too weak to observe due to the subtlety of the modulation. A possible scenario here is the formation of two-dimensionally ordered HS:LS Hofmann layers, e.g., with alternation of HS/LS sites in one (striped) or two (checkboard) directions within the layers, with there being no long-range correlation in the third, interlayer direction, due to the comparative weakness of the interlayer coupling and, again, to the mismatch of the crystallographic periodicity. Notably, in both scenarios the elastic coupling inherent within the Hofmann lattice to some large extent overrides any tendency the Fe<sup>II</sup> sites may have to transition based on the inequivalence of their local geometries. This situation is similar in one sense to the behaviour seen in [Fe<sub>3</sub>(saltrz)<sub>6</sub>(Pd(CN)<sub>4</sub>)<sub>3</sub>]·8H<sub>2</sub>O,<sup>22</sup> in which inequivalent Fe<sup>II</sup> sites transition within single steps of the multistep transition, but different in another in that in  $[Fe_3(saltrz)_6(Pd(CN)_4)_3] \cdot 8H_2O^{22}$  some partial degree of threedimensional coherence of HS and LS sites was observed, albeit with some crystallographic sites being mixed spin-state arrays.

### Experimental

#### General

Chemical and solvents were an analytical grade, commercially available and used without further purifications.

Caution: Iron(n) perchlorate is potentially explosive, carefully handle and the minimum amount was used to avoid any explosion.

#### Preparation of nitrocinnamaldehyde

Nitrocinnamaldehyde was synthesized using a modified reported method.35 A round bottom flask was charged with 1.32 g (10 mmol) cinnamaldehyde and 5.35 mL acetic anhydride and cooled in an ice bath while stirring. When the temperature reached 0 °C, a solution of concentrated nitric acid (0.42 mL) in glacial acetic acid (1.19 mL) was added via a dropping funnel over 2 hours with vigorous stirring and ensuring the temperature remained below 5 °C. After the addition, the resulting mixture was stirred for an additional 30 min and then allowed to warm up gradually to room temperature and allowed to stand for 24 h. Finally, 40% HCl was cautiously added keeping the temperature below 5 °C until a precipitate appeared. The solution was cooled (refrigerated) overnight to completely precipitate the solid. The crude product was washed with excess water, filter and recrystallize in hot ethanol. The bright-yellow needles were collected, dried in air and store at 4 °C. <sup>1</sup>H NMR (400 MHz, *d*-CDCl<sub>3</sub>, ppm):  $\delta$  = 9.77 (d, 1H), 8.10-8.04 (dd, 1H), 7.99-7.56 (m, 4H), 6.65-6.57 (q,

1H). <sup>13</sup>C NMR:  $\delta$  193.31, 147.48, 134.01, 132.86, 131.33, 129.27, 125.42. IR (cm<sup>-1</sup>): 1678 (s), 1569 (w), 1504 (s), 1435 (w), 1340 (m), 1312 (w), 1119 (s), 975 (m), 863 (w), 828 (w), 786 (m), 734 (s), 694 (m), 672 (m), 597 (w). ESI-MS (ESI<sup>+</sup>, *m/z*): calculated for [M + H]<sup>+</sup> C<sub>9</sub>H<sub>7</sub>O<sub>3</sub>N 177.16, found 178.38. Melting point: 128.0 °C (lit. 127–129 °C).

#### Preparation of (E)-3-(2-nitrophenyl)acrylaldehyde (N-cintrz)

A general method was adopted to synthesize the Schiff base of (E)-3-(2-nitrophenyl)acrylaldehyde. An equal amount of nitrocinnamaldehyde 1.77 g (10 mmol) and 4-amino 1,2,4-triazole 0.840 g (10 mmol) were dissolved in 30 mL of ethanol and refluxed with a catalytic amount of conc. sulfuric acid (2-3 drops) at 80 °C for 5 h. The yellow precipitate was collected by filtration. The crude product was washed with cold ethanol and recrystallized from hot ethanol yielded yellow needleshaped microcrystals of N-cintrz (yield: 2.04 g, 83.8%). <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO, ppm):  $\delta$  = 8.78 (s, 2H), 8.61–8.59 (d, 1H), 8.08-8.06 (ddd, 1H), 7.85-7.54 (m, 4H) 6.98-6.92 (q, 1H). <sup>13</sup>C NMR: δ 195, 154.77, 149.69, 148.77, 147.75, 134.40, 132.61, 132.09, 129.78, 129.47, 125.27, 109.27. IR (cm<sup>-1</sup>): 1510 (s), 1340 (s), 1248 (w), 1171 (s), 1051 (s), 995 (w), 979 (w), 935 (w), 862 (m), 848 (w), 832 (w), 759 (w), 731 (s), 695 (w), 614 (s), 516 (m). Elemental analysis calculated for  $C_{11}H_9N_5O_2$  (%): C 54.32; N 28.79; H 3.73; found (%): C 54.13; N 29.28; H 3.56. ESI-MS (ESI<sup>+</sup>, m/z): calculated for  $[M + H]^+$  C<sub>11</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub> 243.22, Found 244.08. Melting point: 230.5 °C.

#### Synthesis of [Fe<sub>3</sub>(N-cintrz)<sub>6</sub>(Pd(CN)<sub>4</sub>)<sub>3</sub>]·6H<sub>2</sub>O

A bulk crystalline sample was prepared by vial-in-vial slow diffusion methods. A large vial was prepared containing a mixture of N-cintrz (38.9 mg, 0.16 mmol) and  $K_2[Pd(CN)_4]$  (23.0 mg, 0.08 mmol) and small vial was prepared containing  $Fe(ClO_4)_2 \cdot xH_2O$  (20.1 mg, 0.08 mmol). The small vial was inserted carefully into a large vial and then both vials were filled with a mixture of an EtOH :  $H_2O$  (50 : 50) solution. Over a period of 8 weeks red square-shaped crystals were formed. Elemental anal. calcd for  $FePdC_{26}H_{18}N_{14}O_4 \cdot 3H_2O$  (%): C: 38.67; H: 2.97; N: 24.29. Experimental (%): C: 38.60; H: 2.50; N: 25.54. IR bands (cm<sup>-1</sup>): 2170(m), 1631(w), 1513(s), 1338(s), 1175(s), 1053(s), 978(m), 864(s), 620(s), 504(w).

#### Characterisation

Elemental analysis was performed at the Mark Wainwright analytical centre (UNSW) or at The Campbell Microanalytical Laboratory (University of Otago). Fourier transformation (FTIR) were recorded on a Thermo-Fisher Nicolet-iS5 spectrometer in the range of 400–4000 cm<sup>-1</sup> which was equipped with a smart iD7 diamond attenuated total reflectance (ATR) window. NMR spectra were recorded on a Bruker 400 MHz NMR equipped with an autosampler in  $d_6$ -DMSO as a solvent. Mass spectroscopy was performed on a Thermo-Fisher mass spectrometer (m/z 50–2000) under the positive ion mode with the ESI source using methanol as eluent. Melting points were determined using an OptiMelt (SRS MPA 100) apparatus in an open borosilicate capillary tube. Thermogravimetric analysis was carried out on a Mettler-Toledo TGA/SDT851e analyser (30-600 °C at 1 °C min<sup>-1</sup>) using an alumina sample holder (N<sub>2</sub> flow of 10 mL min<sup>-1</sup>). Differential scanning calorimetry measurements were performed using a Netzsch DSC 204 instrument (100 to 250 K; rate of 10 K min<sup>-1</sup>; 20 mL min<sup>-1</sup> N<sub>2</sub> atmosphere). The low temperature was obtained with a liquid nitrogen cryostat cooling system attached with an instrument. The measurement was carried out with 12.2 mg of crystalline sample sealed in an aluminium pan with a mechanical crimp and an empty pan used as a reference. The data were analysed with the Netzsch Proteus Analysis 2019. The Hirshfeld surface of the asymmetric unit was generated by crystal Explorer 17.5 software which comprised 3D  $d_{norm}$  surface plots and 2D histogram of de and di fingerprints plot.<sup>29,30</sup> Single crystal CIFs were used as input file for analysis.

#### Magnetic susceptibility

Variable temperature magnetic susceptibility data were collected using a Quantum Design Versalab equipped with a vibrating sample mount (VSM) under a constant applied magnetic field of 3000 Oe. The crystalline sample was retained in a small amount of mother liquor and sealed in a polyethylene tube design for measurement to present solvent loss. The data were collected continuously (rate of 2 K min<sup>-1</sup>, 300–50–300 K).

#### Single crystal X-ray diffraction

A single crystal was mounted on a cryoloop with the paratone-N oil. Data collection was carried out on a Bruker D8 Quest diffractometer equipped with a graphite monochromatic Mo-Kα ( $\lambda$  = 0.71073 Å) X-ray generator and PHOTON II CPAD detector. The crystal was positioned at 40 mm from the detector and the spots were measured using 10 s exposure time. The data were collected on a  $0.152 \times 0.75 \times 0.025 \text{ mm}^3$  red block crystal at 250 K, 150 K and 100 K. An Oxford cryo-stream controller was used. The APEX3 crystallographic software (v2018.1.0, Bruker AXS Inc.) was used for data integration and scaling and XPREP software was employed for space-group determination.36,37 All structures were solved by the direct method using ShelXT and refined on  $F^2$  by full-matrix leastsquare with ShelXL using the X-Seed 4000 and OLEX2 interfaces.<sup>38-41</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atom in the ligands were placed at idealized positions and refined using a riding model with isotropic thermal parameters, except the hydrogen atoms of the disordered water molecules (O9A and O9B). Details of the crystallographic data collection and refinement parameters are summarised in Table S1,† selected structural parameters are given in Table S2,† and hydrogen bonding interactions are given in Table S3.† The crystallographic information files (CIF) have been deposited in the Cambridge Crystallographic Database (CCDC) and are freely the available under CCDC reference numbers: 2045470-2045472.\*

#### Powder diffraction using synchrotron radiation

Variable temperature X-ray powder diffraction data were collected on the Powder Diffraction beamline (BL-10; 20.99 keV and 0.5903 Å) at the Australian Synchrotron.<sup>42</sup> A polycrystalline sample was ground gently into a slurry using a mortar and pestle, packed into borosilicate glass capillary tube (0.5 mm diameter) and mounted onto the powder diffraction beamline. The capillary was rotated at *ca*. 1 Hz during data collection to aide powder averaging. The wavelength was determined accurately using NIST SRM LaB<sub>6</sub> 660b standard. Temperaturedependent data were collected upon cooling and warming in steps of 120 K h<sup>-1</sup> from 100-280-100 K. Data were collected using the Mythen microstrip detector<sup>43</sup> from 1.5 to  $75^{\circ}$  in  $2\theta$ . To cover the gaps between detector modules, two data sets, each of 60 seconds in duration, were collected with the detector set 5° apart and these were then merged to give a single data set. A slit size of 2 mm was used, to ensure that the fraction of the capillary illuminated by the X-ray beam is the same as the isothermal zone on the cryostream. The obtained raw data were merged using in-house software PDViPER and further process with the Surfer software package. Le-Bail analysis and peak fitting were performed using TOPAS<sup>44</sup> software package.

### Conclusions

The targeted incorporation of an organic ligand with two modes of supramolecular contacts (1,2,4-triazole and nitrogroups) has led to a 2-D Hofmann framework which exhibits characteristics of extreme elastic frustration. Highlighting this are the two distinct  $Fe^{II}$  sites in a rare 2:1 ratio, an array of ligand conformations and layer distortion such that interlayer contacts are dominated by hydrogen-bonding rather than aromatic contacts observed in classic Hofmann frameworks. There are many ligand-ligand and ligand-water interactions involving the 1,2,4-triazole and nitro-groups resulting in a structural complexity where all the interactions cannot be simultaneously minimised, resulting in elastic competition between ferro- and anti-ferro elastic interactions. The resultant temperature-induced SCO behaviour is multistepped, supporting the expanding body of theoretical and experimental evidence showing that elastically frustrated structures drive and support multi-stepped transitions and hence mixed spin-state species. Of additional importance in this study is the finding that the elastic competition, which includes 3-D intermolecular communication channels, overrides the periodic ordering of mixed spin-state species at intermediate temperatures leading to a disordered intermediate phase. The disparity between structural and spin-state periodicity in this structure, which we hypothesise underlies the absence of long-range spin-state ordering, is a new feature of multi-stepped transition materials, hence future work on this system will include detailed calculations that test this premise.

## Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

JKC, BJP, CJK and SMN acknowledge support from Fellowships and Discovery Project funding from the Australian Research Council (ARC). Access and use of the facilities of the Australian Synchrotron was supported by ANSTO. JKC acknowledges the support of the ARC through LE170100144.

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