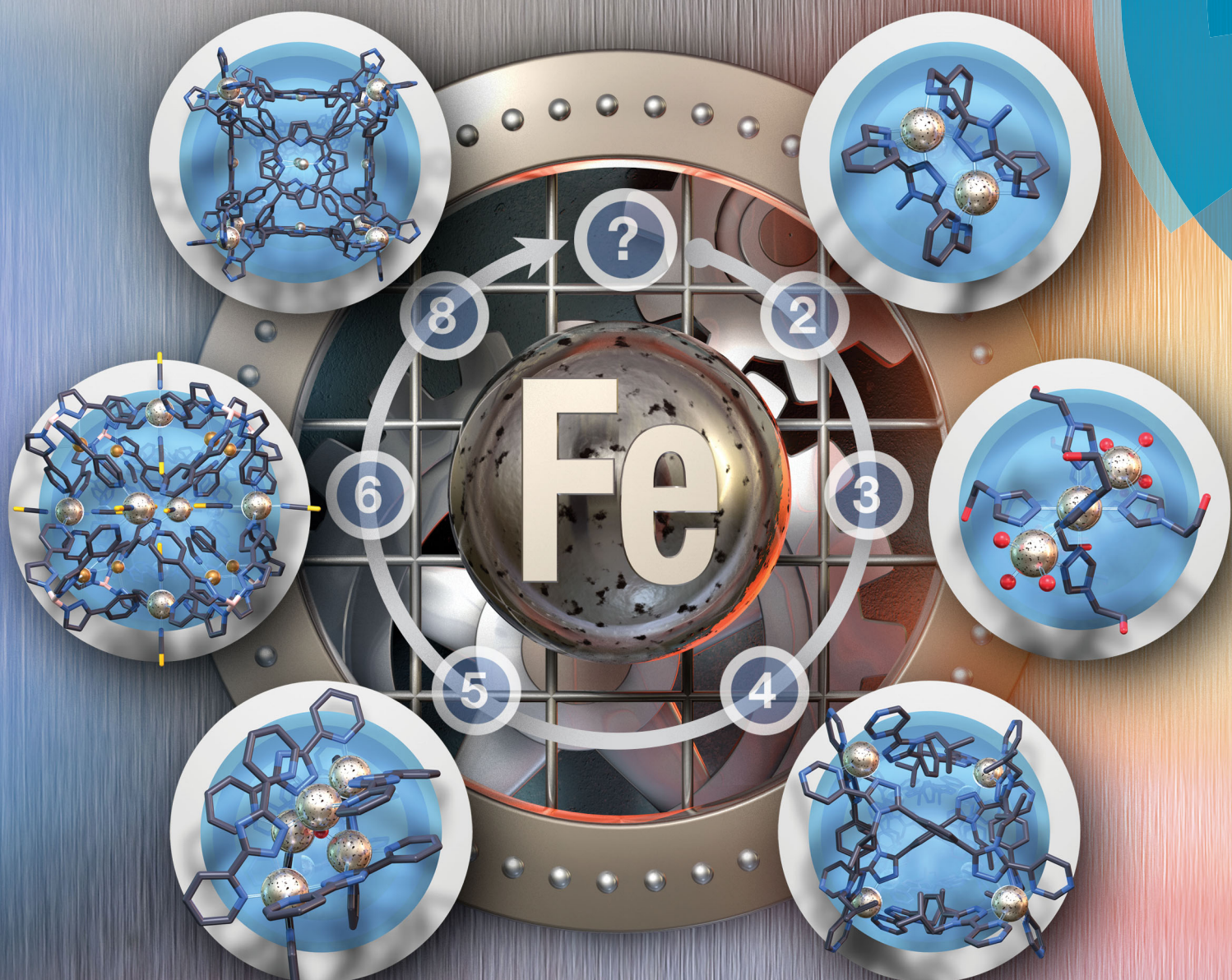


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Spin crossover in discrete polynuclear iron(II) complexes



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## Spin crossover in discrete polynuclear iron(II) complexes†

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Iron(II) spin crossover (SCO) materials have been widely studied as molecular switches with a wide variety of potential applications, including as displays, sensors, actuators or memory components. Most SCO materials have been either monometallic or polymeric, and it is only relatively recently that chemists have really started to focus on linking multiple metal centres together within the one, discrete, molecule in an effort to enhance the SCO properties, such as abrupt, hysteretic, and multistep switching, as well as the potential for quantum cellular automata, whilst still being readily amenable to characterisation. Here we present a review of the ligand designs of the last two decades that have led to self assembly of discrete di- to poly-nuclear iron(II) complexes of helicate, cage, cube, and other supramolecular architectures with rich SCO activity, and to an increased focus on host–guest interactions. Analysis of selected octahedral distortion parameters ( $\Sigma$ , CShM) reveals interesting differences between these structural types, for example that the iron(II) centres in grids are generally significantly more distorted than those in squares or cages, yet are still SCO-active. Of the 127 complexes reviewed (79 published 2012–Feb. 2018), 54% are dinuclear, 10% trinuclear, 31% tetranuclear, and the remaining 5% are penta, hexa and octanuclear. Of the 93 designer ligands utilised in these polynuclear architectures: 60 feature azoles; 55 provide all donors to the Fe(II) centres (no co-ligands coordinated) and form exclusively 5-membered chelate rings via either bidentate azole-imine/pyridine or tridentate heterocycle-imine/amine/thioether/pyridine-heterocycle binding pockets.

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*“Discrete polynuclear complexes: from spin crossover to hydrogen evolution”, was placed on the list of exceptional theses. Ross is currently a postdoctoral fellow working on inorganic materials for non-aqueous redox flow batteries with Dr Kathryn Toghill at Lancaster University, United Kingdom.*



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*she qualified CSIR-UGC NET. In 2017 she moved to Dunedin, New Zealand, to take up a University of Otago PhD scholarship in Professor Sally Brooker's research group, working on the self-assembly of discrete polynuclear spin crossover complexes using designer polytopic ligands.*



# Introduction

## General introduction to spin crossover

Spin crossover (SCO) complexes are an interesting class of materials exhibiting molecular bistability with potential applications in nanotechnological devices such as memory storage units, sensors, actuators or displays.<sup>1–8</sup> The bistability arises from their ability to be switched between two electronic states – high spin (HS) and low spin (LS) – by external stimuli such as a change in temperature or pressure, or light irradiation or guest presence/absence, in a readily detectable and reversible way.

For octahedral  $3d^4$ – $3d^7$  transition metal ions, there are two ways that electrons can populate the  $t_{2g}$  and  $e_g$  orbitals (Fig. 1), depending on ligand field splitting ( $\Delta_O$ ) and the energy cost associated with pairing two electrons in the same orbital, the pairing energy ( $P$ ). If strong field ligands are present,  $\Delta_O$  is large so the lowest energy configuration involves the pairing of electrons in the  $t_{2g}$  set being favoured over population of the  $e_g$  set ( $\Delta_O > P$ ), resulting in the maximum amount of paired electrons and thus a LS state. On the contrary, if weak field ligands are present,  $\Delta_O$  is small and the maximum number of unpaired electrons, *i.e.* the HS state, is the lowest energy configuration as populating the  $e_g$  set costs less energy than pairing the electrons in the  $t_{2g}$  set ( $\Delta_O < P$ ).<sup>9</sup>

When  $\Delta_O$  is of a comparable magnitude to  $P$ , the possibility of inducing switching between the HS and LS states arises, *i.e.* SCO, by perturbing the system through application of an external stimulus (Fig. 1). SCO can be induced by pressure, magnetic or electric field, light irradiation, and the presence/absence of guest molecules, however, the most common perturbation is a change in temperature, due in large part to facile application and measurement.<sup>1</sup>

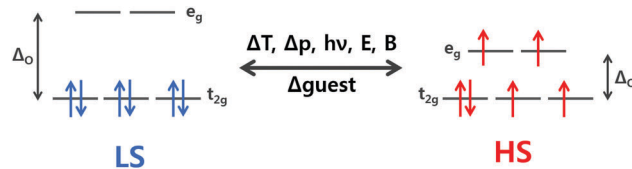


Fig. 1 The d orbital splitting diagram for an octahedral Fe(II) ion. When  $\Delta_O$  is large, the LS state is adopted (left); when  $\Delta_O$  is small, the HS state is adopted (right). When  $\Delta_O$  is tuned for SCO, a change in temperature, pressure, magnetic or electric field, light irradiation, or guest molecules, can result in the switching between HS and LS states.

The HS and LS states have different physical properties, which allows for detection and quantification of SCO by many different methods. Fe(II) SCO compounds often exhibit thermochromism, as the LS state absorbs visible light more strongly than the HS state and usually at distinctly different wavelengths, making UV-vis spectroscopy a useful tool for observing SCO.<sup>9</sup> The HS state has more electrons in the antibonding  $e_g$  orbitals than the LS state so has longer metal–ligand bond lengths. Hence X-ray crystallography, often done at more than one temperature, can be used to determine the spin state. This powerful technique can also pinpoint within a structure which ions are HS and which are LS in a mixed spin state system.<sup>10</sup> A direct and detailed readout of the spin state of a SCO compound is the molar magnetic susceptibility ( $\chi_M$ ). In the case of Fe(II) the HS state ( $S = 2$ ) is paramagnetic, while the LS state ( $S = 0$ ) is diamagnetic, so for Fe(II) SCO switches the paramagnetism “on” and “off”. The most convenient way to quantify SCO is therefore variable temperature  $\chi_M T$  (the product of molar magnetic susceptibility and temperature) measurements, which are routinely performed on modern SQUID, PPMS, or Versalab magnetometers. UV-vis,<sup>9</sup> IR,<sup>11</sup> Raman,<sup>12</sup> NMR,<sup>13–16</sup> Mössbauer,<sup>17</sup> and fluorescence<sup>18</sup> spectroscopies, as well as PXRD<sup>19</sup> and DSC,<sup>20,21</sup> can also be invaluable tools for monitoring SCO.

## Advantages of discrete polynuclear systems for SCO

From a materials perspective, SCO systems were identified as potential molecular switch components in memory storage devices some time ago.<sup>22</sup> Hence the development of spin crossover research is heavily influenced by the target of molecular switch and memory applications, with a drive towards SCO which is complete, abrupt, hysteretic, and ideally switchable about room temperature.<sup>23,24</sup> Complete transitions are favoured, as they allow for easier and unambiguous detection of distinct fully HS and fully LS states, while abrupt transitions allow for a large change in output (*e.g.* colour,  $\chi_M T$ ) for a small input (*e.g.* small change in temperature). A thermal hysteresis provides a memory effect, where the spin state depends on the thermal history of the complex. Hence at temperatures within the hysteresis loop the system is bistable and there is the potential for binary information storage. The design of ligands which not only provide the right  $\Delta_O$  for SCO, but will also facilitate cooperativity within or between complexes which may in turn facilitate abrupt and/or hysteretic spin transitions, is the main goal of many SCO chemists.<sup>25</sup>



Sally Brooker

Professor Sally Brooker (MNZM, FRSNZ, FNZIC, FRSC) studied at the University of Canterbury, New Zealand [BSc(Hons) first class; PhD with Professor Vickie McKee]. After postdoctoral research at Georg-August-Universität Göttingen, Germany with Professor George M. Sheldrick, she took up a Lectureship at the University of Otago where she is now a full Professor. She has been the recipient of numerous awards, most recently including a 2017

Queens Birthday Honour for services to science (MNZM), the 2017 Hector Medal (RSNZ) and 2017 Burrows Award (RACI). Her research interests concern the design, synthesis and full characterisation of, primarily paramagnetic, di- and poly-metallic complexes of transition metal and lanthanide ions with polydentate acyclic and macrocyclic ligands, as these have interesting redox, magnetic, catalytic and photophysical properties ([otago.ac.nz/brooker](http://otago.ac.nz/brooker)).



Cooperativity arising from crystallographic disorder, crystal packing interactions, or large molecular size/shape differences between HS and LS states, can have a significant influence on SCO properties of complexes, including mononuclear and polymeric complexes, in the solid state.<sup>26</sup> Cooperativity may also be imparted by covalently linking multiple metal centres in a polynuclear or polymeric architecture – but it must be noted that this approach is certainly not guaranteed to lead to cooperativity. That said, a beautiful illustration of the successful application of this ‘linking’ approach is provided by the now famous Fe(II) 4-R-1,2,4-triazole 1-D chain polymers,  $[\text{Fe}(\text{Rtz})_3]^{2+}$ , which feature triply-triazole bridged Fe(II) centres and have remarkably large hysteresis loops around room temperature.<sup>22–24,27–29</sup> A single crystal structure of these widely studied  $[\text{Fe}(\text{Rtz})_3]^{2+}$  chains was only obtained recently, as despite considerable attention these polymers had resisted all attempts at crystallisation until then.<sup>30</sup>

Discrete polynuclear complexes, in which multiple metal centres are covalently bridged in order to enhance cooperativity, have advantages over polymeric systems in that the design and synthesis can be more controlled, and the characterisation more straightforward.<sup>31–35</sup> Polynuclear complexes, discrete or polymeric, have the added bonus of potential polynary, rather than binary, information storage as multiple spin states can be accessed by multi-step SCO.<sup>23,36,37</sup> Furthermore the geometric arrangement of HS and LS Fe(II) centres within one complex molecule could be used in quantum cellular automata,<sup>38,39</sup> potentially leading to logic gates consisting of only a few molecules.<sup>40,41</sup>

### Scope of this review of SCO-active discrete polynuclear Fe(II)

Iron(II) complexes are by far the most common SCO systems studied<sup>1</sup> (of the order of >90%), and almost all subsequent in depth studies by physicists and materials scientists are done on iron(II) systems.<sup>7</sup> Most SCO-active Fe(II) complexes are mononuclear or polymeric, while discrete di to poly-nuclear complexes (Fig. 2) are much rarer.<sup>7,25,31,35,42–44</sup>

This is also true for Fe(III), Co(II), and Mn(II), where only a handful of polynuclear SCO systems are known.<sup>35</sup> In 2013<sup>35</sup> we reviewed the development of discrete polynuclear SCO-active complexes, focussing mainly on the 90 new complexes reported over the period 2004–2011: all of the new complexes were either Fe(II) (68) or Fe(III) (22), and the nuclearities ranged from 63 dinuclear to 3 trinuclear to 14 tetranuclear, with another 10 in an assortment of higher nuclearities including mixed metal clusters. Here we review the various classes of structurally characterised, SCO-active, discrete di- to poly-nuclear complexes, specifically of Fe(II), focussing mostly on those published 2012–2017, as there has been considerable growth in this field since our previous review, including an expansion of the range of architectures employed and the setting of a new record for the largest number of metal centres in a discrete SCO-active complex = 8.<sup>45</sup> The 127 complexes included in this review were identified by a CSD search (version 5.38, November 2016) for dinuclear and trinuclear iron(II) 1,2,4-triazoles (as structural search fragments) and a Scifinder search (28 February, 2018) for

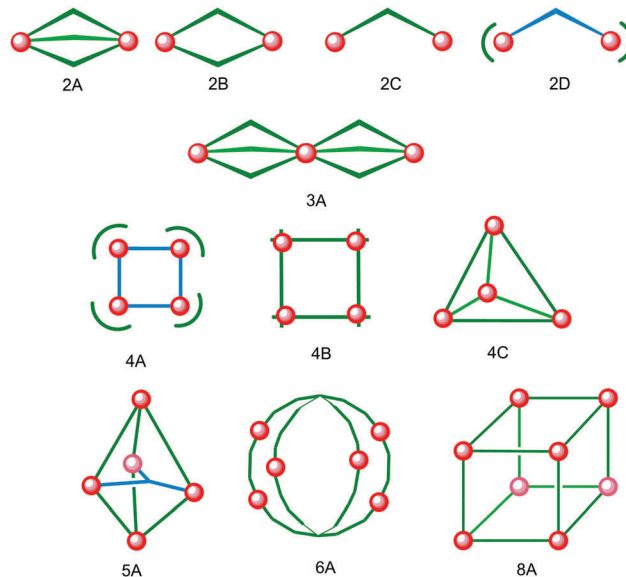


Fig. 2 Topologies observed for the discrete polynuclear SCO-active complexes reviewed herein: dinuclear (2A–2D); trinuclear (3A); tetranuclear squares (4A), grids (4B), tetrahedral cages (4C); pentanuclear cage (5A), hexanuclear nanoball (6A) and octanuclear cube (8A). Green = di- to polydentate N-donor ligand. Blue = bridging anion.

the keywords “Fe(II) or iron(II)” and “dinuclear or trinuclear or tetranuclear or pentanuclear or hexanuclear or septanuclear or nanoball or octanuclear” and “spin crossover or spin-crossover or spin cross-over or spin transition or spin equilibrium”, followed by manually sorting through the resulting ‘hits’. The resulting family of 79 discrete polynuclear SCO-active Fe(II) complexes published from 2012 to February 2018, along with selected examples published before then, brings the total reviewed here to 127. They are reviewed in order of increasing nuclearity: dinuclear (2A–2D), trinuclear (3A), tetranuclear squares (4A)/grids (4B)/cages (4C), pentanuclear (5A), hexanuclear ‘nanoballs’ (6A), and octanuclear cubes (8A) (Fig. 2).

Of these groups, dinuclear remains the most common of the nuclearities seen for discrete SCO-active complexes. A range of structural types can be identified within this dinuclear class: triply bridged triazole  $[\text{Fe}_2\text{L}_5(\text{NCE})_4]$  and helicate  $[\text{Fe}_2\text{L}_3]$  (Fig. 2, 2A), doubly bridged helicate and PMRT-type and pyridine bridged  $[\text{Fe}_2\text{L}_2]$  (Fig. 2, 2B), singly ligand linked dinuclear  $[\text{Fe}_2\text{L}]$  (Fig. 2, 2C) and assorted anion bridged dinuclear complexes with capping ligands (Fig. 2, 2D).

### Dinuclear triply triazole-bridged $\text{Fe}_2\text{L}_5(\text{NCE})_4$

Fundamental questions in the field of SCO materials are; what factors influence the spin transition temperature ( $T_{1/2}$ ) and transition profile.<sup>29,46</sup> Therefore it is important to study structurally and magnetically similar series of complexes with minor changes in substituents, counterions, and/or solvent molecules. The triply triazole bridged dinuclear complexes (Fig. 2, 2A) are one type of dinuclear family suitable for such studies, for which crystal structures can be readily determined.

As mentioned in the introduction, the use of  $N^4$ -substituted triazoles to form 1D polymers of triply triazole bridged iron(II) is



well known, with wide thermal hysteresis loops and tuneable transition temperatures near room temperature, based on the choice of  $N^4$  substituent.<sup>47</sup> But it is interesting to note that those 1D-chain complexes resisted single crystal X-ray characterisation until 2011.<sup>30</sup> In contrast, dinuclear systems tend to more readily characterised, and facilitate the probing of cooperative effects between the two metal ions.

Here, in the seven examples, plus a solvatomorph, of dinuclear SCO-active  $[\text{Fe}_2\text{L}_5(\text{NCE})_4]$  with  $\text{L} = \text{L1-L7}$  (Chart 1), three of the 1,2,4-triazoles provide short  $N^1N^2$ , and fairly rigid, bridges between the iron(II) centres, and two more triazoles act as terminal monodentate ligands. The somewhat distorted octahedral geometry of each iron(II) centre is completed by two NCE mono-anions, affording  $N_6$  coordination spheres (Fig. 3). All eight of these complexes showed an abrupt one-step incomplete spin transition, with  $T_{1/2}$  in the range of 100–165 K, with no hysteresis loops observed and Fe–Fe distances in same range, 3.6–4.0 Å (Table 1).<sup>18,48–50</sup> As expected, the octahedral distortion parameters ( $\Sigma$ , defined as the sum of the absolute values of the difference of each of the 12 *cis* angles from  $90^\circ$ ) for the Fe(II) centres range from 12–19° for LS to the somewhat higher values of 14–35° for HS (Table 1). Some additional details are provided below.

The first of this family of SCO-active dinuclear Fe(II) triply triazole bridged complexes, phenol  $N^4$ -substituent (**L1**, Chart 1),  $[\text{Fe}_2\text{L1}_5(\text{NCS})_4]\cdot 4\text{MeOH}$  in the low-spin and high-spin states, was reported in 2011 by Garcia and co-workers.<sup>18</sup> SQUID magnetometry revealed a sharp [HS–HS] to [LS–LS] transition with  $T_{1/2} = 150$  K (Fig. 4a) and the complex was also structurally

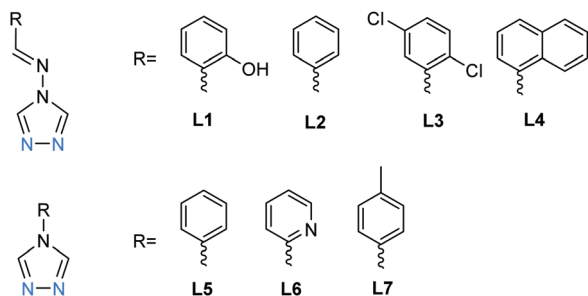


Chart 1 The seven ligands, **L1–L7**, all of which are  $N^4$ -substituted 1,2,4-triazoles, reported in the literature to form SCO-active triply-triazole bridged dinuclear complexes.

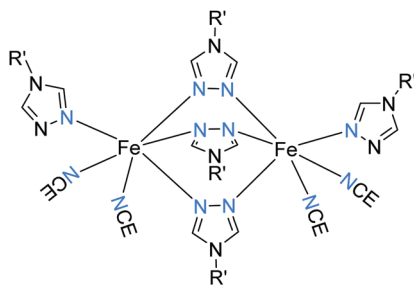


Fig. 3 Schematic representation of  $[\text{Fe}_2\text{L}_5(\text{NCE})_4]$  where  $\text{L} = \text{L1-L7}$ ,  $\text{E} = \text{S}$  or  $\text{Se}$  ( $\text{L} = \text{L4}$ ).

characterised in both spin states, at 100 and 200 K respectively (Table 1). DSC measurements showed a single phase transition at  $T_{\text{max}} = 155$  K (Fig. 4a inset). The SCO event was also able to be monitored by variable temperature fluorescence of the enol, as a bathochromic shift of 20 nm is observed in the emission band across the temperature range of 135–179 K (Fig. 4b).

Fresh crystals of  $[\text{Fe}_2\text{L2}_5(\text{NCS})_4]\cdot 5\text{MeOH}$  showed a gradual, approximately half, SCO centred at 115 K.<sup>50</sup> In contrast, a bulk powder sample of unsolvated  $[\text{Fe}_2\text{L2}_5(\text{NCS})_4]$  remained [HS–HS] to low temperature. By introducing electron withdrawing chloride substituents (**L3**, Chart 1), the ligand field was adjusted, giving a more complete spin transition, with  $T_{1/2} = 150$  K. The LIESST (light-induced excited spin state trapping) effect was also seen for the  $[\text{Fe}_2\text{L3}_5(\text{NCS})_4]$  system: irradiating with 532 nm light at 5 K the  $\chi_{\text{m}}T$  value increased abruptly to  $4.6 \text{ cm}^3 \text{ K mol}^{-1}$ , which was attributed to SCO of the two Fe(II) centres from LS to HS\*, with a  $T_{(\text{LIESST})}$  of 61 K.<sup>48</sup>

Liu and co-workers used a naphthalene group as the  $N^4$  substituent, generating  $[\text{Fe}_2\text{L4}_5(\text{NCS})_4]\cdot 2\text{DMF}\cdot 2\text{H}_2\text{O}$  (**L4**, Chart 1) which showed an abrupt [HS–HS] to [LS–LS] SCO with  $T_{1/2} = 164$  K (Fig. 5a).<sup>49</sup> They also studied the photoinduced SCO. Upon irradiation with 532 nm light at 10 K for 2 h,  $\chi T$  increased max. to  $2.5 \text{ cm}^3 \text{ K mol}^{-1}$  at 48 K, consistent with the LS Fe(II) centres undergoing partial conversion to metastable HS\*. At 10 K, cycles of irradiation at 532 nm followed by irradiation at 808 nm switched the  $\chi T$  value reversibly between 1.23 to  $0.47 \text{ cm}^3 \text{ K mol}^{-1}$  implying reversible SCO between metastable HS\* and LS (Fig. 5b).<sup>49</sup>

Wang and co-workers studied the effect of differing solvents of crystallisation, comparing  $[\text{Fe}_2\text{L5}_5(\text{NCS})_4]\cdot \text{MeOH}\cdot \text{EtOH}$  and  $[\text{Fe}_2\text{L5}_5(\text{NCS})_4]\cdot 2\text{EtOH}$  and showing that the  $T_{1/2}$  value for the observed half SCO increased slightly, from 116 K to 122 K.<sup>51</sup> Changing the  $N^4$  substituent from phenyl (**L5**) to 2-pyridyl (**L6**, Chart 1) resulted in a negligible effect magnetically, with the  $T_{1/2}$  remaining at 116 K.<sup>52</sup> In contrast, changing from a phenyl (**L5**) to *p*-tolyl (**L7**)<sup>53</sup>  $N^4$  substituent (Chart 1), had a dramatic impact, with two dinuclear  $\text{Fe}_2\text{L7}_5(\text{NCS})_4$  units bridged by hydrogen bonding to the coordinated water molecules of a mononuclear  $\text{FeL7}_2(\text{NCS})_2(\text{H}_2\text{O})_2$  unit. But the magnetic behaviour of the resulting material is not much different from other triply triazole bridged dinuclear Fe(II) complexes; it undergoes SCO centred at 111 K, with variable temperature magnetometry and Mössbauer spectroscopy both consistent with four out of five Fe(II) centres transitioning from HS to LS, *i.e.* the dinuclear  $\text{Fe}_2\text{L7}_5(\text{NCS})_4$  units are SCO-active while the mononuclear  $\text{FeL7}_2(\text{NCS})_2(\text{H}_2\text{O})_2$  unit remains HS to low temperature.<sup>53</sup>

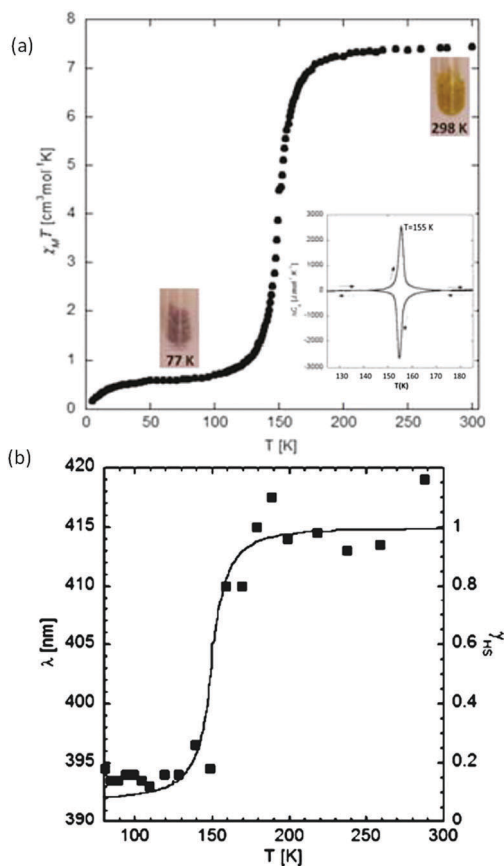
### Dinuclear triply stranded helicates $\text{Fe}_2\text{L}_3$

The other type of triply bridged dinuclear Fe(II) SCO-active complex is the helicate architecture,  $\text{Fe}_2(\text{L})_3$  (Fig. 2, 2A). Helicates are made through controlled and predictable self assembly of carefully designed components. They are intrinsically stable, and have wide ranging properties owing to their versatility with respect to choice of metal ion.<sup>54–60</sup> Through careful design of the polydentate ligand, the cavity of such helicates can be optimised for favourable host–guest interactions, which can



**Table 1** Selected parameters for SCO-active triply-triazole bridged dinuclear Fe(II) complexes (Fig. 2, 2A). LS centres in italics

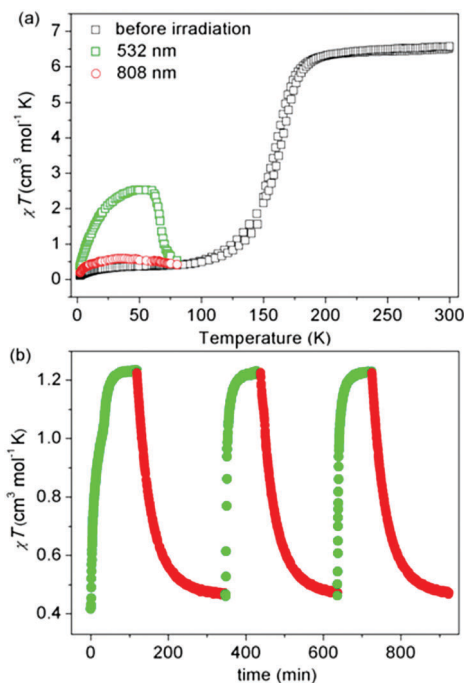
| Complex   | <i>T</i> (K) | Fe–Fe (Å) | $\Sigma$ (°) | Spin state | <i>T</i> <sub>1/2</sub> (K) | Lit. |
|---|--------------|-----------|--------------|------------|-----------------------------|------|
| [Fe <sub>2</sub> L1 <sub>5</sub> (NCS) <sub>4</sub> ] <sub>4</sub> ·4MeOH   | 100          | 3.65      | 15           | 2LS        | 150                         | 18   |
| [Fe <sub>2</sub> L2 <sub>5</sub> (NCS) <sub>4</sub> ] <sub>4</sub> ·3.5MeOH   | 100          | 3.97      | 19           | 2HS        | 115                         | 50   |
|   | 250          | 3.97      | 23/23        | HS–HS      |                             |      |
| [Fe <sub>2</sub> L3 <sub>5</sub> (NCS) <sub>4</sub> ] <sub>4</sub> ·H <sub>2</sub> O  | 100          | 3.72      | 13/13        | LS–LS      | 150                         | 48   |
|   | 180          | 3.96      | 17/35        | LS–HS      |                             |      |
| [Fe <sub>2</sub> L4 <sub>5</sub> (NCSe) <sub>4</sub> ] <sub>4</sub> ·2DMF·2H <sub>2</sub> O                                   | 92           | 3.63      | 12/13        | LS–LS      | 164                         | 49   |
|   | 280          | 3.95      | 24/20        | HS–HS      |                             |      |
| [Fe <sub>2</sub> L5 <sub>5</sub> (NCS) <sub>4</sub> ] <sub>4</sub> ·MeOH·EtOH   | 100          | 3.92      | 19/24        | LS–HS      | 116                         | 51   |
|   | 296          | 3.99      | 16/26        | HS–HS      |                             |      |
| [Fe <sub>2</sub> L5 <sub>5</sub> (NCS) <sub>4</sub> ] <sub>4</sub> ·2EtOH   | 296          | 3.97      | 14/19        | HS–HS      | 122                         | 51   |
| [Fe <sub>2</sub> L6 <sub>5</sub> (NCS) <sub>4</sub> ] <sub>4</sub> ·MeOH·EtOH   | 173          | 3.92      | 19/24        | LS–HS      | 116                         | 52   |
| 2[Fe <sub>2</sub> L7 <sub>5</sub> (NCS) <sub>4</sub> ][FeL7 <sub>2</sub> (NCS) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] | 295          | 3.94      | 23/24/8      | HS–HS, HS  | 111                         | 53   |



**Fig. 4** Data obtained on [Fe<sub>2</sub>L<sub>5</sub>(NCS)<sub>4</sub>]<sub>4</sub>·4MeOH: (a) plot of  $\chi_m T$  vs. *T*. The inset shows the DSC peaks, both exothermic and endothermic. (b)  $\lambda_{\max}$  of the emission spectrum vs. *T* (black dots), follows the  $\gamma_{\text{HS}}$  determined from the SQUID data (solid line). (a) Adapted and (b) reproduced with permission from ref. 18. Copyright 2011 ACS.

dictate the self-assembly process, and can also be exploited for tuning of the metal ion properties.<sup>61–65</sup> In line with the theme of this review, only Fe(II) examples of this architecture which are SCO-active are discussed herein.

A reliable route to such helicates is the 2 : 3 combination of octahedral Fe(II) ions and bis-bidentate linker ligands to give dinuclear Fe<sub>2</sub>L<sub>3</sub> helicates, of which only a handful of examples, 14, have been reported to be SCO-active. Indeed only nine



**Fig. 5** Data obtained on [Fe<sub>2</sub>L<sub>4</sub><sub>5</sub>(NCSe)<sub>4</sub>]<sub>4</sub>·2DMF·2H<sub>2</sub>O: (a)  $\chi T$  vs. *T* (black), including before and after irradiation at 10 K at the stated wavelengths (green and red). (b)  $\chi T$  vs. time during cycles of successive irradiation at 532 nm (green) and 808 nm (red) at 10 K. (a and b) Reproduced with permission from ref. 49. Copyright 2017 ACS.

ligands (Chart 2) have been used to produce all of the SCO-active Fe<sub>2</sub>L<sub>3</sub> helicates reported to date,<sup>61,66–72</sup> the first of which was reported in 1998.<sup>66</sup> In these helicates the three ligands provide all of the donor atoms to the two Fe(II) centres which results in greatly increased  $\Sigma$  values (54–94°, Table 2; 64–159°, Table 3; 59–116°, Table 4) compared to those in the triply bridged triazoles with monodentate co-ligands (12–35°, Table 1).

Williams and co-workers reported the first SCO-active Fe(II) dinuclear triply stranded helicate, based on the bis[2-(pyrid-2'-yl)benzimidazol-5-yl]methane ligand L8 (Chart 2).<sup>66,73</sup> The SCO was monitored in CD<sub>3</sub>CN solution by the Evans method, and revealed a gradual and far from complete spin transition over the measured temperature range (240–330 K). Interestingly, the mononuclear analogue of the 2-(pyrid-2-yl)benzimidazole



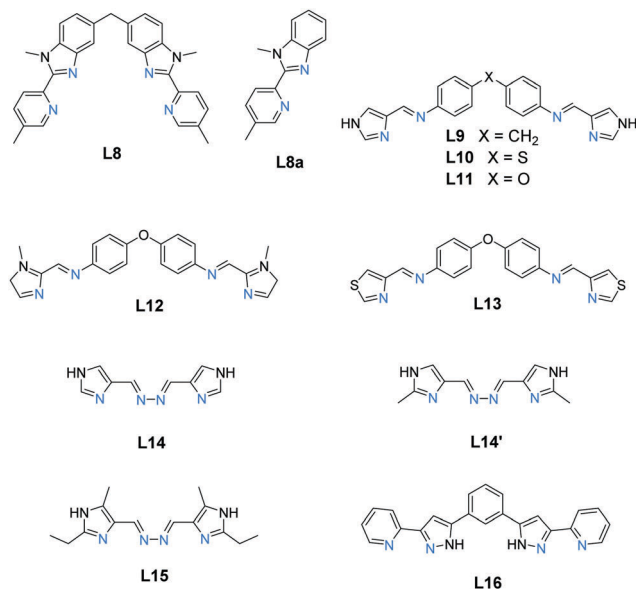


Chart 2 The nine ligands, **L8–L16**, reported in the literature to form SCO-active  $\text{Fe}_2\text{L}_3$  helicates. All are bis-bidentate and provide  $\text{N}_6$  donor sets to the octahedral  $\text{Fe}(\text{II})$  metal ions.

“half” ligand,  $[\text{FeL8a}_3](\text{ClO}_4)_2$ , was also studied, and it was found that the LS state is better stabilised in the dinuclear  $[\text{Fe}_2(\text{L8})_3]^{4+}$  helicate than in mononuclear  $[\text{FeL8a}_3](\text{ClO}_4)_2$ .

A family of  $[\text{Fe}_2(\text{L9})_3]\text{X}_4$  helicates prepared using a neutral bis-imidazoleimine ligand which features a central methylene linker (**L9**, Chart 2; bis-imine made from 4(5)-imidazolecarboxaldehyde and 4,4'-methylenedianiline) was reported by Hannon and co-workers in 2004 (Fig. 6a).<sup>67</sup> Variation of the counter-anion X ( $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ) led to different solid state SCO behaviours being observed (Fig. 6b). While the use of  $\text{PF}_6^-$  or  $\text{BF}_4^-$  resulted in SCO transitions from fully HS to ~20% HS, centred at approximately 200 K and 150 K respectively, the  $\text{ClO}_4^-$  analogue underwent a HS to ~50% HS transition, *i.e.* half SCO, centred around 150 K (Fig. 6b). Subsequent Mössbauer experiments indicated that for  $[\text{Fe}_2\text{L9}_3](\text{ClO}_4)_4$ , the half SCO occurs *via* half of the helicates undergoing a complete [HS–HS] to [LS–LS] transition and the other half remaining [HS–HS], giving 1:1 [HS–HS]:[LS–LS], as no localised [HS–LS] species was detected.<sup>74</sup>

The ditopic ligand scaffold of **L9** is well predisposed to forming  $\text{Fe}_2\text{L}_3$  helicates, so it is unsurprising that several more recent examples of SCO-active complexes have employed thioether and ether analogues of **L9**, **L10–L13** (Chart 2).

Li and co-workers recently reported the  $\text{Fe}_2\text{L}_3$  helicates of the most closely related thioether and ether analogues of **L9**, **L10** and **L11**, which differ only in the linker (methylene *vs.* thioether *vs.* ether), whilst providing the same imidazole-imine binding pocket.<sup>71</sup> The magnetic properties of  $[\text{Fe}_2(\text{L10})_3](\text{BF}_4)_4$  and  $[\text{Fe}_2(\text{L11})_3](\text{BF}_4)_4$  were compared to that of a re-synthesised sample of the  $[\text{Fe}_2(\text{L9})_3](\text{BF}_4)_4$  helicate originally reported by Hannon and co-workers. All three samples were found to undergo a [HS–HS]  $\rightarrow$  [HS–LS] transition with a 15 K wide hysteresis loop, but with  $T_{1/2}$  values which varied by 40 K. Changing the linker

group of the ligand from methylene to thioether to ether was shown to influence the crystal packing and the intramolecular Fe–Fe separation varied by up to 0.16 Å (Table 2) and the inter-helicate Fe–Fe separation by up to 0.75 Å. But these structural differences were difficult to correlate to the SCO behaviours, which are possibly influenced more heavily by harder to predict inter-helicate interactions *e.g.* CH– $\pi$  or hydrogen bonding interactions. This is perhaps illustrated by the differences in the packing and SCO of  $[\text{Fe}_2(\text{L9})_3](\text{BF}_4)_4$  seen in the reports of Hannon *versus* Li. While Hannon crystallised  $[\text{Fe}_2(\text{L9})_3](\text{BF}_4)_4$  from acetonitrile by diisopropyl ether vapour diffusion and observed a hydrogen bonded 2D network of helicates (through imidazole-NH and  $\text{BF}_4^-$  counteranions) which exhibited abrupt SCO,<sup>67</sup> Li crystallised the material by diethyl ether vapour diffusion, observed no hydrogen-bonded network, and a less abrupt SCO.<sup>71</sup>

While most SCO-active  $\text{Fe}_2\text{L}_3$  helicates exhibit [HS–HS] to 50% HS transitions (half SCO), a desolvated  $[\text{Fe}_2(\text{L12})_3](\text{ClO}_4)_4$  complex based on the methylimidazole analogue of **L11**, **L12** (Chart 2, bis-imine made from 1-methyl-2-imidazole-carboxaldehyde and 4,4'-oxydianiline), was shown by Kruger and co-workers to undergo a complete SCO (Fig. 7b).<sup>69</sup> The  $\chi T$  value at 300 K was  $6.6 \text{ cm}^3 \text{ K mol}^{-1}$ , consistent with two uncoupled HS  $\text{Fe}(\text{II})$  ions. At 80 K, all HS transit into LS with  $T_{1/2}$  140 K. At low temperature, a metastable fully [HS–HS] state can be populated by light irradiation, providing a remarkable example of the LIESST effect. Subsequently, when the complex was instead obtained as  $[\text{Fe}_2\text{L12}_3](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ , only half SCO was achieved, and the  $T_{1/2}$  value was found to be dependent on the degree of hydration, thus the helicate exhibits moisture-sensitive SCO.<sup>75</sup>

In 2018, Li and co-workers went on to report the  $[\text{Fe}_2(\text{L13})_3](\text{BF}_4)_4$  helicate of a thioazoly-imine analogue, **L13**, of the ligand **L11** (Chart 2).<sup>72</sup> The complex,  $[\text{Fe}_2(\text{L13})_3](\text{BF}_4)_4$ , was structurally characterised in the [LS–LS] state at 100 K, and again at 298 K at which temperature it showed slightly increased Fe–N bond lengths and octahedral distortion parameter at one of the  $\text{Fe}(\text{II})$  centres, consistent with slight population of a [HS–LS] state. Indeed, the magnetic data show that at 298 K there is an onset of a SCO, which becomes complete above room temperature, with  $T_{1/2} = 348 \text{ K}$ . This complete [LS–LS] to [HS–HS] SCO was also observed by X-ray photoelectron spectroscopy (XPS). This report provides a nice example of deliberately tuning the  $T_{1/2}$  of a SCO-active complex, in this case by ~200 K, by changing the ligand field strength of these ether linked ditopic ligands upon changing the terminal imidazole group of the **L11** and **L12** ligands to the stronger ligand field thiazole group of **L13** (Chart 2).

Abrupt SCO was achieved for two complexes of a ‘tight’  $\text{Fe}_2\text{L}_3$  helicate architecture derived from the relatively short **L14** ligand (Chart 2) reported by Sunatsuki, Kojima, and co-workers.<sup>68</sup> This short, conjugated, ditopic **L14** ligand is prepared by the 2:1 condensation of imidazole-4-carbaldehyde with hydrazine hydrate. In order to bind in a bis-bidentate manner, and provide a two-atom NN bridge between the two iron(II) centres, the ligand twists significantly away from being flat, forming the triple



**Table 2** Selected parameters for SCO-active triply-stranded helicate dinuclear Fe(II) complexes (Fig. 2, 2A). LS centres in italics

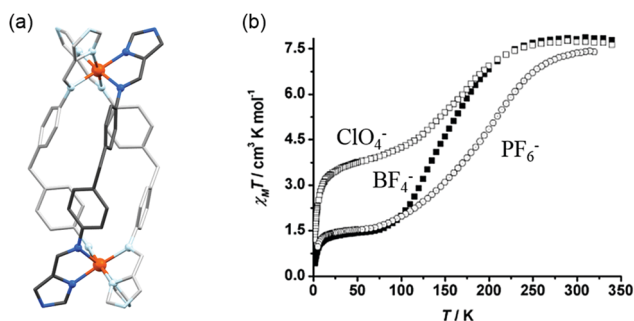
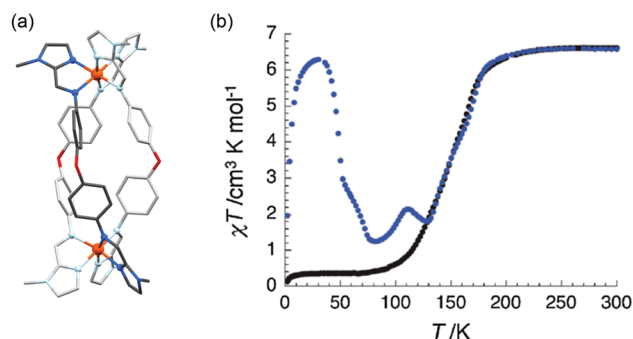
|   | <i>T</i> (K) | $\Sigma$ (°) | Fe–Fe (Å) | Spin state | <i>T</i> <sub>1/2</sub> (K) | Lit.      |
|---|--------------|--------------|-----------|------------|-----------------------------|-----------|
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L8</b> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>4</sub>                       | 295          | 62           | 9.16      | 2LS        | 341, 402                    | 66 and 73 |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L9</b> ) <sub>3</sub> ](PF <sub>6</sub> ) <sub>4</sub>                        | 180          | 64           | 11.40     | 2LS        | Not stated                  | 67        |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L9</b> ) <sub>3</sub> ](BF <sub>4</sub> ) <sub>4</sub>                        | 180          | 63, 83       | 11.56     | LS–HS      | Not stated                  |           |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L9</b> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>4</sub>                       | 180          | 76, 94       | 11.58     | HS–HS      | Not stated                  |           |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L9</b> ) <sub>3</sub> ](BF <sub>4</sub> ) <sub>4</sub>                        | 100          | 76           | 11.71     | 2HS/LS     | ↓155<br>↑170                | 71        |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L10</b> ) <sub>3</sub> ](BF <sub>4</sub> ) <sub>4</sub>                       | 100          | 60, 90       | 11.78     | LS–HS      | ↓115<br>↑130                | 71        |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L11</b> ) <sub>3</sub> ](BF <sub>4</sub> ) <sub>4</sub>                       | 100          | 84.9, 74.5   | 11.62     | HS–HS/LS   | ↓150<br>↑165                | 71        |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L12</b> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·2MeCN               | 150          | 65, 62       | 11.45     | LS–LS      | 140                         | 69        |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L12</b> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·1.5H <sub>2</sub> O | 150          | 62, 85       | 11.45     | LS–HS      | 210–265                     | 75        |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L13</b> ) <sub>3</sub> ](BF <sub>4</sub> ) <sub>4</sub>                       | 100          | 54, 65       | 11.33     | LS–LS      | 348                         | 72        |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L13</b> ) <sub>3</sub> ](BF <sub>4</sub> ) <sub>4</sub>                       | 298          | 58, 70       | 11.36     | LS–LS/HS   |                             |           |

**Table 3** Selected parameters for SCO-active triply-stranded 'tight' helicate dinuclear Fe(II) complexes (Fig. 2, 2A) of the 'short' **L14**–**L15** ligands (Chart 2). LS centres in italics

|  | <i>T</i> (K) | $\Sigma$ (°) | Fe–Fe (Å) | Spin state | <i>T</i> <sub>1/2</sub> (K) | Lit. |
|--|--------------|--------------|-----------|------------|-----------------------------|------|
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L14</b> ) <sub>3</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2MeNO <sub>2</sub> ·1H <sub>2</sub> O | 173          | 66, 159      | 3.87      | LS–HS      | ↑190<br>↓183                | 68   |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L14</b> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·5MeNO <sub>2</sub>                   | 103          | 64, 152      | 3.85      | LS–HS      | 240                         |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L15</b> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·3MeCN·0.5H <sub>2</sub> O (plate)    | 163          | 116, 124     | 4.04      | HS–HS      |                             | 70   |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>L15</b> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·2MeCN (block)                        | 113          | 132, 135     | 4.178     | HS–HS      | HS                          | 70   |

**Table 4** Selected parameters for SCO-active triply-stranded helicate dinuclear Fe(II) complexes (Fig. 2, 2A) of the **L16** ligand (Chart 2) which can encapsulate a halide ion. LS centres in italics

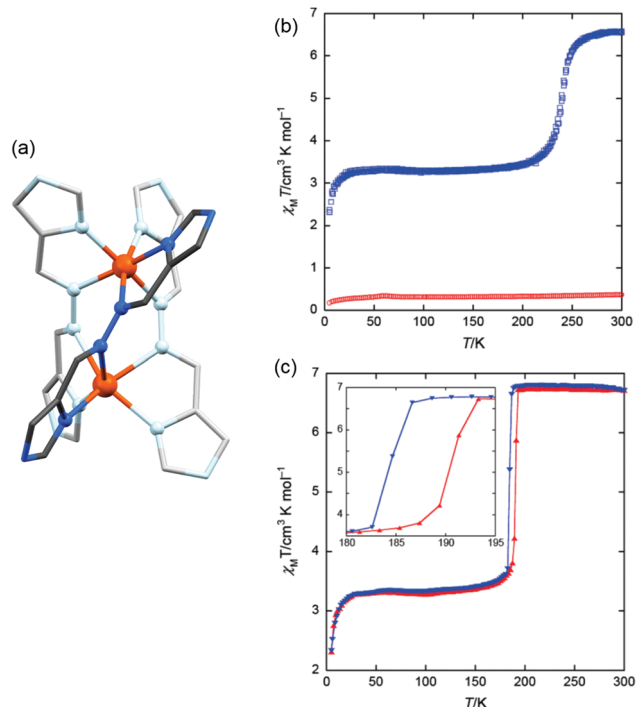
|  | <i>T</i> (K) | $\Sigma$ (°) | Fe–Fe (Å) | Spin state | <i>T</i> <sub>1/2</sub> (K) | Lit. |
|--|--------------|--------------|-----------|------------|-----------------------------|------|
| Cl@[Fe <sub>2</sub> ( <b>L16</b> ) <sub>3</sub> ]Cl(PF <sub>6</sub> ) <sub>2</sub> ·5.7MeOH                | 100          | 116, 59      | 9.73      | HS–LS      | 302                         | 61   |
|  | 280          | 113, 62      | 9.73      | HS–LS      |                             |      |
| Cl@[Fe <sub>2</sub> ( <b>L16</b> ) <sub>3</sub> ]Cl(PF <sub>6</sub> ) <sub>2</sub> ·3MeOH·H <sub>2</sub> O | 90           | 62           | 9.67      | 2LS        | 160, 265                    |      |
|  | 300          | 95           | 9.80      | 2HS        |                             |      |
| Br@[Fe <sub>2</sub> ( <b>L16</b> ) <sub>3</sub> ]Br(PF <sub>6</sub> ) <sub>2</sub> ·4MeOH                  | 100          | 114, 61      | 9.67      | HS–LS      | 258                         |      |
|  | 280          | 110, 84      | 9.70      | HS–HS      |                             |      |
| Br@[Fe <sub>2</sub> ( <b>L16</b> ) <sub>3</sub> ]Br(PF <sub>6</sub> ) <sub>2</sub> ·MeOH·H <sub>2</sub> O  | 90           | 64           | 9.69      | 2LS        | 200                         |      |
|  | 296          | 97           | 9.79      | 2HS        |                             |      |

**Fig. 6** Data obtained on the family of three [Fe<sub>2</sub>(**L9**)<sub>3</sub>]X<sub>4</sub> helicates: (a) the structure of the [Fe<sub>2</sub>(**L9**)<sub>3</sub>]<sup>4+</sup> cation. (b)  $\chi_M T$  vs. *T* for the [Fe<sub>2</sub>(**L9**)<sub>3</sub>]X<sub>4</sub> helicates where X = PF<sub>6</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup> or ClO<sub>4</sub><sup>−</sup>. Structure redrawn from CCDC data.<sup>67</sup> (b) Adapted with permission from ref. 67. Copyright 2004 John Wiley and Sons.**Fig. 7** Data obtained on [Fe<sub>2</sub>(**L12**)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub> (a) structure of the [Fe<sub>2</sub>(**L12**)<sub>3</sub>]<sup>4+</sup> cation. (b) Thermal SCO (black data) and LIESST (blue data) behaviour of desolvated [Fe<sub>2</sub>(**L12**)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>. Structure redrawn from CCDC data.<sup>69</sup> (b) Adapted with permission from ref. 69. Copyright 2009 RSC.

helicate complex, [Fe<sub>2</sub>(**L14**)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub> (Fig. 8a) with very short Fe–Fe distances  $\sim 4$  Å (Table 3) for a helicate (Tables 2 and 4).

This undergoes an abrupt [HS–HS] to 50% HS transition at 240 K (Fig. 8b, blue data), while the BF<sub>4</sub><sup>−</sup> analogue has a lower *T*<sub>1/2</sub>,



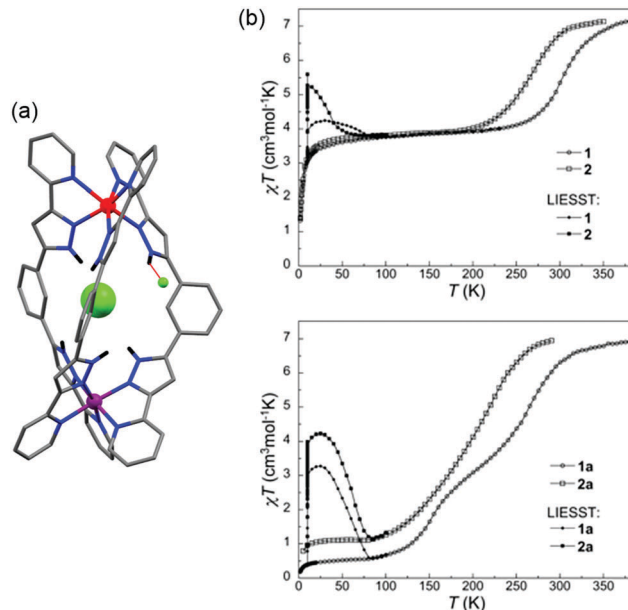


**Fig. 8** Data obtained on  $[\text{Fe}_2(\text{L14})_3](\text{ClO}_4)_4$ ,  $[\text{Fe}_2(\text{L14})_3](\text{BF}_4)_4$  and  $[\text{Fe}_2(\text{L14}')_3](\text{ClO}_4)_4$ : (a) structure of the cation of the  $[\text{Fe}_2(\text{L14})_3]^{4+}$  helicate. (b)  $\chi_M T$  vs.  $T$  for  $[\text{Fe}_2(\text{L14})_3](\text{ClO}_4)_4$  in blue, and the methylimidazole analogue,  $[\text{Fe}_2(\text{L14}')_3](\text{ClO}_4)_4$  helicate, in red. (c)  $\chi_M T$  vs.  $T$  for  $[\text{Fe}_2(\text{L14})_3](\text{BF}_4)_4$ . Structure redrawn from CCDC data.<sup>68</sup> (b and c) Reproduced with permission from ref. 68. Copyright 2009 ACS.

at 190 K, with a hysteresis loop 7 K wide (2 K  $\text{min}^{-1}$  scan rate) (Fig. 8c). The methylimidazole analogue of L14, L14' results in a [LS-LS] complex (no SCO) in the analogous perchlorate complex,  $[\text{Fe}_2(\text{L14}')_3](\text{ClO}_4)_4$  (Fig. 8b, red data), which the authors attribute to being a direct result of tuning of the ligand field by introduction of an electron donating group to the ligand scaffold.

A follow-up publication from the same authors reported the SCO-active dinuclear helicate  $[\text{Fe}_2(\text{L15})_3](\text{ClO}_4)_4$ -solvents based on the (electron donating) ethyl/methyl substituted analogue, L15, of the bis-imidazole ligand L14 (Chart 2).<sup>70</sup>  $[\text{Fe}_2(\text{L15})_3](\text{ClO}_4)_4$ -solvents crystallised as two solvatomorphs, block shaped and plate crystals, both of which were structurally characterised (Table 3). The plate crystals,  $[\text{Fe}_2(\text{L15})_3](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ , undergo a half SCO from [HS-HS] to [HS-LS] at 120 K, with a localised [HS-LS] state confirmed by X-ray crystallography, and no [LS-LS] state is accessible. On the other hand, the block shape crystals,  $[\text{Fe}_2(\text{L15})_3](\text{ClO}_4)_4 \cdot \frac{1}{2} \text{CH}_3\text{CN}$ , remain [HS-HS] to low temperature, as observed by SQUID magnetometry and X-ray crystallography. These results highlight the large influence that crystal packing and/or lattice solvent content can have on the SCO properties of a system, in this case overruling the expected electronic influence of methyl/ethyl substituents.

An example of a SCO-active  $\text{Fe}_2\text{L}_3$  helicate which is triply switchable – by temperature, light, and guests – was reported by Aromi and co-workers in 2016.<sup>61</sup> Here the ligand strand, L16 (Chart 2), consists of two bidentate pyrazole-pyridine units,



**Fig. 9** (a) [HS-LS]  $\{\text{Cl}@[\text{Fe}_2(\text{L16})_3]\text{Cl}(\text{PF}_6)_2 \cdot 5.7\text{MeOH}\}$  structure ( $\text{PF}_6^-$  anions and solvents omitted), showing the encapsulated  $\text{Cl}^-$  (spacefill) nearer the HS  $\text{Fe}(\text{II})$  (red) than the LS  $\text{Fe}(\text{II})$  (purple), and also the external  $\text{Cl}^-$  which interacts with one pyrazole NH closer to HS  $\text{Fe}(\text{II})$  (red dashed line). (b) Thermal SCO and LIESST effect of the helicates  $\{\text{Cl}@[\text{Fe}_2(\text{L16})_3]\text{Cl}(\text{PF}_6)_2 \cdot 5.7\text{MeOH}\}$  (**1** in this figure) and  $\{\text{Br}@[\text{Fe}_2(\text{L16})_3]\text{Br}(\text{PF}_6)_2 \cdot 4\text{MeOH}\}$  (**2** in this figure), and the corresponding SCSC generated helicates  $\{\text{Cl}@[\text{Fe}_2(\text{L16})_3]\text{Cl}(\text{PF}_6)_2 \cdot 3\text{MeOH} \cdot \text{H}_2\text{O}\}$  (**1a** in this figure) and  $\{\text{Br}@[\text{Fe}_2(\text{L16})_3]\text{Br}(\text{PF}_6)_2 \cdot \text{MeOH} \cdot \text{H}_2\text{O}\}$  (**2a** in this figure). Structure redrawn from CCDC data.<sup>61</sup> (b) Reproduced with permission from ref. 61. Copyright 2016 John Wiley and Sons.

linked by a central 1,3-benzene group, and features two internally facing 'spare' NH moieties. Due to these NH groups, the resulting triply stranded dinuclear helicates,  $\{\text{X}@[\text{Fe}_2(\text{L16})_3]\text{X}(\text{PF}_6)_2$  ( $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ ), can encapsulate a halide counteranion. One halide ion is encapsulated inside the cavity defined by the three ligand strands and the other is external (Fig. 9a). For the as-synthesised helicate structures, the encapsulated halide ion interacts with the six pyrazole rings through hydrogen bonding to the internally facing NH moieties, and is closer to one of the two  $\text{Fe}(\text{II})$  centres. The external halide counteranion is closer to the same  $\text{Fe}(\text{II})$  centre, and has one  $\text{X} \cdots \text{H}-\text{N}$  interaction with a pyrazole ring. These out-of-sphere interactions stabilise this  $\text{Fe}(\text{II})$  centre in the HS state down to low temperatures, and, as such, only a half SCO, to a localised [HS-LS] state, as determined by an X-ray structure determination at 100 K (Fig. 9a), is observed (Table 4).

The  $\text{X} = \text{Cl}^-$  and  $\text{X} = \text{Br}^-$  helicates are isostructural, with the only difference being the nature of the encapsulated/external halide ions, yet the  $T_{1/2}$  of the SCO is shifted down by 40 K on changing from  $\text{X} = \text{Cl}^-$  to  $\text{Br}^-$ , highlighting the significant impact of the out-of-sphere interactions on the ligand field strength and hence SCO properties. In both compounds, a single crystal to single crystal (SCSC) transformation of the helicate, by partial methanol solvent loss and uptake of water, results in the encapsulated halide ions being equidistant to the two  $\text{Fe}(\text{II})$  centres, thus breaking the structural non-equivalence, and full



[HS–HS] to [LS–LS] SCO is observed (Fig. 9b and Table 4). Attempts to encapsulate the larger  $\Gamma^-$  anion were unsuccessful and instead yielded complexes with external  $\text{I}_3^-$  counteranions. These persisted in the [HS–HS] state to low temperatures.

### Doubly stranded dinuclear helicates, $\text{Fe}_2\text{L}_2$

While there are numerous examples of SCO-active dinuclear  $\text{Fe}(\text{II})$  triply stranded helicates made from bis-bidentate ligands, doubly stranded systems are rare (Fig. 2, 2B). For just two ligand strands to complete the octahedral coordination sphere of two octahedral  $\text{Fe}(\text{II})$  centres in a helicate complex, the ditopic ligand must be bis-terdentate. To date, only two such ligands, the neutral 1,2,3-triazole-based ligands **L17** and **L18** (Chart 3), have been reported to give SCO-active  $\text{Fe}_2\text{L}_2$  helicates.<sup>76,77</sup>

In 2016 Hagiwara, Tanaka and Hora reported the first SCO-active dinuclear double helicate,  $[\text{Fe}_2(\text{L17})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  (Fig. 10a).<sup>76</sup> X-ray structural analysis at 120 K revealed two identical LS  $\text{Fe}(\text{II})$  centres in the dication, and no higher temperature structures could be obtained due to loss of crystallinity upon desorption of lattice solvent molecules. SQUID magnetometry on  $[\text{Fe}_2(\text{L17})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  showed that the helicate remains [LS–LS] to 300 K, but measurements above room temperature revealed an unusual two-step SCO. Upon warming from 300 K to 435 K, the  $\chi_{\text{M}}T$  value increases steadily from

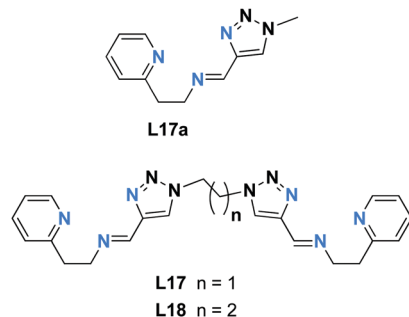


Chart 3 The two ditopic 1,2,3-triazole-based ligands, **L17** and **L18**, known to give dinuclear  $\text{Fe}(\text{II})$  doubly stranded double helicates. Both are bis-terdentate and provide  $\text{N}_6$  donor sets to the octahedral  $\text{Fe}(\text{II})$  metal ions.

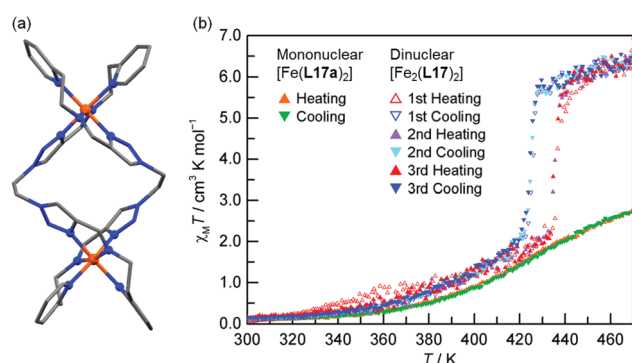


Fig. 10 (a) Structure of the cation  $[\text{Fe}_2(\text{L17})_2]^{4+}$  of  $[\text{Fe}_2(\text{L17})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  (b)  $\chi_{\text{M}}T$  vs.  $T$  for  $[\text{Fe}_2(\text{L17})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  and the mononuclear analogue  $[\text{Fe}(\text{L17a})_2](\text{PF}_6)_2$ . Structure redrawn from CCDC data.<sup>76</sup> (b) Adapted, with permission, from ref. 76. Copyright 2016 RSC.

Table 5 Selected parameters for SCO-active doubly-stranded helicate dinuclear  $\text{Fe}(\text{II})$  complexes (Fig. 2, 2B) of **L17–L18** (Chart 3). LS centres in italics

|   | $T$ (K) | $\Sigma$ ( $^\circ$ ) | Fe–Fe ( $\text{\AA}$ ) | Spin state | $T_{1/2}$ (K)    | Lit. |
|---|---------|-----------------------|------------------------|------------|------------------|------|
| $[\text{Fe}_2^{\text{II}}(\text{L17})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  | 120     | 43                    | 7.85                   | 2LS        | $\uparrow$ 437   | 76   |
|   |         |                       |                        |            | $\downarrow$ 426 |      |
| $[\text{Fe}_2^{\text{II}}(\text{L18})_2](\text{AsF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$ | 120     | 48, 48                | 10.87                  | LS–LS      | $\uparrow$ 485   | 77   |
|   |         |                       |                        |            | $\downarrow$ 401 |      |

0.1 to 2.6  $\text{cm}^3 \text{K mol}^{-1}$ , consistent with a gradual SCO to  $\sim 40\%$  HS (Fig. 10b, red data). An abrupt second step is then observed between 435 and 443 K, with  $\chi_{\text{M}}T$  increasing to 5.6  $\text{cm}^3 \text{K mol}^{-1}$ , before again increasing gradually to 6.5  $\text{cm}^3 \text{K mol}^{-1}$  at 470 K (Fig. 10b, red data), consistent with a [HS–HS] state. In cooling mode (Fig. 10b, blue data), the abrupt transition occurs at 426 K giving the double helicate an 11 K wide hysteresis loop: importantly this behaviour is also shown to be reversible over three cycles (Fig. 10b). Another key component of this report was the comparison of these SCO properties with those of the analogous mononuclear  $\text{Fe}(\text{II})$  complex,  $[\text{Fe}(\text{L17a})_2](\text{PF}_6)_2$ , where **L17a** is a monotopic terdentate ligand with a  $\text{CH}_3$  group in place of the ethylene linker of **L17**.  $[\text{Fe}(\text{L17a})_2](\text{PF}_6)_2$  undergoes a gradual SCO from LS to HS that is very similar to the first SCO step of  $[\text{Fe}_2(\text{L17})_2](\text{PF}_6)_4$  between 300 and 435 K, however in the mononuclear compound there is no abrupt second step (Fig. 10b green/orange data). This example clearly demonstrates the enhanced SCO properties that can be achieved by linking two  $\text{Fe}(\text{II})$  centres together in a dinuclear complex, in this case by simply joining two SCO-active mononuclear units through an ethylene linker. The resulting dinuclear double helicate is also remarkable for the high temperature SCO which occurs ( $T_{1/2} \uparrow$  437 and  $T_{1/2} \downarrow$  426 K) with an 11 K thermal hysteresis loop.

In a follow-up study, Hagiwara and Hora changed the linker length in the ligand from ethylene in **L17** to propylene in **L18**, and assembled the second example of an SCO-active double helicate,  $[\text{Fe}_2(\text{L18})_2](\text{AsF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$ .<sup>77</sup> The change in linker from ethylene (**L17**) to propylene (**L18**) has changed the Fe–Fe distance from 7.85 to 10.87  $\text{\AA}$  (Table 5). This new double helicate is also [LS–LS] at 300 K, but above room temperature it undergoes an abrupt SCO to [HS–HS] with a remarkably wide hysteresis loop of 84 K ( $T_{1/2} \uparrow = 485 \text{ K}$ ,  $T_{1/2} \downarrow = 401 \text{ K}$ ). But in this case, upon further cycling in the SQUID, the SCO becomes more gradual and the hysteresis loop becomes narrower, due to lattice solvent loss and/or loss of crystallinity at high temperatures – once again highlighting the sensitivity of polynuclear SCO compounds to crystal packing and solvent content.

The use of these bis-terdentate ligands (Chart 3) results in higher  $T_{1/2}$  values and less distorted  $\text{Fe}(\text{II})$  centres in the resulting doubly-stranded helicates (43–48 $^\circ$ , Table 5), than in the triply-stranded helicates (54–159 $^\circ$ , Tables 2–4) formed using bis-bidentate ligands (Chart 2).

### Dinuclear $\text{Fe}_2\text{L}_2$ : PMRT and related ligands

Grouped together here are a range of bis-terdentate ligands, generated since the first SCO-active complex of such a PMRT-type



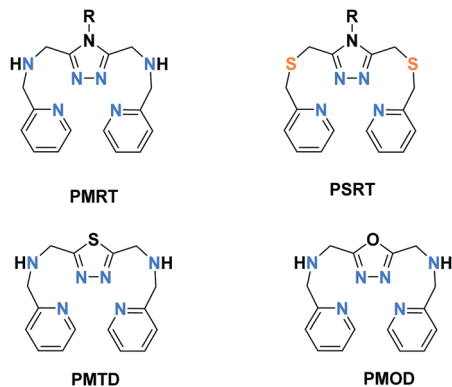


Chart 4 Bis-terdentate **PMRT** and **PSRT** (which vary in the choice of **R**, including **PMAT** where **R** =  $\text{NH}_2$ ) and **PMTD** and **PMOD** ligands.

ligand was reported in 2005,<sup>10</sup> that provide an  $\text{N}^1\text{N}^2$ -bridge (of a five-membered heterocycle) between the binding pockets (Chart 4) forming doubly-bridged  $\text{Fe}_2\text{L}_2$  complexes (Fig. 2, 2B).

Of these ligands (Chart 4), the bis-terdentate 4-substituted-3,5-bis-[(2-pyridylmethyl)-amino]methyl)-4H-1,2,4-triazole ligands (**PMRT**, Chart 4)<sup>10,78–82</sup> have been widely studied within the present authors group since we first reported them in 2005.<sup>10,78</sup> The bis-terdentate ligand scaffold is strongly predisposed to forming dinuclear complexes. Key features include: two **PMRT** ligands provide all 12 N donors to the two octahedral metal ions, and double triazole bridges between them, and the **R** group can be widely varied (Fig. 2, 2B). The  $[\text{Fe}_2^{\text{II}}(\text{PMAT})_2](\text{BF}_4)_4 \cdot \text{DMF}$  (**PMRT** with **R** =  $\text{NH}_2$ ) complex undergoes an abrupt half-SCO at 224 K. The half SCO was determined to be to a localised [HS–LS] state,<sup>10</sup> rather than a 50:50 mixture of complexes in the [HS–HS] and [LS–LS] states,<sup>83</sup> by X-ray crystallography. The LS Fe(II) centre has a more regular octahedral coordination sphere, and hence a smaller octahedral distortion parameter,  $\Sigma$ , as well as shorter metal–ligand bond lengths (Fig. 11 and Table 6). This was the first report of a crystal structure of a localised mixed spin state dinuclear complex.<sup>10</sup> The localised mixed spin state was later further confirmed by standard Mössbauer spectroscopy, as the HS ion in the [HS–LS] state gave a distinct signal to that of the HS ions in the [HS–HS] state – the first time such a distinction had been made for a dinuclear complex without the use of an applied field.<sup>79</sup>

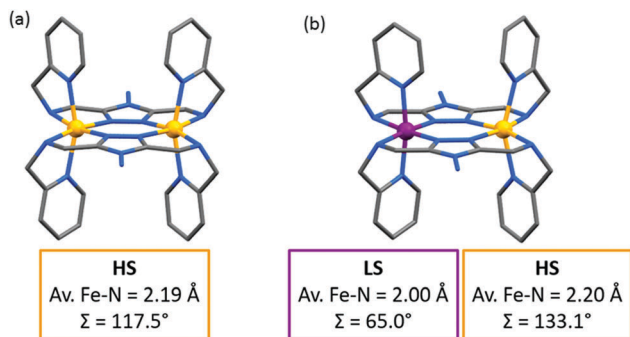


Fig. 11 (a) The [HS–HS] 298 K structure and (b) [HS–LS] 123 K structure of  $[\text{Fe}_2^{\text{II}}(\text{PMAT})_2](\text{BF}_4)_4 \cdot \text{DMF}$ . Structures redrawn from CCDC data.<sup>10</sup>

Variation of the  $\text{N}^4$  substituent, **R**, to give other **PMRT** ligands was shown to greatly affect the SCO properties of the resulting dinuclear iron(II) complexes,  $[\text{Fe}_2^{\text{II}}(\text{PMRT})_2]\text{X}_4$ , despite **R** being physically and electronically (when **R** is a ring it is usually almost at right angles to the triazole, switching off any possible resonance effects) remote from the donor atoms (Fig. 12).<sup>84</sup>

When the **R** group of **PMRT** was the 4-(*tert*-butyl)phenyl group, and specifically only for the solvatomorph  $[\text{Fe}_2^{\text{II}}(\text{PM}^t\text{BuPhT})_2](\text{BF}_4)_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , an abrupt half SCO was observed with a wide thermal hysteresis loop of 22 K – at the time a record equalling hysteresis loop width for a dinuclear complex.<sup>85</sup> Hysteresis loops are a kinetic phenomenon so typically become narrower with a decreasing rate of change of temperature,<sup>6</sup> ultimately closing entirely (but potentially only after a very long time). However, remarkably, upon decreasing the temperature scan rate of the SQUID measurements on  $[\text{Fe}_2^{\text{II}}(\text{PM}^t\text{BuPhT})_2](\text{BF}_4)_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$  only the cooling mode narrows, while the  $T_{1/2}$  of the warming mode is unchanged (Fig. 13).

The family of dinuclear iron(II) complexes of **PMRT** has revealed many interesting SCO features, with highlights including the first example of a localised [HS–LS] state to be identified by X-ray crystallography (Fig. 11) and Mössbauer spectroscopy (no applied field), and an example of unique thermal hysteresis behaviour (Fig. 12). However, in no case could the second potential SCO event, to the [LS–LS] state, be accessed, most probably because of the steric restraint of having all twelve donors to the two iron(II) centres, and two  $\text{N}^1\text{N}^2$ -triazole bridges between them, provided by just two ligands. These features lead to a significantly increased distortion at the HS centre in the [HS–LS] state, over that in the [HS–HS] state, which stabilises the mixed spin state and prevents the second HS centre from undergoing SCO (Table 6). Indeed, even under the immense pressure of 1.03 GPa and at the extremely low temperature of 4 K, the [LS–LS] state was inaccessible for  $[\text{Fe}_2^{\text{II}}(\text{PMAT})_2](\text{BF}_4)_4 \cdot \text{DMF}$ .<sup>82</sup> It is clear that the very constraining **PMRT** ligand family is extremely good at communicating the structural effects that SCO from HS to LS at the first metal ion induces, to the second metal ion such that it becomes even more distorted away from octahedral and therefore remains HS (Table 6).

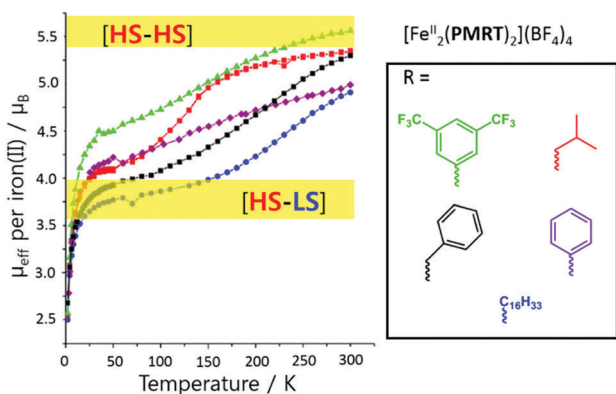
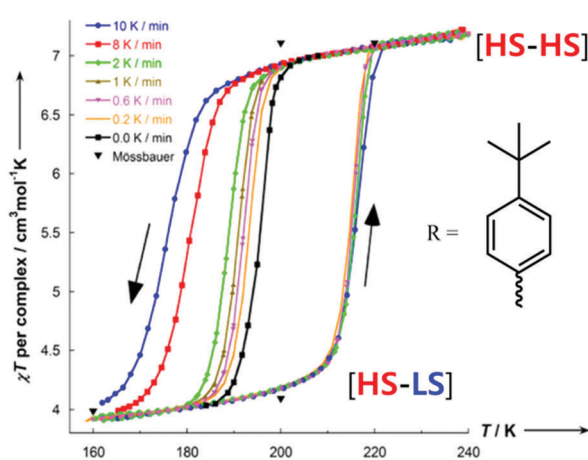
The [LS–LS] state was recently accessed by changing the amino linkages to the pyridine side-arms of **PMRT** to thioether linkages in the **PSRT** family (Chart 4).<sup>86</sup> This change resulted in a more flexible ligand framework, due to longer C–S bonds compared to C–N bonds. In the corresponding  $[\text{Fe}_2(\text{PSRT})_2](\text{BF}_4)_4$  complexes (Fig. 14a), not only was SCO retained upon changing from the  $\text{N}_6$  donor sphere provided by the **PMRT** family to  $\text{N}_4\text{S}_2$ , but, for the first time in complexes of this kind, all three of the possible spin states – [HS–HS], [HS–LS] and [LS–LS] – were accessible.

The complex  $[\text{Fe}_2(\text{PSPht})_2](\text{BF}_4)_4$  in particular had interesting SCO properties, undergoing a multistep [HS–HS]  $\rightarrow$  [HS–LS]  $\rightarrow$  [LS–LS] transition (Fig. 14b). Unfortunately, the  $[\text{Fe}_2(\text{PSRT})_2](\text{BF}_4)_4$  complexes are only SCO active after MeCN solvent loss, which is associated with a loss of crystallinity, and no structural observations of the multistep SCO could be made. From the [HS–HS]

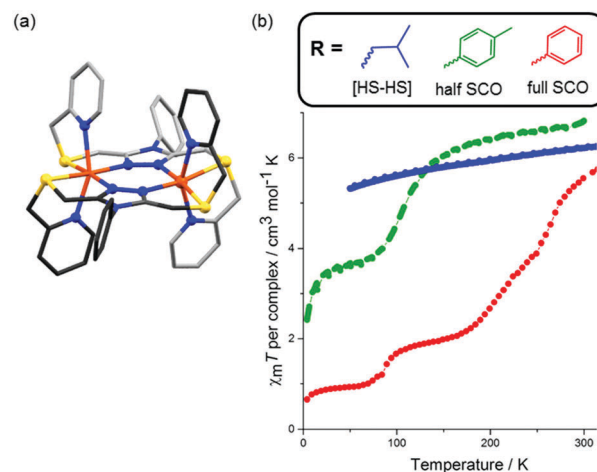


Table 6 Selected parameters for SCO-active doubly-bridged dinuclear Fe(II) complexes (Fig. 2, 2B) of PMRT-type ligands (Chart 4). LS centres in italics

|  | <i>T</i> (K) | $\Sigma$ (°) | Fe-Fe (Å) | Spin state | <i>T</i> <sub>1/2</sub> (K) | Lit. |
|--|--------------|--------------|-----------|------------|-----------------------------|------|
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMAT</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·DMF  | 123          | 65, 133      | 4.212     | LS-HS      | 224                         | 10   |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMBzT</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2CH <sub>3</sub> CN   | 298          | 117          | 4.296     | 2HS        |                             |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMPH</b> <sup>tBu</sup> <b>T</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·3CH <sub>3</sub> CN·0.5Et <sub>2</sub> O | 91           | 99           | 4.178     | 2HS        | 147                         | 84   |
|  | 91           | 118          | 4.262     | 2HS        | ↑ 217<br>↓ 194              | 85   |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PSPht</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2MeCN·H <sub>2</sub> O  | 100          | 110          | 4.216     | 2HS        | 265, 210 and 87             | 86   |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PSPht</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2.5MeCN·0.5H <sub>2</sub> O·THF                                 | 100          | 105          | 4.231     | 2HS        | Not stated                  |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PS</b> <sup>Me</sup> <b>PhT</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2MeCN                                     | 100          | 88           | 4.189     | 2LS/HS     | 109                         |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMTD</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·0.75MeOH·0.5H <sub>2</sub> O                                     | 173          | 58, 65       | 3.946     | LS-LS      | Not stated                  | 88   |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMTD</b> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·0.75MeOH·0.5H <sub>2</sub> O                                    | 173          | 59, 66       | 3.952     | LS-LS      | Not stated                  |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMTD</b> ) <sub>2</sub> ](OTf) <sub>4</sub> ·1.5MeOH·0.5CH <sub>2</sub> Cl <sub>2</sub>                                    | 173          | 61, 58       | 3.948     | LS-LS      | Not stated                  |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMTD</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·4DMF   | 173          | 59, 60       | 3.950     | LS-LS      | 380                         | 89   |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMTD</b> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·4DMF  | 193          | 59, 60       | 3.953     | LS-LS      | 380                         |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMOD</b> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·4MeCN   | 193          | 121          | 4.402     | 2HS        | 150                         | 90   |
|  | 100          | 70, 137      | 4.326     | LS-HS      |                             |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMOD</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2MeCN  | 173          | 126          | 4.378     | 2HS        | Not stated                  |      |
| [Fe <sub>2</sub> <sup>II</sup> ( <b>PMOD</b> ) <sub>2</sub> ](OTf) <sub>4</sub> ·2MeCN   | 193          | 125          | 4.361     | 2HS        | 150                         |      |

Fig. 12 Effective magnetic moment per iron(II) centre vs. *T* for the SCO-active complexes [Fe<sub>2</sub><sup>II</sup>(**PSRT**)<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub>, where **R** is one of the five moieties shown in the box. Figure adapted with permission from ref. 84. Copyright 2013 ACS.Fig. 13 Scan rate dependence of the thermal hysteresis loop of [Fe<sub>2</sub><sup>II</sup>(**PM**<sup>t-Bu</sup>**PhT**)<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub>·3½H<sub>2</sub>O. Figure adapted with permission from ref. 85. Copyright 2014 ACS.

structures (MeCN solvated), however, one can observe the enhanced flexibility of these **PSRT** dinuclear systems, over the

Fig. 14 (a) Structure of the complex cation of [Fe<sub>2</sub>(**PSPht**)<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub>, with carbons shaded dark/light grey on opposite ligands to highlight the *trans*-axial binding mode. (b) Solid state SCO of [Fe<sub>2</sub>(**PSRT**)<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub> complexes with varying **R**. Structure redrawn from CCDC data.<sup>86</sup> (b) Adapted with permission from ref. 86. Copyright 2016 ACS.

**PMRT** analogues, and this is believed to facilitate the observed complete [HS-HS] → [LS-LS] SCO. The Fe-N bond lengths in the **PSRT** structures are completely within the range expected for HS Fe(II) (Table 6). Furthermore, while **PMRT** ligands have always been observed to bind two Fe(II) metals in a bis-terdentate fashion and in a *cis*-axial mode (both pyridine arms up, but note that an alternative binding mode has been seen for an Fe(III) oxo product<sup>87</sup>), the more flexible **PSRT** ligands were observed to bind in bis-terdentate fashion and either a *cis*-axial mode or *trans*-axial mode (pyridine arms up/down, Fig. 14a). In addition to solid state SCO-activity, the [Fe<sub>2</sub>(**PSRT**)<sub>2</sub>](BF<sub>4</sub>)<sub>4</sub> complexes exhibit SCO in MeCN solution, induced by both temperature and pressure, with more electron donating **R** groups predictably favouring LS more.<sup>16,86</sup>

The Rentschler group has reported an interesting family of **PMRT**-like complexes of a thiadiazole analogue of **PMRT**,



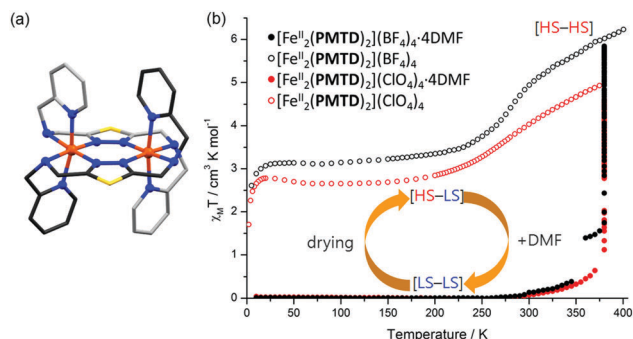


Fig. 15 (a) Structure of the cation of  $[\text{Fe}_2^{\text{II}}(\text{PMTD})_2]\text{X}_4$ , with carbons shaded dark/light grey on opposite ligands to highlight the *trans*-axial binding mode. (b)  $[\text{Fe}_2^{\text{II}}(\text{PMTD})_2]\text{X}_4$ -solvent  $\chi_{\text{MT}}$  vs.  $T$  data sets showing the DMF sensing ability of the complexes. Structure redrawn from CCDC data.<sup>88</sup> (b) Adapted with permission from ref. 89. Copyright 2016 ACS.

2,5-bis[[2-pyridylmethyl]amino]methyl-1,3,4-thiadiazole (**PMTD**, Chart 4). The bis-terdentate **PMTD** ligand differs from **PMRT** ligands in that there is a non-coordinating sulphur atom in place of the non-coordinating  $N^4\text{-R}$  moiety of **PMRT**. It was shown to produce  $[\text{Fe}_2^{\text{II}}(\text{PMTD})_2]\text{X}_4$  complexes with the *trans*-axial binding mode (Fig. 15a, like the thioether **PSRT** systems), revealing more flexibility than in the analogous **PMRT** complexes (always *cis*-axial mode), and thus giving access to the fully [LS-LS] state.

The impact of the larger S heteroatom in the central five membered ring of **PMTD** (over the N atom in **PMRT**) on the overall flexibility can also be seen in the angle at which the amino side arms protrude from the thiadiazole/triazole, with  $N_{\text{azole}}\text{-}N_{\text{azole}}\text{-}N_{\text{amino}}$  angles averaging  $176.04^\circ$  for LS **PMTD** complexes and  $172.30^\circ$  for [HS-LS]  $[\text{Fe}_2(\text{PMAT})_2](\text{BF}_4)_4$ . Indeed, all three  $[\text{Fe}_2^{\text{II}}(\text{PMTD})_2]\text{X}_4$  complexes highly favour the [LS-LS] state and undergo a gradual SCO starting above 250 K, not reaching the [HS-LS] state (or the [HS-HS] state) at the limit of the measurement, 380 K.<sup>88</sup> In 2016, the DMF solvates of  $[\text{Fe}_2^{\text{II}}(\text{PMTD})_2](\text{BF}_4)_4$  and  $[\text{Fe}_2^{\text{II}}(\text{PMTD})_2](\text{ClO}_4)_4$ , which are both [LS-LS], were shown to undergo a transition to the [HS-HS] state upon thermal desolvation of the DMF molecules, and to subsequently undergo a half-SCO to the [HS-LS] state upon cooling (Fig. 15b and Table 6).<sup>89</sup>

The Rentschler group further investigated the effect of changing the non-coordinated-heteroatom in the five-membered ring, this time to an oxygen atom, generating the oxadiazole analogue, 2,5-bis[[2-pyridylmethyl]amino]methyl-1,3,4-oxadiazole (**PMOD**, Chart 4). The more electronegative oxygen (*cf.* the sulphur atom of **PMTD**) was anticipated to decrease the ligand field strength at the N donor atoms of the heterocycle, and indeed the HS state is stabilised in comparison to the thiadiazole **PMTD** complexes: all three  $[\text{Fe}_2(\text{PMOD})_2]\text{X}_4$  ( $\text{X} = \text{ClO}_4^-$ ,  $\text{BF}_4^-$ , or  $\text{CF}_3\text{SO}_3^-$ ) complexes are [HS-HS] at room temperature. While the  $\text{X} = \text{BF}_4^-$  complex remains HS to low temperatures, the  $\text{X} = \text{ClO}_4^-$  and  $\text{X} = \text{CF}_3\text{SO}_3^-$  complexes undergo abrupt [HS-HS] to [HS-LS] SCO centred about 150 K, with a 26 K wide hysteresis loop for  $[\text{Fe}_2(\text{PMOD})_2](\text{CF}_3\text{SO}_3)_4$ . The [LS-LS] state was inaccessible due to steric constraints imposed by the rigid ligand: the smaller oxygen heteroatom tightens the angle of the

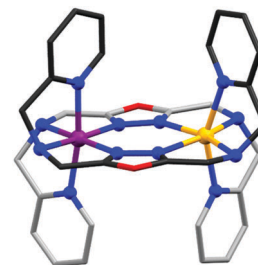


Fig. 16 Structure of the cation of  $[\text{Fe}_2^{\text{II}}(\text{PMOD})_2]\text{X}_4$ , (yellow HS and purple LS Fe<sup>II</sup> centre) with carbons shaded dark/light grey on opposite ligands to highlight the *cis*-axial binding mode.<sup>90</sup> Structure redrawn from CCDC data.

amino side arms relative to that in **PMTD**, as seen by a reduction of the  $N_{\text{azole}}\text{-}N_{\text{azole}}\text{-}N_{\text{amino}}$  angle from  $177$  to  $168^\circ$ , and by the *cis*-axial binding mode (Fig. 16). As was seen with the **PMRT** ligands, the transition to the [HS-LS] state for  $[\text{Fe}_2(\text{PMOD})_2](\text{ClO}_4)_4$  is associated with an increase in octahedral distortion parameter at the residual HS Fe(II) centre ([HS-HS] @ 193 K,  $\Sigma_{\text{HS}} = 121^\circ$ ; [HS-LS] @ 100 K,  $\Sigma_{\text{HS}} = 137^\circ$  Fig. 16 yellow,  $\Sigma_{\text{LS}} = 70^\circ$  Fig. 16 purple; Table 6). Crystal packing appears to have a large influence on the SCO behaviour. A hydrogen bonding network for one of the compounds, linking amino NH groups on neighbouring  $[\text{Fe}_2(\text{PMOD})_2]^{4+}$  cations *via*  $\text{CF}_3\text{SO}_3^-$  counteranions, infers high cooperativity and results in the hysteresis loop. Also, all three compounds contain two or four solvent MeCN molecules, and although no significant interactions to the cations are obvious, SCO is lost upon desolvation.

#### Dinuclear $\text{Fe}_2\text{L}_2$ formed by assorted other ligands

Further examples of dinuclear  $\text{Fe}_2\text{L}_2$  type complexes (Fig. 2, 2B) are formed by the diverse family of ligands **L19**–**L21** (Chart 5).

Murray, Kepert and co-workers have reported a pyridyl rich ligand, **L19** (Chart 5), which binds in a bis-bidentate manner, forming a SCO active dinuclear  $\text{Fe}_2\text{L}_2$  complex,  $[\text{Fe}_2(\text{L19})_2(\text{NCS})_4] \cdot 4\text{CH}_2\text{Cl}_2$  (Fig. 17a).<sup>91</sup> It undergoes a two-step SCO with all three spin states accessed: [HS-HS], [HS-LS], and [LS-LS]. The plateaus occurred at 110 and 140 K with  $T_{1/2} = 80$  and 180 K (Fig. 17b, a circle). The authors traced the magnetic behaviour with  $\Sigma$  angle at different temperatures (Table S1, ESI<sup>†</sup>). At 25 K both Fe(II) centres

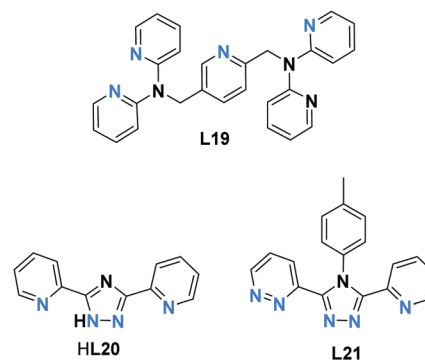


Chart 5 Assorted other ligands, **L19**–**L21**, forming SCO-active  $\text{Fe}_2\text{L}_2$  type dinuclear Fe(II) complexes (Fig. 2, 2B).



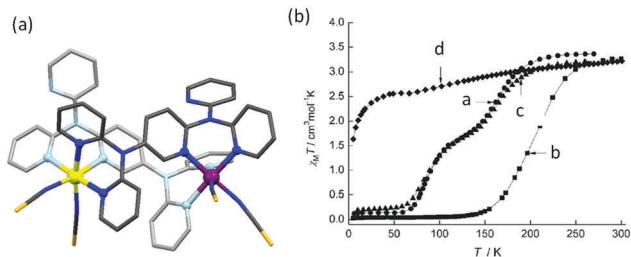


Fig. 17 (a)  $[\text{Fe}_2^{\text{II}}(\text{L19})_2\text{NCS}_4]$  structure, with carbons shaded dark/light grey. (b) Plots of  $\chi_{\text{m}}T$  per  $\text{Fe}^{\text{II}}$  vs.  $T$ , for complex  $[\text{Fe}_2(\text{L19})_2(\text{NCS})_4] \cdot x\text{CH}_2\text{Cl}_2$  (a)  $x = 4$  (circle), (b)  $x = 1$  (square) (c) re-solvated,  $x = 4$  (triangle) (d)  $x = 1$  (rhombus). Structure redrawn from CCDC data and (b) adapted from ref. 91 with permission. Copyright 2006 John Wiley and Sons.

were in the LS state with  $\Sigma = 28.4^\circ$  and  $35.2^\circ$ . The intermediate [HS–LS] state observed at 123 K has  $\text{Fe}_{\text{LS}} \Sigma = 27.7^\circ$  (Fig. 17a, purple) and  $\text{Fe}_{\text{HS}} \Sigma = 45.9^\circ$  (Fig. 17a, yellow). Furthermore, heating from 123 K to 250 K the geometry around Fe2 is slightly changed from  $45.9^\circ$  to  $46.7^\circ$ ,  $\text{Fe1} = 41.8^\circ$ . The partially de-solvated compound underwent a one-step SCO with increased transition temperature,  $T_{1/2}$  of 200 K (Fig. 17b, b square). Furthermore, immersion of partially de-solvated compound into dichloromethane reverted the two-step SCO (Fig. 17b, c triangle). The fully de-solvated compound lost its SCO nature and remained HS all over the temperature range,  $\chi_{\text{m}}T = 3.15 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K (Fig. 17b, d rhombus).

Murray and co-workers also reported, in 2013, a triazolate bridged dinuclear complex of anionic **L20**, Chart 5 (Fig. 18a). Single crystal and powder forms of  $[\text{Fe}_2(\text{L20})_2(\text{NCBH}_3)_2(\text{py})_2]$  showed distinctly different degrees of thermally induced SCO behaviour with different  $T_{1/2}$  values. The powder sample showed a two-step complete SCO at  $T_{1/2} = 194$  and 151 K (Fig. 18b) whereas the crystal form showed an abrupt half step SCO at  $T_{1/2}$  102 K (Fig. 18c).<sup>92</sup>

Brooker and co-workers reported another kind of  $\text{Fe}_2\text{L}_2$  type SCO– $\text{Fe}(\text{II})$  complex in 2016, by employing **L21** (Chart 5).<sup>93</sup> The resulting dark red dinuclear complex  $[\text{Fe}_2(\text{L21})_2(\text{MeCN})_4](\text{BF}_4)_4$ .

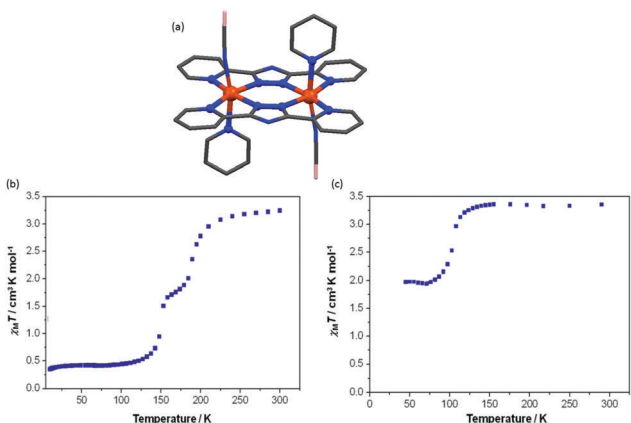


Fig. 18 (a) The crystal structure of  $[\text{Fe}_2(\text{L20})_2(\text{NCBH}_3)_2(\text{py})_2]$ . (b)  $\chi_{\text{m}}T$  vs.  $T$  plot for powder sample and (c) crystal form. Structure redrawn from CCDC data. (b and c) Adapted from reference, with permission.<sup>92</sup> Copyright 2016 John Wiley and Sons.

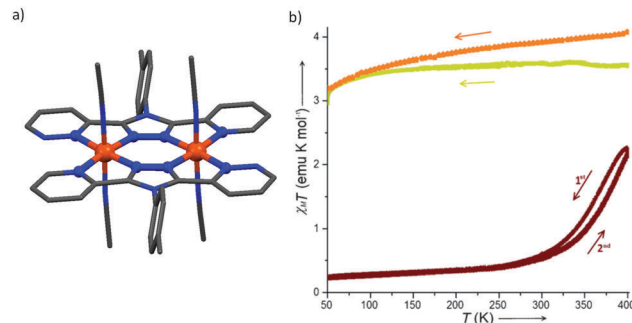


Fig. 19 Data for  $[\text{Fe}_2(\text{L21})_2(\text{MeCN})_4](\text{BF}_4)_4 \cdot 2\text{MeCN}$ : (a) structure of the tetracation. (b)  $\chi_{\text{m}}T$  (per Fe) vs.  $T$  plot (maroon). Structure redrawn from CCDC data and (b) adapted from reference, with permission.<sup>93</sup> Copyright 2013 John Wiley and Sons.

$2\text{MeCN}$  was shown by a crystal structure determination to be [LS–LS] at 100 K (Fig. 19a). It underwent a gradual SCO with a 13 K wide thermal hysteresis loop, at  $T_{1/2} \downarrow = 356 \text{ K}$  and  $T_{1/2} \uparrow = 369 \text{ K}$  (Fig. 19b, maroon curve). The  $\chi_{\text{m}}T$  was  $2.45 \text{ emu mol}^{-1} \text{ K}$  at 400 K, indicating about 80% conversion from [LS–LS] to [HS–HS]. Guest exchange, by reversible SCSC transformations, gave two other complexes, orange  $[\text{Fe}_2(\text{L21})_2(\text{EtOH})_4](\text{BF}_4)_4$  and yellow polymer  $\{[\text{Fe}_2(\text{L21})_2(\text{H}_2\text{O})_4](\text{BF}_4)_4\}_\infty$ , both of which were [HS–HS] at all temperatures 50–400 K (Fig. 19b, orange and yellow curves, respectively).

### Dinuclear singly N-ligand linked $\text{Fe}_2\text{L}$

Grouped together in this section are the  $\text{Fe}_2\text{L}$  dinuclear complexes in which the two  $\text{Fe}(\text{II})$  centres are linked by a single ligand **L** that provides some, or all, of the N-donors (Fig. 2, 2C). The ligands employed vary considerably, ranging from bis-monodentate, to bis-bi-, bis-tri-, bis-tetra- and bis-hexa-dentate (Chart 6), but all give rise to dinuclear  $\text{M}_2\text{L}$  complexes of type 2C (Fig. 2).

In 2015, Meyer and co-workers reported a dinuclear  $\text{Fe}_2\text{L}$  complex (Fig. 2, 2C) of a bis-terdentate pyrazolate ligand, **HL22** (Chart 6).<sup>94</sup> **HL22** is deprotonated and provides a single pyrazolate bridge between the two  $\text{Fe}(\text{II})$  centres as well as meridionally coordinated  $\text{N}_2\text{P}$  donors to each of them, in  $[\text{Fe}_2 \text{L22}(\text{OTf})_3(\text{CH}_3\text{CN})]$  (Fig. 20a). In addition to the bridging pyrazolate, the  $\text{Fe}(\text{II})$  centres are also bridged by two triflate anions, and the octahedral geometry of HS Fe1 is completed by a terminal triflate ( $\text{O}_3\text{N}_2\text{P}$ ), and that of Fe2 by a MeCN ligand ( $\text{O}_2\text{N}_3\text{P}$ ). The magnetic behaviour of this complex was studied in both solid and solution (Fig. 20b). In the solid state it remains fully high spin, due to the O-donors. In contrast, in MeCN solution, the complex exchanges the triflate anions for MeCN solvent molecules, becoming  $\text{N}_5\text{P}$ -coordinated and enabling it to undergo a reversible and complete thermally induced SCO (Fig. 20b).<sup>94</sup>

Sato and co-workers<sup>95</sup> studied the pyrazine-bridged  $\text{Fe}_2\text{L}$  dinuclear complexes (Fig. 2, 2C)  $[\text{Fe}_2\text{L}(\text{NCS})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}$ , of the bis-tetradentate pyrazine ligands **L** = **L23**, **L24** (Chart 6). The dinuclear complex of the 2,5-substituted pyrazine ligand **L23**,  $[\text{Fe}_2\text{L23}(\text{NCS})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}$ , underwent a one-step SCO at around 180 K (Fig. 21, red circles). After being heated to 400 K, desolvated



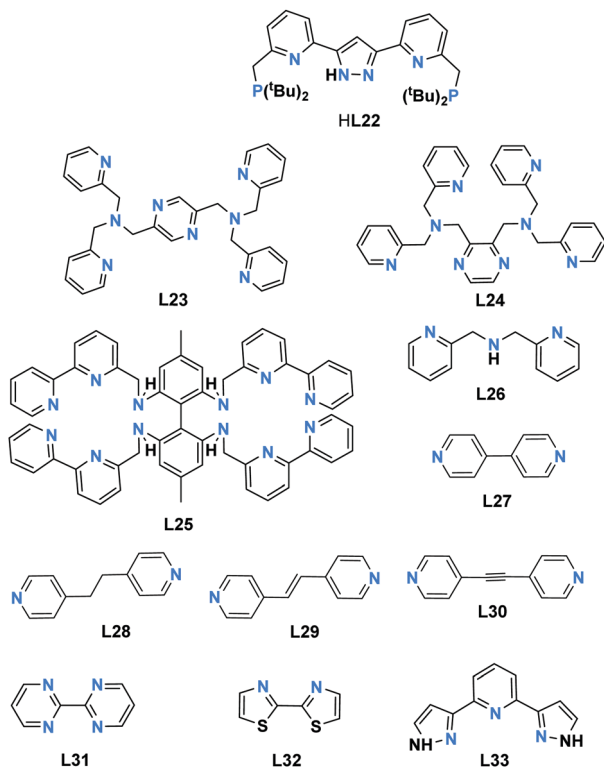


Chart 6 Ligands used to link two Fe(II) ions forming SCO-active singly-ligand linked dinuclear  $\text{M}_2\text{L}$  complexes (Fig. 2, 2C).

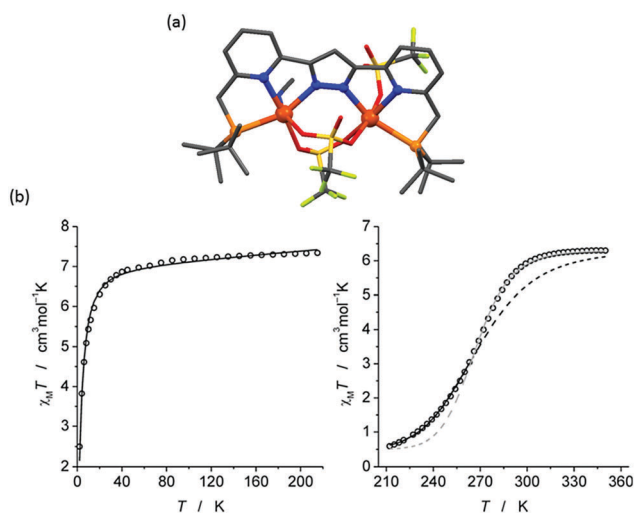


Fig. 20 (a) The solid state structure of  $[\text{Fe}_2\text{L22}(\text{OTf})_3(\text{CH}_3\text{CN})]$ . (b)  $\chi_{\text{m}}T$  vs.  $T$  plot in the solid state (left) and MeCN solution (right). Structure redrawn from CCDC data. (b) Reproduced from reference, with permission.<sup>94</sup> Copyright 2015 John Wiley and Sons.

$[\text{Fe}_2\text{L23}(\text{NCS})_4]$  showed a different SCO curve, with an abrupt transition ( $T_{1/2}\uparrow = 189$ ,  $T_{1/2}\downarrow = 184$  K) and 5 K wide hysteresis loop (Fig. 21, inset). In the case of the 2,3-substituted pyrazine ligand L24, the resulting complex displayed a gradual two step SCO,  $[\text{HS}\text{--}\text{HS}] \leftrightarrow [\text{LS}\text{--}\text{HS}] \leftrightarrow [\text{LS}\text{--}\text{LS}]$ .<sup>95</sup> At 300 K,  $\chi_{\text{m}}T$  value is  $5.58 \text{ cm}^3 \text{ K mol}^{-1}$ , consistent with the  $[\text{HS}\text{--}\text{HS}]$  state, and decreases gradually to  $0.71 \text{ cm}^3 \text{ K mol}^{-1}$  at 70 K, consistent

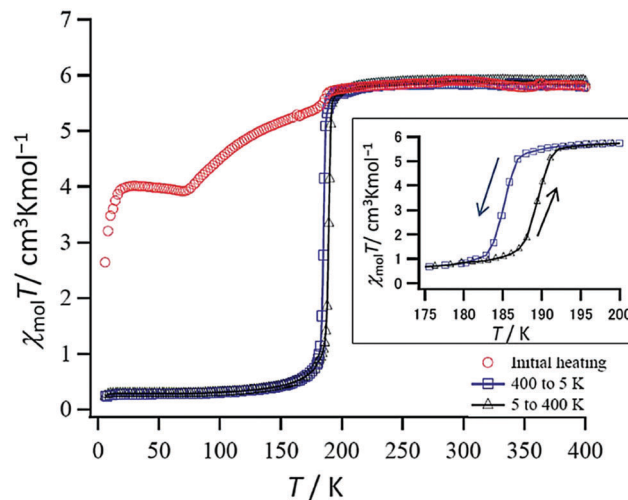


Fig. 21  $\chi_{\text{m}}T$  vs.  $T$  for  $[\text{Fe}_2\text{L23}(\text{NCS})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}$  (initial heating: red circles; cooling cycle: blue squares, heating cycles: black triangles (on heated sample)). Figure reproduced from ref. 95. Copyright 2013 John Wiley and Sons.

with the  $[\text{LS}\text{--}\text{LS}]$  state, however with a change in slope occurring at approximately  $\chi_{\text{m}}T = 3 \text{ cm}^3 \text{ K mol}^{-1}$ , 185 K, indicating that the Fe(II) centres undergo SCO at differing temperatures. The LIESST studies on this pair of complexes gave pairs of thermal transition temperature ( $T_{1/2}$ ) and photo-induced transition temperature ( $T_{\text{LIESST}}$ ) values for desolvated  $[\text{Fe}_2\text{L23}(\text{NCS})_4]$  (192, 70 K) and for  $[\text{Fe}_2\text{L24}(\text{NCS})_4] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}$  (210 and 56 K; 130 and 71 K). These fall close to the  $T_0 = 120$  K line of the correlation,  $T_{\text{LIESST}} = T_0 - 0.3T_{1/2}$ , earlier identified by Létard and co-workers.<sup>96</sup>

In 2013, Petzold and co-workers reported a dinuclear  $\text{Fe}_2\text{L}$  complex of a bis-hexadentate, biphenyl-linked, L25 (Chart 6), in which the two Fe(II) centres are linked by this single ligand.<sup>97</sup> Remarkably L25 provides all twelve N-donors to the two octahedral Fe(II) centres in  $[\text{Fe}_2(\text{L25})](\text{BPh}_4)_4$ . The structure determination shows the complex to be fully LS at 153 K (Fig. 22a) whereas mononuclear  $[\text{Fe}(\text{L25})](\text{BPh}_4)_2$  was paramagnetic at room temperature. In MeCN solution there is a very gradual, partial SCO towards HS as the temperature is raised from 298 (25 °C) to 348 K (75 °C), with the fraction HS rising from 0.05 to 0.15 (Fig. 22b).

Some of the 4,4'-bi-pyridine-like bridged SCO-active  $\text{Fe}_2\text{L}$  complexes were covered in our previous review,<sup>35</sup> but for completeness are also included here. Matouzenko and co-workers studied a series of dinuclear  $\text{Fe}_2\text{L}$  complexes,  $[\{\text{Fe}(\text{L26})(\text{NCX})_2\}_2(\text{L})] \cdot n\text{MeOH}$  ( $\text{X} = \text{S}$  and  $\text{BH}_3$ ;  $\text{L} = \text{L27}\text{--}\text{L30}$ , Chart 6) varying the length of the bipyridyl-like bridges L, between the Fe(II) centres (Fig. 2, 2C), and employing L26 capping ligands (Chart 6). They first reported this kind of complex in 2009, with  $\text{X} = \text{S}$  and L27.<sup>98</sup>

Then in 2011 they replaced the L27 bridge by L29 (Chart 6), retaining  $\text{X} = \text{S}$ , generating three forms of  $[\{\text{Fe}(\text{L26})(\text{NCS})_2\}_2 \cdot (\text{L29})] \cdot n\text{MeOH}$ , a pair of solvent-free polymorphs ( $n = 0$ ) and a solvatomorph ( $n = 2$ ), which displayed different SCO behaviours. The two solvent-free polymorphs were dark vinous (red-wine coloured) prismatic versus brown crystals. The crystal structures



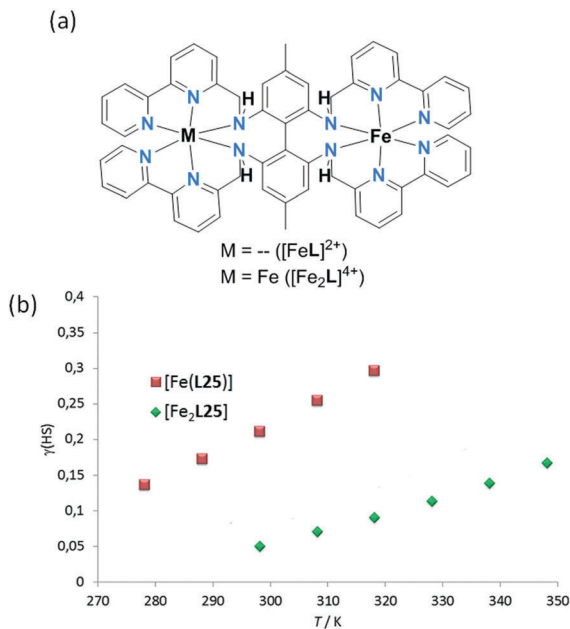


Fig. 22 (a) Binding sites in mononuclear and dinuclear Fe(II) complexes of hexadentate **L25**; dinuclear singly-ligand linked (Fig. 2, **2C**). (b) Evans measurements on mononuclear [Fe(**L25**)](BPh<sub>4</sub>)<sub>2</sub> and dinuclear [Fe<sub>2</sub>(**L25**)](BPh<sub>4</sub>)<sub>4</sub>. Figure adapted from reference, with permission.<sup>97</sup> Copyright 2013 John Wiley and Sons.

of the vinous polymorph at 300 K, 183 K and 90 K, revealed [HS–HS], localised [HS–LS], and [LS–LS] spin states, respectively. This is consistent with the occurrence of a two-step SCO, separated by a subtle inflection point with  $T = 182$  K as revealed by the magnetic study. The brown crystals remained high spin. In contrast, the red-brown crystals of the methanol solvate underwent a complete one step transition, without hysteresis, at 159 K.<sup>99</sup>

The following year they instead employed a **L30** bridge (Chart 6), again retaining X = S, and generating two solvatomorphs,  $n = 0$  and  $n = 2$  (Fig. 23a), which differed in SCO

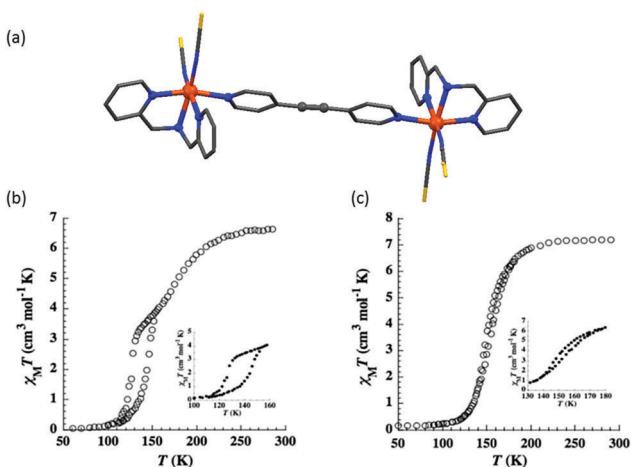


Fig. 23 (a) Crystal structure of [Fe(**L26**)(NCS)<sub>2</sub>]<sub>2</sub>(**L30**). (b)  $\chi_M T$  vs.  $T$  plot for  $n = 0$  and (c)  $n = 2$ . Structure redrawn from CCDC data. (b and c) Reproduced with permission.<sup>100</sup> Copyright 2012 John Wiley and Sons.

behaviour. The solvent free complex underwent a two-step SCO, with 50% spin conversion and short plateau at 145 K, with a 17 K wide hysteresis loop for the lower temperature SCO event ( $T_{1/2\downarrow} = 126$  and  $T_{1/2\uparrow} = 143$  K) (Fig. 23b). The methanol solvate, [Fe(**L26**)(NCS)<sub>2</sub>]<sub>2</sub>(**L30**)·2MeOH, undergoes a one-step SCO with a narrow 4 K hysteresis loop ( $T_{1/2\downarrow} = 150$  and  $T_{1/2\uparrow} = 154$  K; Fig. 23c).<sup>100</sup>

Then in 2013 they changed to using cyanoborohydride anions, generating a set of three complexes which varied in the choice of L (L = **L27**, **L28**, **L30**), [Fe(**L26**)(NCBH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(L). The complex with an L = **L27** bridge showed abrupt two step SCO with an inflection point at 210 K whereas with the complexes with an L = **L28** or **L30** bridge showed gradual one step transitions with  $T_{1/2}$  of 241 and 290 K, respectively.<sup>101</sup>

Pressure induced SCO is less commonly studied. A key early study carried out on bipymidine-bridged SCO-active Fe<sub>2</sub>L complexes {[Fe(L)(NCE)<sub>2</sub>]<sub>2</sub>L31}, where E = S or Se and the capping ligands were L = **L31** or **L32** (Chart 6), was reported in 2001 by Gutlich, Real and co-workers (Fig. 24).<sup>102</sup>

At ambient pressure {[Fe(**L31**)(NCS)<sub>2</sub>]<sub>2</sub>L31} was paramagnetic 4–300 K (Fig. 24a). In contrast, at 8.9 kbar it showed incomplete one-step SCO behaviour,  $T_{1/2} \approx 150$  K. At ambient

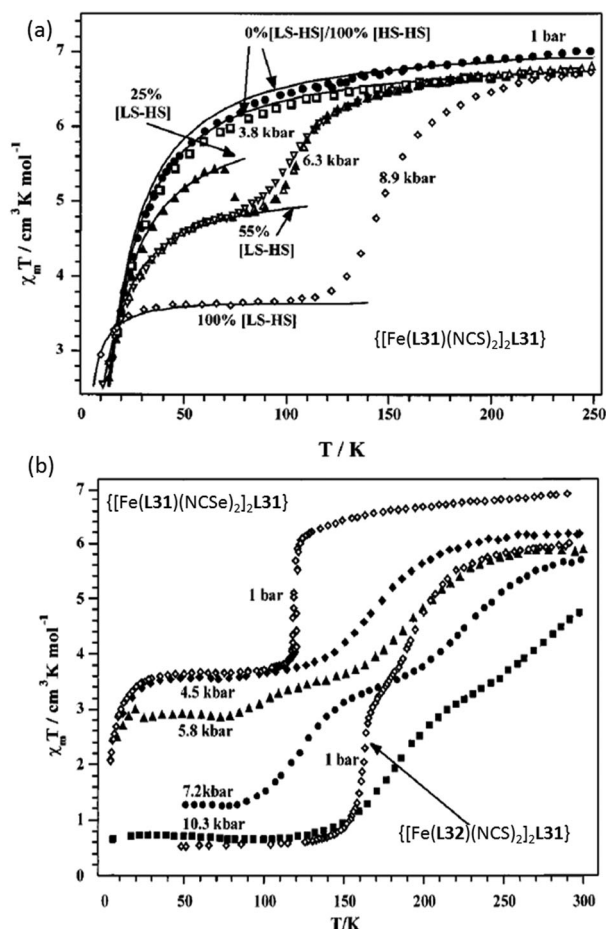


Fig. 24 (a)  $\chi_M T$  vs.  $T$  plot of [Fe(**L31**)(NCS)<sub>2</sub>]<sub>2</sub>L31 and (b) [Fe(**L31**)(NCS)<sub>2</sub>]<sub>2</sub>L31 and [Fe(**L32**)(NCS)<sub>2</sub>]<sub>2</sub>L31 at various pressures. (a and b) Adapted with permission from ref. 102. Copyright 2001 ACS.



pressure (1 bar) the X = Se analogue,  $\{[\text{Fe}(\text{L31})(\text{NCSe})_2]_2\text{L31}\}$ , undergoes a 50% spin transition at  $T_{1/2} = 120$  K (Fig. 24b).<sup>102</sup> The complex featuring bis-thiazole capping ligands (L32, Chart 6),  $\{[\text{Fe}(\text{L32})(\text{NCS})_2]_2\text{L31}\}$ , underwent an almost complete two step SCO at ambient pressure (Fig. 24b).

In 2012, Molnár, Guionneau and co-workers reported the effect of pressure on the SCO curve of the 4,4'-bipyridine (L27, Chart 6) bridged  $\text{Fe}_2\text{L}$  complex,  $\{[\text{Fe}(\text{L33})(\text{NCS})_2]_2(\text{L27})\} \cdot 2\text{MeOH}$ , which features L33 capping ligands (Chart 6).<sup>103</sup> This complex undergoes thermally and photo-induced incomplete SCO, which was ascribed to a purely structural phase transition and only partial conversion to LS at low temperature.<sup>104</sup> But under the influence of high pressure, this complex showed no crystallographic phase transition. High pressure X-ray diffraction and Raman spectroscopic studies showed that a fully LS state is realised at low temperature, and that SCO is very gradual at pressures between 7 and 25 kbar.<sup>103</sup>

### Assorted anion bridged dinuclear complexes

Non-heterocyclic anion bridged (Chart 7) SCO-active dinuclear  $\text{Fe}(\text{II})$  complexes (Fig. 2, 2D) are rarely reported, with only four cases in the literature, all of which employ polydentate N-donor capping ligands (Chart 8).

In the first case, dicyanamide (dca, Chart 7) acts as the anionic bridge between the two  $\text{Fe}(\text{II})$  centres, with the  $\text{N}_6$  coordination spheres completed by L34 capping ligands (Chart 8).<sup>105</sup> In the second case, cyanocarbanions (A1, Chart 7) doubly bridge the two  $\text{Fe}(\text{II})$  centres, with the  $\text{N}_6$  coordination spheres completed by L35 and L36 capping ligands (Chart 8), giving a neutral complex.<sup>106</sup> In the third case, NCS anions doubly bridge the

$\text{Fe}(\text{II})$  centres with  $\text{N}_5\text{S}$  coordination environments and L37 capping ligands (Chart 8).<sup>107</sup> The fourth example features a diiminoquinonoid-bridges (A2–A5, Chart 7) with L35 capping ligands (Chart 8).<sup>108</sup>

Real and co-workers reported the first example, a dicyanamide bridged  $\text{Fe}(\text{II})$  SCO-active dinuclear complex, in 2005,<sup>105</sup>  $[\text{Fe}_2\text{L34}_2(\text{dca})](\text{PF}_6)_3 \cdot n\text{H}_2\text{O}$  ( $n = 1$  and 0). When  $n = 1$  it remains HS with a constant  $\chi_{\text{M}}T$  value of  $6.7 \text{ cm}^3 \text{ K mol}^{-1}$  from 350 K to 50 K. In contrast,  $n = 0$   $[\text{Fe}_2\text{L34}_2(\text{dca})](\text{PF}_6)_3$  showed a two-step spin transition: at 400 K,  $\chi_{\text{M}}T = 7.0 \text{ cm}^3 \text{ K mol}^{-1}$  indicating all iron centres are HS, then  $\chi_{\text{M}}T$  decreased gradually to  $3.65 \text{ cm}^3 \text{ K mol}^{-1}$  at 250 K with a broad plateau from 285–208 K, then in a second step it decreased gradually to  $0.21 \text{ cm}^3 \text{ K mol}^{-1}$  at 50 K. This SCO response was attributed to 50% spin conversion in each step. Magnetic studies in  $\text{D}_6$ -acetone solution showed the one-step incomplete SCO-behaviour of both solvatomorphs.<sup>105</sup>

In 2016, Triki and co-workers used two types of tetradentate capping ligands, L35 and L36 (Chart 8), to obtain a pair of A1-bridged complexes (A1, Chart 7),  $[\text{Fe}_2\text{L}_2(\text{A1})_2] \cdot n\text{MeOH}$  ( $n = 0.8$  and 2, respectively). The small difference between these tetradentate capping ligands, L35 and L36 (Chart 8), leads to a large change in  $T_{1/2}$  ( $\Delta T_{1/2} > 150$  K), from 365 to 180 K, respectively (Fig. 25), which they attributed to changes in crystal packing. After desolvation of this pair of complexes, the  $T_{1/2}$  values were slightly different, 352 and 196 K, respectively.<sup>106</sup>

Harris and co-workers also employed the tetradentate capping ligand L35, but utilised a series of diiminoquinonoid anion bridges, A2–A5 (Chart 7) to generate dinuclear  $[\text{Fe}_2(\text{L35})_2(\text{A})] \cdot (\text{B}(\text{PhCF}_3)_4)_2$ , with A2–A5, complexes in order to systematically study the effect of varying the electronic effects of substituents on the bridge A on the SCO behaviour (Fig. 26a).<sup>108</sup> They were able to correlate  $T_{1/2}$  and  $\Delta H$  (the latter obtained by fitting the magnetic data to an ideal solution model) (Fig. 26b). They showed that both the  $T_{1/2}$  (from 160–110 K) and  $\Delta H$  (from 11.4–7.5  $\text{kJ mol}^{-1}$ ) values decreased with increasingly electron-withdrawing groups X

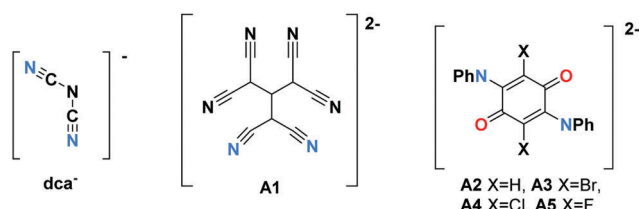


Chart 7 Anions used as bridges in SCO-active dinuclear  $\text{Fe}(\text{II})$  complexes (Fig. 2, 2D).

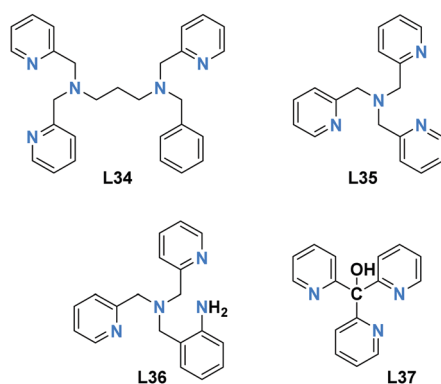


Chart 8 Capping ligands used in anion bridged SCO-active  $\text{Fe}(\text{II})$  dinuclear complexes (Fig. 2, 2D).

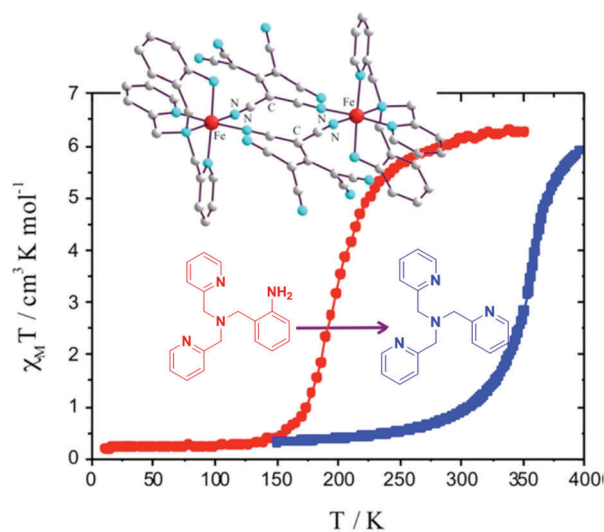


Fig. 25 Plot of  $\chi_{\text{M}}T$  vs.  $T$  of desolvated  $[\text{Fe}_2\text{L}_2(\text{A1})_2]$  [L35 (blue points) and L36 (red points)]. Figure adapted from reference with permission.<sup>106</sup> Copyright 2016 ACS.



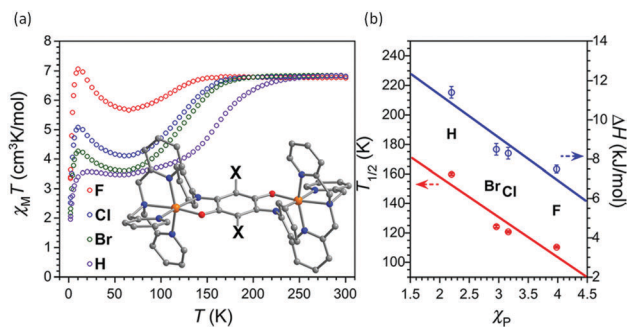


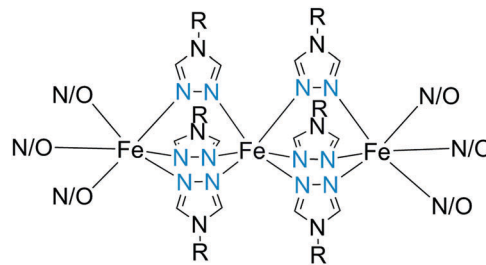
Fig. 26 (a)  $\chi_m T$  vs.  $T$  plot of  $[\text{Fe}_2(\text{A})(\text{L35})_2](\text{B}(\text{PhCF}_3)_4)_2$ , **A2–A5**. (b) Correlation between  $T_{1/2}$  (red points) and  $\Delta H$  (blue points) as a function of Pauling electronegativity ( $\chi_P$ ) of the X substituent (F, Cl, Br, H). (a and b) Adapted with permission from ref. 108. Copyright 2015 ACS.

on the bridging anion **A2–A5** (–H to –Br to –Cl to –F), as measured by the Pauling electronegativity ( $\chi_P$ ).<sup>108</sup> The incorporation of electron withdrawing groups in **A** increases the  $\pi$ -back donation from the **L35** pyridyl capping ligand and stabilises the LS state, hence shifting  $T_{1/2}$  towards higher temperatures.

Another example features bridging  $\text{NCS}^-$  anions, and employs **L37** as capping ligands (Chart 8). The complex  $[\{\text{Fe}(\text{L37})(\text{NCS})-(\mu\text{-NCS})\}_2]$  showed gradual one step SCO,  $[\text{LS}]\text{-}[\text{LS}] \leftrightarrow [\text{HS}]\text{-}[\text{HS}]$ , at 207 K, with no hysteresis loop.<sup>107</sup>

### Trinuclear: triply triazole bridged, $\text{Fe}_3\text{L}_6$

All of the structurally characterized SCO-active trinuclear  $\text{Fe}(\text{II})$  complexes after 2011 are of one structural type: triply triazole-bridged (Fig. 2, **3A**). Like the dinuclear analogues, they are readily structurally characterised, in contrast to the related 1D-chain polymers. To date, 10 different  $N^4$ -substituted 1,2,4-triazoles (Chart 9) have been employed in generating these complexes. In all cases, the six R-triazole ligands provide triple  $N^1N^2$  bridges between the central  $\text{Fe}(\text{II})$  and each of the two terminal  $\text{Fe}(\text{II})$  ions, resulting in an  $N_6$  octahedral central  $\text{Fe}(\text{II})$  ion, and providing 3N donors to each of the terminal  $\text{Fe}(\text{II})$  ions



N/O donor either from solvent or counteranion

Fig. 27 Schematic representation of trinuclear triply-triazole bridged SCO-active  $\text{Fe}(\text{II})$  complexes (Fig. 2, **3A**).

with their octahedral coordination completed by three mono-anions and/or solvent molecules (Fig. 27). Depending on coordinated or non-coordinated anions, the three  $\text{Fe}(\text{II})$  centres are afforded either  $N_3O_3\text{-}N_6\text{-}N_3O_3$ <sup>109–116</sup> or  $N_6\text{-}N_6\text{-}N_6$ <sup>117</sup> or  $N_5O\text{-}N_6\text{-}N_5O$ <sup>118</sup> coordination environments. In all of these trinuclear complexes, the central  $\text{Fe}(\text{II})$  is always  $N_6$ , being triply triazole bridged to each of the other two  $\text{Fe}(\text{II})$  centres. Hence the central  $\text{Fe}(\text{II})$  centre in these complexes is the only one that undergoes SCO – except in the case of  $[\text{Fe}_3\text{L46}_6\text{A6}_4]$ <sup>117</sup> ( $N_6\text{-}N_6\text{-}N_6$ ) where all three of the  $\text{Fe}(\text{II})$  centres underwent SCO. These complexes have shown a range of gradual to abrupt SCO, with  $T_{1/2}$  varying with the **R** group, anions and solvent molecules present.

In 1983, the first structurally characterized trinuclear SCO-active complex,  $[(\text{Fe}_3(\text{L38})_6(\text{H}_2\text{O})_6)](\text{CF}_3\text{SO}_3)_6$ , was reported by Reedijk and co-workers.<sup>109</sup> This complex showed an abrupt SCO of one third of the  $\text{Fe}(\text{II})$  ions, as seen by Faraday balance at 203 K and confirmed by Mössbauer studies. By incorporating a hydroxyl group at C2 of the ethyl group (*i.e.* use of **L39**, Chart 9), the  $T_{1/2}$  was tuned to room temperature (290 K) which was attributed to the incorporation of hydrogen bonding into the system which increased the ligand field strength at the central metal atom.<sup>112</sup>

The effect of anion variation on the complex of **L40** (Chart 9, 4-(4-isopropyl)triazole) was studied by Haasnoot and co-workers.<sup>110</sup>  $[\text{Fe}_3\text{L40}_6(\text{H}_2\text{O})_6]^{6+}$  showed a gradual spin transition at 242 K and 187 K, for the tosylate and triflate anions, respectively. By varying the **R** group from **L41**<sup>111</sup> to **L42**<sup>113</sup> with tosylate anions, the  $T_{1/2}$  values changed slightly to 245 K, which was similar to the case of **L40**, and 148 K, respectively.

Galán-Mascarós and co-workers reported  $[\text{Fe}_3(\text{L43})_6(\text{H}_2\text{O})_6]\cdot 8\text{H}_2\text{O}$  with hysteresis in its partially dehydrated form, where **L43**<sup>–</sup> is anionic in nature with a highly polar functional group at the 4-position. It showed three crystallographic phases with three different magnetic behaviours (Fig. 28a). The original compound had a single step spin transition below 250 K with  $T_{1/2}$  at 150 K. Upon partial dehydration at 320 K the second phase occurred and showed spin transition with hysteresis. The third phase, observed after heating at 393 K, was paramagnetic down to low temperature. For the first phase, the  $\chi_m T$  value at room temperature was  $9.25 \text{ cm}^3 \text{ K mol}^{-1}$ , as expected for three independent HS iron(II) centres. On heating, the  $\chi_m T$  value remained constant from 300 K to 320 K, then decreased to  $6.2 \text{ cm}^3 \text{ K mol}^{-1}$  at 330 K due to partial solvent loss to form the

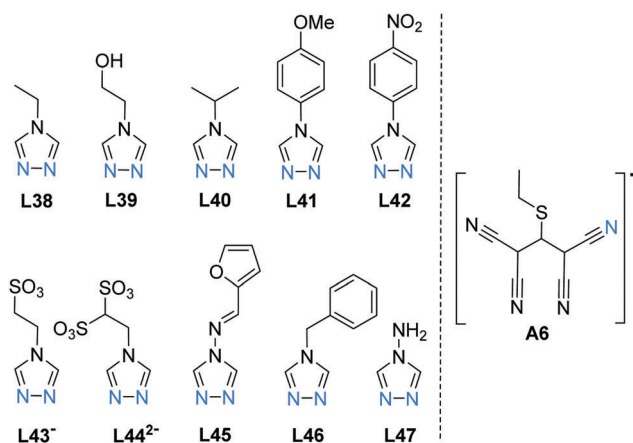


Chart 9 Ligands **L38–L47** reported in the literature to form SCO-active  $\text{Fe}(\text{II})$  trinuclear complexes (Fig. 2, **3A**): in all cases only the central  $\text{Fe}(\text{II})$  site is SCO active – except for **L46** and **A6** which provide all three  $\text{Fe}(\text{II})$  sites with SCO active  $N_6$  coordination environments.



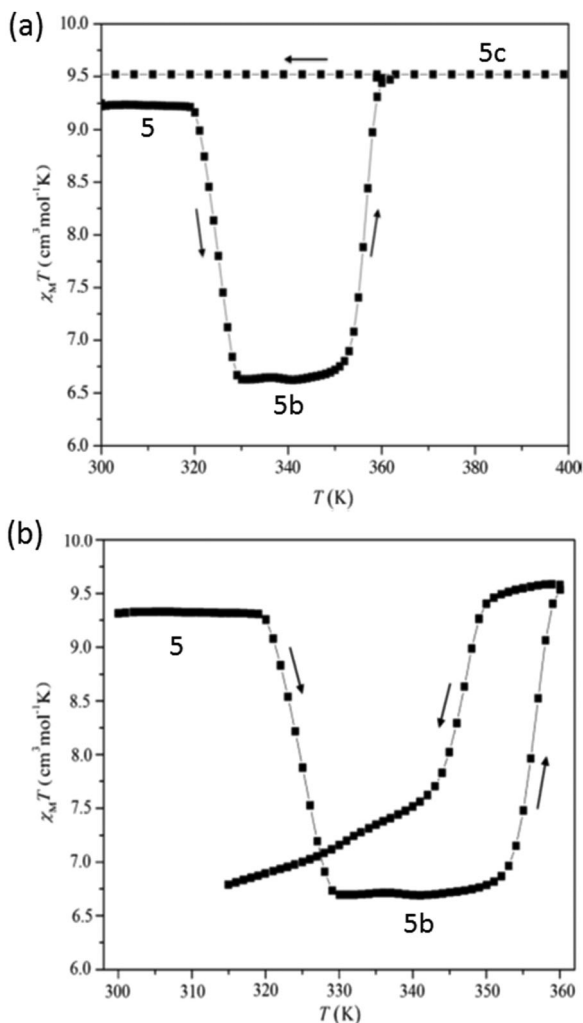


Fig. 28 (a) Plots of  $\chi_m T$  versus  $T$  for  $[\text{Fe}_3\text{L43}_6(\text{H}_2\text{O})_6]\cdot 8\text{H}_2\text{O}$ ; magnetic behaviour of all three crystallographic phases, (b) for  $[\text{Fe}_3\text{L43}_6(\text{H}_2\text{O})_6]\cdot 8\text{H}_2\text{O}$  (5 in this figure) upon heating above room temperature (320 K) showing the transformation into phase partially de-solvated  $[\text{Fe}_3\text{L43}_6(\text{H}_2\text{O})_6]$  (5b in this figure). Figure adapted from ref. 114 with permission. Copyright 2014 John Wiley and Sons.

second phase. This then showed an abrupt increase to  $9.44 \text{ cm}^3 \text{ K mol}^{-1}$  at 360 K, and a 14 K wide hysteresis ( $T_{1/2} \uparrow \downarrow$ : 357, 343 K) on cooling down again (Fig. 28b).<sup>114</sup>

The same group subsequently reported the trinuclear complex of anionic  $\text{L44}^{2-}$  (Chart 9),  $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\text{L44})_6(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}$ , in which the  $N^1$ -substituent is ethanedisulphonate. This compound showed a one step SCO above room temperature, with a 65 K wide thermal hysteresis loop (Fig. 29, inset filled squares). The  $\chi_m T$  value was  $6.37 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K, corresponding to [HS-LS-HS], and remains constant down to 50 K. On heating above 360 K it increased, and reached  $7.92 \text{ cm}^3 \text{ K mol}^{-1}$  at 400 K, consistent with [HS-HS-HS]. Maintaining the sample at 400 K,  $\chi_m T$  kept increasing over time and saturated at  $8.89 \text{ cm}^3 \text{ K mol}^{-1}$  and the cooling cycle showed a 90 K wide and reproducible hysteresis, with  $T_{1/2} \uparrow \downarrow = 400 \text{ K}$  and 310 K (Fig. 29, inset empty squares). They have also studied the temperature induced excited spin transition (TIESST) effect. The excited spin state

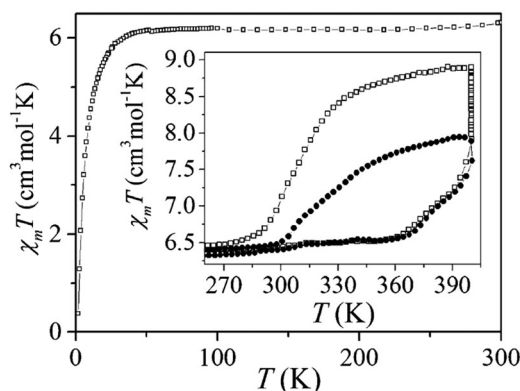


Fig. 29 Plot of  $\chi_m T$  vs.  $T$  for  $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\text{L44})_6(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}$  in the range of 2–300 K. Inset: 270–400 K range, empty squares show the saturated magnetic behaviour of  $(\text{Me}_2\text{NH}_2)_6[\text{Fe}_3(\text{L44})_6(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}$  when maintained at 400 K. Figure is reproduced from ref. 115. Copyright 2015 ACS.

(metastable-HS\*) was thermally trapped and remained HS\* at high temperature,  $T_{\text{TIESST}} = 250 \text{ K}$ , which was the highest value ever reported.<sup>115</sup>

Neville and co-workers have recently reported  $[\text{Fe}_3(\text{L45})_6(\text{p-tol})_2(\text{MeOH})_4](\text{p-tol})_4$  ( $\text{p-tol} = p\text{-tolylsulfonate}$ ), which showed a gradual one step spin transition with no hysteresis. The  $\chi T$  value at 300 K was  $10.2 \text{ cm}^3 \text{ K mol}^{-1}$  indicating fully HS Fe(II), then decreased gradually to  $7.8 \text{ cm}^3 \text{ K mol}^{-1}$  at 50 K, which corresponds to one third of Fe(II) undergoing SCO to LS,<sup>116</sup> as is usual in these trinuclear complexes (see above).

In 2017, Marchivie and co-workers reported that  $[\text{Fe}_3\text{L46}_6(\text{A6})_6]$  (Chart 9,  $\text{A6} = 1,1,3,3\text{-tetracyano-2-thioethylpropene}$ ), with  $\text{N}_3\text{N}_3\text{-N}_6\text{-N}_3\text{N}_3$  coordination spheres around each Fe(II), undergoes an abrupt one-step complete SCO at 318 K,  $3\text{LS} \rightarrow 3\text{HS}$ .<sup>117</sup> At 380 K, the  $\chi_m T$  value was  $9.48 \text{ cm}^3 \text{ K mol}^{-1}$ , attributed to three uncoupled HS Fe(II) centres. The SCO curve decreased sharply at 320 K to  $0.0 \text{ cm}^3 \text{ K mol}^{-1}$ , consistent with complete SCO to fully LS. The structural transition was also monitored by single crystal X-ray crystallography and DSC studies (Fig. 30).

Most recently, Tong, Dong, and co-workers used 4-amino-1,2,4-triazole, **L47** (Chart 9), to generate the trinuclear complex  $[\text{Fe}_3(\text{L47})_6(\text{SCN})_4(\text{H}_2\text{O})_2](\text{SCN})_2\cdot \text{H}_2\text{O}$ .<sup>118</sup> Heating at 400 K caused

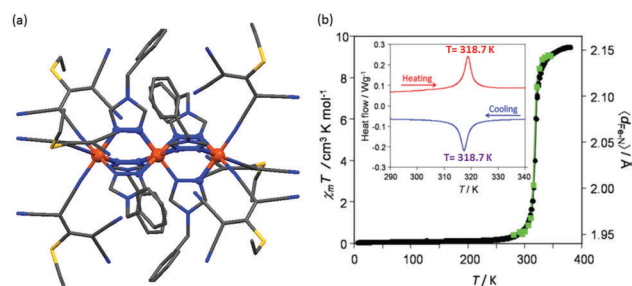


Fig. 30 Data for  $[\text{Fe}_3\text{L46}_6(\text{A6})_6]$ : (a) crystal structure (b) plot of  $\chi_m T$  vs.  $T$  (black circle) and the average Fe–N distances (green squares) around the transition region. Inset: DSC study in both exo- and endo-thermic modes. Structure redrawn from CCDC data. Figure (b) is adapted from ref. 117 with permission. Copyright 2017 RSC.



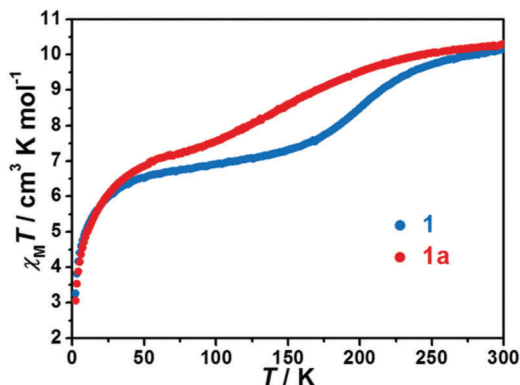


Fig. 31  $\chi_M T$  vs.  $T$  plots for as synthesised  $[\text{Fe}_3(\text{L47})_6(\text{SCN})_4(\text{H}_2\text{O})_2](\text{SCN})_2 \cdot \text{H}_2\text{O}$  (blue, labelled 1 in this figure) and de-solvated  $[\text{Fe}_3(\text{L47})_6(\text{SCN})_5(\text{H}_2\text{O})](\text{SCN})$  (red, labelled 1a in this figure). Figure adapted with permission from ref. 118. Copyright 2018 RSC.

the complex to undergo a thermally induced single crystal-to-single crystal transformation, losing two water molecules and becoming  $[\text{Fe}_3(\text{L47})_6(\text{SCN})_5(\text{H}_2\text{O})](\text{SCN})$ . This changed the SCO  $T_{1/2}$  from 202 to 160 K, with the SCO being gradual and, as usual (see above), only being observed for the central Fe(II) ion in both cases, *i.e.*  $[\text{HS}-\text{HS}-\text{HS}] \leftrightarrow [\text{HS}-\text{LS}-\text{HS}]$  (Fig. 31).<sup>118</sup>

#### Tetrametallic anion-bridged Fe<sub>4</sub> squares

The metal ions in cyanometallates like  $[\text{Fe}(\text{CN})_6]^{4-}$  are LS due to the coordination of six strong field  $\pi$ -acceptor  $\text{CN}^-$  anions.<sup>119</sup> Such cyanometallate polyanions can be used to bridge other metal ions, as both the C and N of the cyanide anion can coordinate, and this has been a profitable line of enquiry for the generation of Single Chain Magnets (SCMs).<sup>120</sup> But to generate SCO-active complexes requires a significant reduction

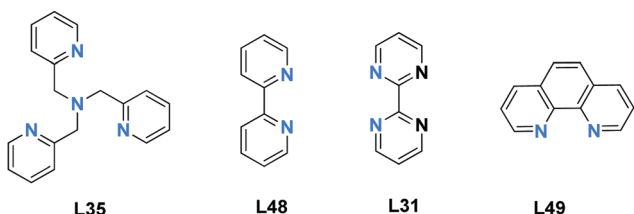


Chart 10 Capping ligands used in anion bridged SCO-active Fe(II) tetrametallic square complexes (Fig. 2, 4A).

in the number of  $\text{CN}^-$  ligands, with weaker field co-ligands being used in place of some of them.<sup>121</sup>

In this section we consider  $\text{CN}^-$  or ( $\text{dca}^-$ , Chart 7) bridged tetranuclear Fe(II) squares (Fig. 2, 4A), featuring an  $\text{Fe}_4(\mu\text{-mono}/\text{di-cyano})_4$  core, with capping ligands (Chart 10) completing the, mixed  $\text{N}_4\text{C}_2\text{-N}_6$  with cyano bridges or all  $\text{-N}_6$  with dicyano bridges, octahedral coordination environments around the Fe(II) centres,<sup>122–125</sup> *i.e.* two *cis*-sites are occupied by N/C of two mono/di-cyanide ions and the remaining four sites are occupied by either one tetradentate or two bidentate ‘capping’ ligands (Chart 10). In the case of  $\mu\text{-CN}$  bridged squares, the  $\text{Fe}\cdots\text{Fe}$  distance is  $\sim 5$  Å, whereas in  $\text{dca}^-$  bridged squares this distance is  $\sim 8$  Å (Table 7). The octahedral distortion  $\Sigma$  of the Fe(II) centres in these squares is modest: LS in the range  $31\text{--}70^\circ$  and HS in the range  $74\text{--}109^\circ$  (Table 7).

Oshio and co-workers have reported several such squares. The first, reported in 2005, featured a mixture of tetradentate L35 and bidentate L48 capping ligands (Chart 10). Initially,  $[\text{Fe}_2\text{L35}(\text{L48})_2(\mu\text{-NC})_2]_2(\text{PF}_6)_4$  was studied, in which  $[\text{FeL35}]^{2+}$  and  $[\text{Fe}(\text{L48})_2]^{2+}$  centres are alternately arranged in the square, and bridged by four cyanide groups – with the carbon atoms of  $\text{CN}^-$  always binding to  $[\text{Fe}(\text{L48})_2]^{2+}$ . This leads to alternating  $\text{N}_4\text{C}_2$  and  $\text{N}_6$  coordination of the four Fe(II) centres in the square. The magnetic studies showed thermally induced two step SCO, with  $T_{1/2} = 160$  K and 380 K. Up to 100 K all Fe<sup>II</sup> sites are LS ( $\chi_M T = 0.3$   $\text{cm}^3$   $\text{mol}^{-1}$  K), then upon warming to 200 K,  $\chi_M T$  increases to  $3.2$   $\text{cm}^3$   $\text{mol}^{-1}$  K, corresponding to one HS iron site. X-ray crystallography at 200 K revealed that this SCO event occurs at one of the two  $[\text{Fe}(\text{L35})]^{2+}$  units (where both CN bridges bond through the N atom). Upon further increasing the temperature, the  $\chi_M T$  remained constant until 300 K, then increased to  $4.9$   $\text{cm}^3$   $\text{mol}^{-1}$  K at 400 K, which corresponds to 57% of the second  $[\text{Fe}(\text{L35})]^{2+}$  unit becoming HS (Fig. 32a).<sup>122</sup>

The authors also monitored SCO by reflectance studies on crystals at 100 K and 300 K on the (001) plane with unpolarised light. At 100 K, the spectra consisted of one sharp peak at 2.13 eV (582 nm) and two broad peaks at 2.3 eV (539 nm) and 2.6 eV (477 nm) (Fig. 32b). These peaks were assigned to d–d transitions of the LS Fe(II) centres in the  $[\text{Fe}(\text{L48})_2]^{2+}$  and  $[\text{Fe}(\text{L35})]^{2+}$  units respectively. At 300 K, two broad peaks merged at 2.40 eV (517 nm) and one new sharp peak appeared at 1.47 eV (843 nm) which was assigned to a d–d transition of a HS Fe(II) of a  $[\text{Fe}(\text{L35})]^{2+}$  moiety (Fig. 32b).

Table 7 Selected parameters for SCO-active tetranuclear Fe(II) squares (Fig. 2, 4A). LS centres in italics

|  | $T$ (K) | Fe–Fe (Å)              | $\Sigma$ ( $^\circ$ ) | Spin state  | $T_{1/2}$ (K) | Lit. |
|--|---------|------------------------|-----------------------|-------------|---------------|------|
| $[\text{Fe}_2\text{L35}(\text{L48})_2(\mu\text{-NC})_2]_2(\text{PF}_6)_4$  | 100     | 5.00, 4.95, 4.99, 4.99 | 52, 61, 47, 45        | LS–LS–LS–LS | 160, 380      | 122  |
|  | 200     | 5.04, 5.02, 4.99, 4.99 | 50, 108, 48, 45       | LS–HS–LS–LS |               |      |
|  | 293     | 5.05, 5.02, 5.0, 4.99  | 49, 109, 46, 47       | LS–HS–LS–LS |               |      |
| $[\text{Fe}_2\text{L31}_2(\text{L48})_2(\text{NC})_2]_2(\text{PF}_6)_4 \cdot 6\text{MeOH} \cdot 4\text{H}_2\text{O}$ | 200     | 4.96, 4.98,            | 49, 56                | 2LS–2LS     | Not stated    | 123  |
| $[\text{Fe}(\text{L35})(\text{CN})]_4(\text{BF}_4)_4 \cdot \text{MeCN} \cdot \text{H}_2\text{O}$                     | 100     | 4.94, 4.97, 4.94, 4.95 | 68, 49, 55, 70        | LS–LS–LS–LS | Not stated    | 124  |
| $[\text{Fe}(\text{L35})(\text{CN})]_4(\text{BF}_4)_4 \cdot 0.75\text{MeCN} \cdot \text{H}_2\text{O}$                 | 210     | 4.59, 4.99, 4.96, 4.98 | 69, 74, 47, 79        | LS–HS–LS–HS |               |      |
| $[\text{Fe}(\text{L35})(\text{dca})]_4(\text{BF}_4)_4 \cdot 2(\text{H}_2\text{O})$                                   | 150     | 8.23, 8.40             | 54, 60                | 2LS–2LS     | 302, 194      | 126  |
|  | 250     | 8.44, 8.36             | 57, 91                | 2LS–2HS     |               |      |
| $[\text{Fe}(\text{L35})(\text{dca})]_4(\text{BF}_4)_4$   | 350     | 8.51, 8.49             | 88, 98                | 2HS–2HS     |               |      |
| $[\text{Fe}_4(\text{L49})_4(\text{L35})_2(\text{CN})_4](\text{PF}_6)_4 \cdot 1\text{MeCN} \cdot \text{H}_2\text{O}$  | 100     | 4.98, 4.99             | 44, 43                | 2LS–2LS     | Not stated    | 125  |
| $[\text{Fe}_4(\text{L49})_4(\text{L35})_2(\text{CN})_4](\text{PF}_6)_4$  | 370     | 5.07, 5.04             | 31, 86                | 2LS–2HS     |               |      |



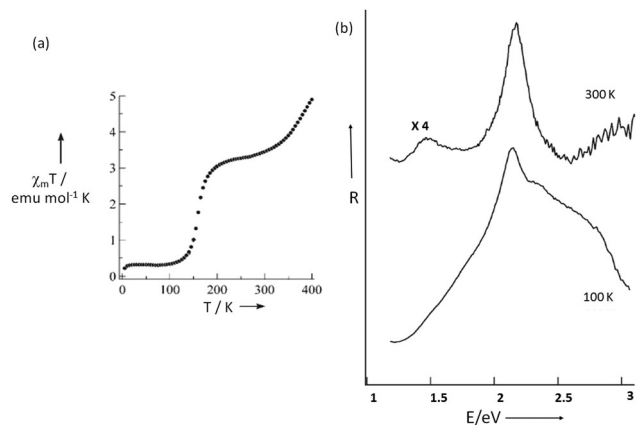


Fig. 32 (a) Plot of  $\chi_m T$  vs.  $T$  for  $[\text{Fe}_2\text{L35}(\text{L48})_2(\text{u-CN})_2]_2(\text{PF}_6)_4$ ; (b) reflectance spectra;  $R$  = reflectivity,  $E$  = photon energy. Figure adapted with permission from ref. 122. Copyright 2005 John Wiley and Sons.

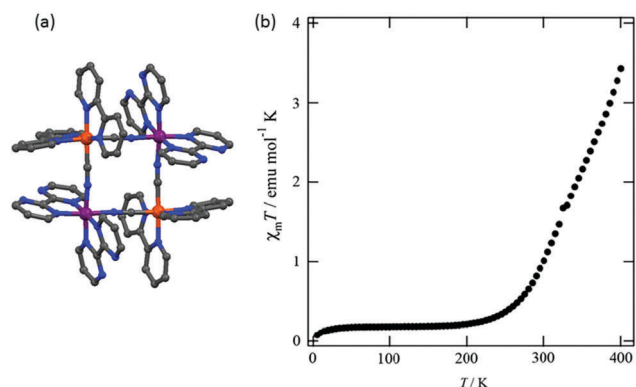


Fig. 33 (a) Crystal structure of the cation of  $[\text{Fe}_4(\text{L48})_2(\text{L31})_2(\text{CN})_4](\text{PF}_6)_4$ , SCO active Fe(II) centres violet (b) plot of  $\chi_m T$  vs.  $T$  for  $[\text{Fe}_4(\text{L48})_2(\text{L31})_2(\text{CN})_4](\text{PF}_6)_4 \cdot 6\text{MeOH} \cdot 4\text{H}_2\text{O}$ . Structure redrawn from CCDC data. (b) Reproduced with permission from ref. 123. Copyright 2009 Elsevier.

The same group has reported a related heteroleptic tetranuclear cyanide bridged square, again using bidentate **L48** but replacing tetradentate **L35** by two bidentate **L31** ligands (Chart 10),  $[\text{Fe}_4(\text{L48})_2(\text{L31})_2(\text{CN})_4](\text{PF}_6)_4 \cdot 6\text{MeOH} \cdot 4\text{H}_2\text{O}$  (Fig. 33a). Again the corners alternate between  $[\text{Fe}(\text{L48})_2]^{2+}$  and  $[\text{Fe}(\text{L31})_2]^{2+}$  around the square. The complex remained LS up to 250 K, then the  $\chi_m T$  product increased gradually to  $3.42 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 400 K. The  $[\text{Fe}(\text{L48})_2]^{2+}$  corners remain LS throughout, whereas the  $[\text{Fe}(\text{L31})_2]^{2+}$  corners undergo SCO to HS in one step (Fig. 33b).<sup>123</sup>

Shatruck and co-workers prepared homoleptic capped  $\text{Fe}_4^{\text{II}}$  squares using the tetradentate capping ligand **L35** (Chart 10).  $[\text{Fe}(\text{L35})(\text{CN})_4]_4 \cdot X_4 \cdot n\text{MeOH}$  ( $X = \text{BF}_4^-$ ,  $\text{ClO}_4^-$ ), revealed SCO curves which were strongly influenced by the presence of solvent MeOH molecules, while counteranion variation had little effect.<sup>124</sup> The  $\chi_m T$  value of both complexes covered in a small amount of MeOH mother liquor at 300 K was  $\sim 7.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  which was consistent with two HS and two LS Fe(II) centres in each cluster. The wet samples showed abrupt SCO with complete one step spin conversion of two  $\text{N}_6$  Fe(II) HS ions to the LS state at

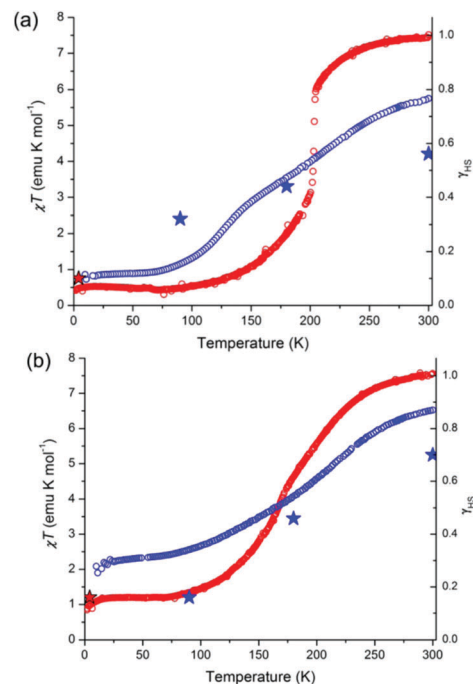


Fig. 34 Plot of  $\chi T$  and the high spin fraction ( $\gamma_{\text{HS}}$ ) vs.  $T$  for the two HS Fe(II) sites attributed to being in  $\text{N}_6$  coordination environments: red curves, as synthesized (wet) samples; blue curves, powder samples (a)  $[\text{Fe}(\text{L35})(\mu\text{-CN})]_4(\text{BF}_4)_4$  and (b)  $[\text{Fe}(\text{L35})(\mu\text{-CN})]_4(\text{ClO}_4)_4$ . Figures adapted with permission from ref. 124. Copyright 2014 ACS.

low temperature. Dry powder samples showed more gradual incomplete one-step spin transition (Fig. 34).<sup>124</sup>

Zheng and co-workers have also used the tetradentate **L35** capping ligand (Chart 10) to prepare a homoleptic capped square, but this time featuring dicyanamide bridges,  $[\text{Fe}(\text{L35})(\text{dca})_2]_4(\text{BF}_4)_4 \cdot 2(\text{H}_2\text{O})$ . In this square all of the Fe(II) centres have  $\text{N}_6$  coordination (Fig. 35a). It exhibits both thermal and light irradiation induced two step, complete SCO in both the hydrated and dehydrated forms. The as-synthesized sample was heated at 350 K to SCSC transform the hydrated crystals to the dehydrated form. The asymmetric unit of the as-synthesised hydrated form contained two crystallographically different Fe(II) centres. At 150 K,  $\Sigma = 60^\circ$  and  $54^\circ$ , which changed to  $91^\circ$  and  $57^\circ$  at 250 K (Table 7), which suggested that two identical iron(II) centres have undergone

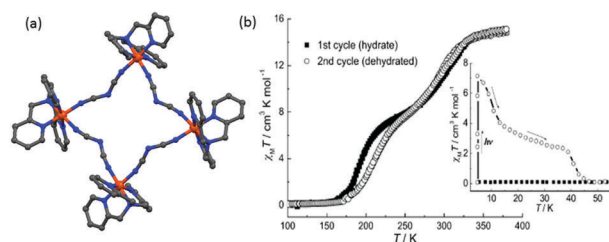


Fig. 35 (a) Crystal structure of the cation of  $[\text{Fe}(\text{L35})(\text{dca})_2]_4(\text{BF}_4)_4 \cdot 2\text{H}_2\text{O}$  (b) plots of  $\chi_m T$  vs.  $T$  for  $[\text{Fe}(\text{L35})(\text{dca})_2]_4(\text{BF}_4)_4$  in two successive temperature cycles 300–100–380 K (square), and 380–100–380 K (circle). Inset: LIESST studies. Structure redrawn from CCDC data. (b) Reproduced with permission from ref. 126. Copyright 2011 John Wiley and Sons.



SCO to HS. At 350 K, solvent molecules are removed but crystal packing remained intact and  $\Sigma$  changed to 98.0 and 88.2° corresponding to all Fe(II) in the HS state. For the two-step SCO of the hydrated square  $T_{1/2} = 302$  and 194 K, and for the dehydrated form  $T_{1/2} = 294$  and 211 K. The  $\chi_m T$  vs.  $T$  curve follows the same route for the cooling and heating processes, except for a 6 K wide hysteresis (Fig. 35b) in the 4LS to 2HS–2LS step. The LIESST effect was studied at 5 K with 457 nm irradiation: the maximum  $\chi_m T$  observed was 7.08 cm<sup>3</sup> K mol<sup>-1</sup>, which was assigned to 47.5% photo-excited HS population. When the light source is switched-off, the metastable HS state relaxed steeply between 5–13 K, then smoothly from 13–33 K, with a plateau at approximately 3 cm<sup>3</sup> mol<sup>-1</sup> K which corresponds to relaxation of half of the metastable HS population (Fig. 35b, inset).<sup>126</sup>

Real and co-workers reported a heteroleptic capped square of **L35** and **L49** (Chart 10), [Fe<sub>4</sub>(μ-CN)<sub>4</sub>(**L49**)<sub>4</sub>(**L35**)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>. Again the cyanide bridges are ordered, binding *via* N to the [Fe(**L35**)]<sup>2+</sup> corners and *via* C to the [Fe(**L49**)<sub>2</sub>]<sup>2+</sup> corners. This complex undergoes incomplete and gradual one-step SCO. The  $\chi_m T$  value at 400 K was 5.3 cm<sup>3</sup> K mol<sup>-1</sup>, which corresponds to a value just below that expected for a 2HS–2LS state, and decreased to 0.5 cm<sup>3</sup> K mol<sup>-1</sup> at 4 K, *i.e.* fully LS. The crystal structure investigation showed that the two N<sub>6</sub>-coordinated [Fe(**L35**)]<sup>2+</sup> units are SCO active, while the two N<sub>4</sub>C<sub>2</sub>-coordinated [Fe(**L49**)<sub>2</sub>]<sup>2+</sup> units remain LS up to 370 K.<sup>125</sup> The authors also studied the magnetic behaviour on changing the ligand field strength by varying the extent of methyl substitution at the 6-position of one or two of the pyridine groups of **L35**. They observed that these methyl substituents increased the steric constraint which led to longer Fe–N bond distances, weakening the ligand strength and stabilising the HS state of [FeN<sub>6</sub>] and LS [FeN<sub>4</sub>C<sub>2</sub>] centres all over the temperature range.<sup>125</sup>

### Tetranuclear [2 × 2] grids Fe<sub>4</sub>L<sub>4</sub>

Like the tetrametallic squares, tetrametallic [2 × 2] grids (Fig. 2, 4B) are an appealing architecture for SCO design, with the possibility of multistability being exhibited in an array of four addressable metal ion sites.<sup>42,43</sup> The combination of octahedral Fe(II), the most commonly studied SCO metal ion, with bis-terdentate rigid linear bridging ligands to, in a controlled way, self-assemble Fe<sub>4</sub>L<sub>4</sub> grids is therefore a very attractive pursuit in SCO research. Again this is a relatively young area of investigation, with few reported Fe<sub>4</sub>L<sub>4</sub> grids in the literature, and even fewer examples that exhibit SCO. In fact only 21 ligands (Chart 11) have been reported to produce SCO-active Fe<sub>4</sub> grids,<sup>39,127–137</sup> the first of which was reported in 2000 – this was also the first example of an SCO-active tetranuclear complex,<sup>127</sup> and held the record for the largest nuclearity discrete SCO-active complex until 2009 (see the ‘nanoball’ later). Interestingly, 16 of the ligands employed to date feature pyrimidine-bridging moieties **L50–L65**<sup>–</sup> (only 6 of the resulting grids have been structurally characterised, one in two different spin states, Table 8), whilst the other 5 ligands, **L66**<sup>–</sup> to **L70** (all of the resulting grids have been structurally characterised, Table 9), present a wide range of different bridging moieties (Chart 11).

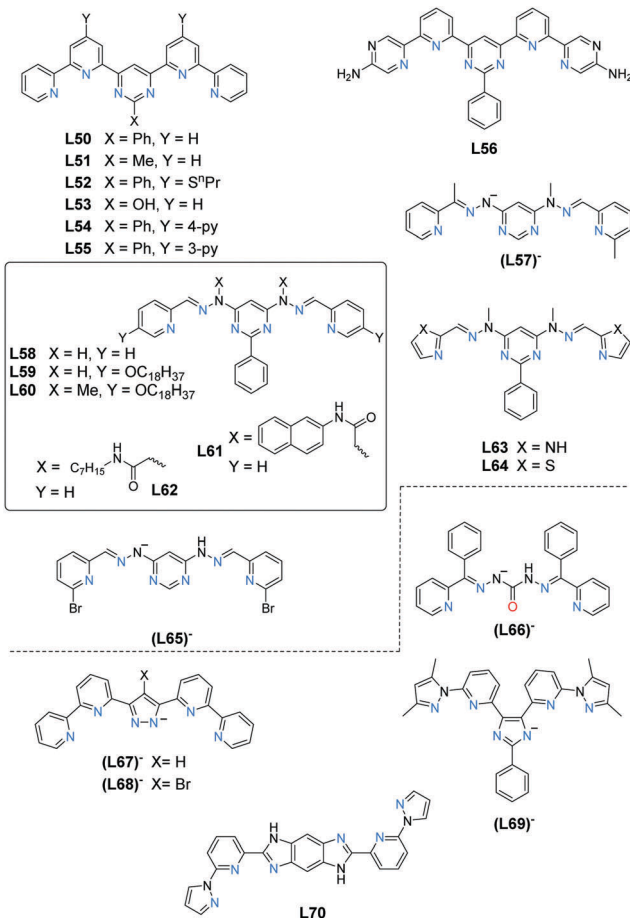


Chart 11 The 21 bis-terdentate ligands known to form SCO-active Fe<sub>4</sub>L<sub>4</sub> grids (Fig. 2, 4B). All ligands provide N<sub>6</sub> donor sets to the octahedral Fe(II) centres, except (**L66**)<sup>–</sup> which provides a N<sub>4</sub>O<sub>2</sub> donor set, to the octahedral Fe(II) centres, so no co-ligands are bound.

In each case the ligand is bis-terdentate and as such the four ligands in the corresponding Fe<sub>4</sub>L<sub>4</sub> grid complexes provide all of the donor atoms to the Fe(II) centres with no co-ligands bound. This, coupled with the fact that all ligands contain either a heterocyclic or single atom bridging moiety, results in a very rigid coordination environment and significant octahedral distortions at the Fe(II) centres. As a result, these grids impose much larger  $\Sigma$  values on the Fe(II) centres (LS 84–125°, HS 129–176°; Tables 8 and 9) than those observed in the other tetranuclear architectures, squares (LS 31–70°, HS 79–109°; Table 7) and cages (LS 43–75°, HS 69–121°; see later, Tables 10 and 11).

In 2000, Lehn, Gütllich and co-workers reported the first SCO-active Fe(II) [2 × 2] grid.<sup>127</sup> The grid was assembled from the linear bis-terdentate ligand 4,6-bis(2,2′-bipyridin-6-yl)-2-phenylpyrimidine (**L50**, Chart 11), and the structure of [Fe<sub>4</sub>(**L50**)<sub>4</sub>]<sup>8+</sup> was determined by X-ray crystallography (Fig. 36a). Analysis of the Fe–N bond lengths at 293 K clearly revealed three of the Fe(II) centres were HS while the fourth had bond lengths intermediate between those typical for HS and LS states. In contrast, at 100 K three of the Fe(II) centres have intermediate Fe–N bond lengths (but closer to LS) and one is HS, indicating that a thermal SCO has occurred. Variable temperature magnetic susceptibility



**Table 8** Selected parameters for the structurally characterised SCO-active tetranuclear Fe(II)  $2 \times 2$  grids (Fig. 2, **4B**) of pyrimidine-based ligands **L50–L65** (Chart 11, NB). The grids of pyrimidine-based ligands **L55–L64** were not structurally characterised. See Table 9 for grids of the non-pyrimidine-based ligands (Chart 11). LS centres in italics

|  | <i>T</i> (K) | Fe–Fe (Å)              | $\Sigma$ (°)       | Spin state | <i>T</i> <sub>1/2</sub> (K) | Lit.        |
|--|--------------|------------------------|--------------------|------------|-----------------------------|-------------|
| [Fe <sup>II</sup> ( <b>L50</b> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>8</sub> ·9MeCN·1.25H <sub>2</sub> O                | 100          | 6.42, 6.35, 6.32, 6.42 | 88, 87, 91, 146    | HS–3LS     | Not stated                  | 127         |
|  | 293          | 6.43, 6.47, 6.50, 6.47 | 137, 109, 143, 146 | 3HS–LS     |                             |             |
| [Fe <sup>II</sup> ( <b>L53</b> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>8</sub> ·3MeCN·5H <sub>2</sub> O                   | 120          | 6.27, 6.33, 6.42, 6.39 | 160, 146, 125, 98  | 2HS–2LS    | Not stated                  | 128         |
| [Fe <sup>II</sup> ( <b>L54</b> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>7</sub> (Cl)·7MeNO <sub>2</sub> ·6H <sub>2</sub> O | 120          | 6.30, 6.35             | 85, 84             | 2LS–2LS    | Not stated                  | 128 and 129 |
| [Fe <sup>II</sup> ( <b>L65</b> ) <sub>4</sub> ]Cl <sub>4</sub> ·9H <sub>2</sub> O  | 153          | 5.93, 5.98             | 88, 91             | 2LS–2LS    | Not stated                  | 135         |
| [Fe <sup>II</sup> ( <b>L65</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·7H <sub>2</sub> O                          | 153          | 6.07, 6.06             | 86                 | 4LS        | Not stated                  | 135         |

**Table 9** Selected parameters for the structurally characterised SCO-active tetranuclear Fe(II)  $2 \times 2$  grids (Fig. 2, **4B**) of non-pyrimidine-based ligands **L66** to **L70** (Chart 11). See Table 8 for grids of the pyrimidine-based ligands (Chart 11). LS centres in italics

|   | <i>T</i> (K) | Fe–Fe (Å) | $\Sigma$ (°) | Spin state           | <i>T</i> <sub>1/2</sub> (K) | Lit. |
|---|--------------|-----------|--------------|----------------------|-----------------------------|------|
| [Fe <sup>II</sup> ( <b>L66</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·MeOH·2H <sub>2</sub> O  | 123          | 3.77      | 105          | 2LS–2HS              | 175                         | 134  |
|   |              | 3.84      | 129          |                      |                             |      |
|   |              | 3.87      | 149          |                      |                             |      |
|   |              | 3.75      | 113          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L66</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·MeOH·2H <sub>2</sub> O  | 283          | 3.84      | 149          | HS–HS–HS–HS          |                             |      |
|   |              | 3.73      | 147          |                      |                             |      |
|   |              | 3.86      | 146          |                      |                             |      |
|   |              | 3.88      | 150          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L67</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·4DMF  | 133          | 4.52      | 145          | 3HS–LS               | Not stated                  | 39   |
|   |              | 4.51      | 97           |                      |                             |      |
|   |              | 4.42      | 144          |                      |                             |      |
|   |              | 4.57      | 156          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L67</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·4DMF  | 233          | 4.88      | 151          | HS–HS–HS–HS          |                             |      |
|   |              | 4.45      | 137          |                      |                             |      |
|   |              | 4.45      | 149          |                      |                             |      |
|   |              | 4.51      | 152          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L67</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>6</sub> ·3CH <sub>3</sub> CN   | 133          | 4.53      | 92           | 2LS–2HS              | LS–HS                       | 39   |
|   |              | 4.59      | 148          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>HL67</b> ) <sub>2</sub> ( <b>L67</b> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2CH <sub>3</sub> CN                      | 133          | 4.59      | 95           | 2LS–HS               | ↑ ↓ 355, 329                | 138  |
|   |              | 4.54      | 94           |                      |                             |      |
|   |              |           | 142          |                      |                             |      |
|   |              |           | 99           |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L68</b> ) <sub>4</sub> ](PF <sub>6</sub> ) <sub>4</sub> ·DMF·THF   | 133          | 4.50      | 99           | 2LS–2HS              | 2LS–2HS                     | 133  |
|   |              | 4.48      | 170          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L68</b> ) <sub>4</sub> ](PF <sub>6</sub> ) <sub>4</sub> ·4DMF  | 133          | 4.42      | 150          | HS–HS–HS–HS–HS–HS–HS | HS                          | 133  |
|   |              | 4.35      | 153          |                      |                             |      |
|   |              | 4.36      | 153          |                      |                             |      |
|   |              | 4.40      | 159          |                      |                             |      |
|   |              | 4.36      | 159          |                      |                             |      |
|   |              | 4.39      | 139          |                      |                             |      |
|   |              | 4.40      | 148          |                      |                             |      |
|   |              | 4.37      | 155          |                      |                             |      |
|   |              | 4.41      | 152          |                      |                             |      |
|   |              | 4.48      | 142          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L68</b> ) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>4</sub> ·0.25DMF·DME  | 133          | 4.48      | 150          | 6HS–2LS              | 3HS–1LS                     | 133  |
|   |              | 4.50      | 90           |                      |                             |      |
|   |              | 4.50      | 91           |                      |                             |      |
|   |              | 4.51      | 173          |                      |                             |      |
|   |              | 4.46      | 136          |                      |                             |      |
|   |              | 4.47      | 159          |                      |                             |      |
|   |              | 4.44      | 150          |                      |                             |      |
|   |              | 4.53      | 105          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L68</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·THF·4H <sub>2</sub> O   | 293          | 4.44      | 150          | 4HS                  | 250                         | 133  |
|   |              | 4.41      | 176          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L68</b> ) <sub>4</sub> ]Br <sub>4</sub> ·4DMF·2H <sub>2</sub> O  | 133          | 4.41      | 176          | LS–HS–HS–HS          | Not stated                  | 133  |
|   |              |           | 160          |                      |                             |      |
|   |              |           | 131          |                      |                             |      |
|   |              |           | 145          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L69</b> ) <sub>4</sub> ](BF <sub>4</sub> ) <sub>4</sub> ·2MeCN   | 293          | 6.48      | 131          | HS–HS–HS–HS          | Not stated                  | 136  |
|   |              | 6.44      | 145          |                      |                             |      |
|   |              | 6.51      | 144          |                      |                             |      |
|   |              | 6.42      | 147          |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L70</b> ) <sub>4</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>8</sub> ·12MeNO <sub>2</sub> ·C <sub>6</sub> H <sub>14</sub> O | 180          | 9.16      | 87           | 2LS–2LS              | 310                         | 137  |
|   |              | 9.05      | 85           |                      |                             |      |
| [Fe <sup>II</sup> ( <b>L70</b> ) <sub>4</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> (F) <sub>3</sub> ·2MeNO <sub>2</sub> ·H <sub>2</sub> O | 180          | 7.33      | 167          | 2HS–2HS              | HS                          | 137  |
|   |              | 7.22      | 152          |                      |                             |      |

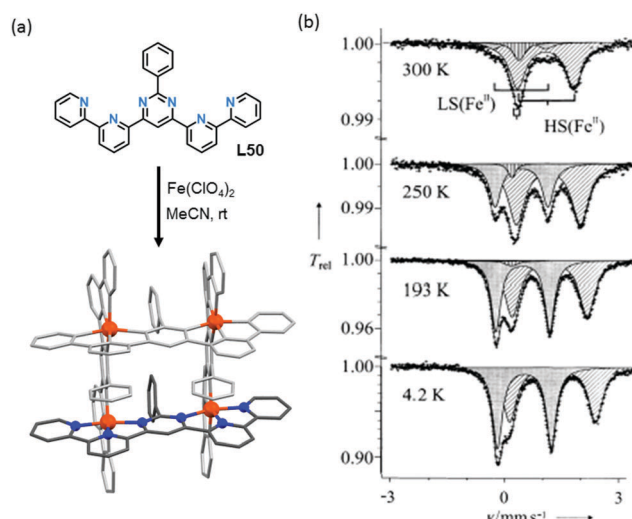


**Table 10** Selected parameters for SCO-active tetranuclear Fe(II) tetrahedral cages (Fig. 2, **4C**) of the tri-topic, face bridging, ligands **L71–L74** (Chart 12). See Table 11 for the di-topic, edge bridging, ligands. LS centres in italics

|  | <i>T</i> (K) | Fe–Fe (Å)   | $\Sigma$ (°)                                       | Spin state | Lit. |
|--|--------------|---|--|------------|------|
| $[\text{Fe}_4^{\text{II}}(\text{L71})_4](\text{BF}_4)_8 \cdot 14.75\text{MeCN} \cdot 4.5\text{C}_6\text{H}_6 \cdot 3\text{H}_2\text{O}$          | 153          | 14.28, 14.28, 14.28, 13.99, 14.14, 13.98                            | <i>61, 60</i>                                      | 2LS–2LS    | 140  |
| $[\text{Fe}_4^{\text{II}}(\text{L71})_4](\text{BF}_4)_8 \cdot 14.75\text{CH}_3\text{CN} \cdot 4.5\text{C}_6\text{H}_6 \cdot 3\text{H}_2\text{O}$ | 293          | 14.46, 14.29, 14.11, 14.52, 14.46, 14.11                            | 66, 69   | 2LS/HS–2HS | 140  |
| $\text{Fe}_4^{\text{II}}(\text{L73})(\text{CF}_3\text{SO}_3)_8$  | 100          | 6 × 11.85   | 65   | 4LS        | 141  |
| $[\text{Fe}_4^{\text{II}}(\text{L74})_4](\text{BF}_4)_4 \cdot 16\text{CH}_3\text{CN}$  | 100          | 3 × 14.61, 3 × 14.78, 3 × 14.54,<br>3 × 14.94, 3 × 14.56, 3 × 15.14 | 2 × 82, 2 × 67, 2 × 70,<br>2 × 121, 2 × 86, 2 × 75 | 6LS–6HS    | 142  |

**Table 11** Selected parameters for SCO-active tetranuclear Fe(II) tetrahedral cages (Fig. 2, **4C**) of the di-topic, edge bridging, ligands **L75–L78** (Chart 12). See Table 10 for the tri-topic, face bridging, ligands. LS centres in italics

|   | <i>T</i> (K) | Fe–Fe (Å)   | $\Sigma$ (°)                  | Spin state | Lit. |
|---|--------------|---|-------------------------------|------------|------|
| $[\text{Fe}_4^{\text{II}}(\text{L75})_6](\text{ClO}_4)_8$ ( <i>R</i> )  | 150          | 3 × 9.56, 3 × 9.67  | <i>61, 49</i>                 | LS–LS      | 143  |
| $[\text{Fe}_4^{\text{II}}(\text{L75})_6](\text{ClO}_4)_8$ ( <i>S</i> )  | 123          | 3 × 9.66, 3 × 9.48  | <i>60, 42</i>                 | LS–LS      | 143  |
| $[\text{Fe}_4^{\text{II}}(\text{L76})_6](\text{ClO}_4)_8 \cdot 11.59\text{MeCN} \cdot 2\text{C}_4\text{H}_{10}\text{O} \cdot \text{H}_2\text{O}$ ( <i>R</i> ) | 123          | 9.66, 9.45, 9.70, 9.59, 9.64, 9.79                                | <i>56, 58, 56, 64</i>         | 4LS        | 143  |
| $[\text{Fe}_4^{\text{II}}(\text{L76})_6](\text{ClO}_4)_8 \cdot 6\text{MeCN}$ ( <i>S</i> )   | 123          | 9.74, 9.70, 9.68, 9.41, 9.77, 9.76                                | <i>56, 55, 60, 63</i>         | 4LS        | 143  |
| $[\text{Fe}_4^{\text{II}}(\text{L77})_6](\text{ClO}_4)_8 \cdot 2\text{MeCN}$ ( <i>S</i> )   | 123          | 3 × 9.53, 3 × 9.81  | <i>55, 57</i>                 | 2LS        | 143  |
| $[\text{Fe}_4^{\text{II}}(\text{L78})_6](\text{ClO}_4)_8 \cdot 2\text{MeCN}$  | 173          | 11.35, 11.04, 11.90, 11.73, 11.95,<br>11.18, 3 × 11.97, 3 × 11.78 | <i>43, 45, 49, 43, 53, 50</i> | 6LS        | 144  |



**Fig. 36** (a) Reaction of 4,6-bis(2,2'-bipyrid-6-yl)-2-phenyl-pyrimidine (**L50**) with iron(II) perchlorate in acetonitrile at room temperature to produce the corresponding  $[\text{Fe}_4(\text{L50})_4](\text{ClO}_4)_8$  [ $2 \times 2$ ] grid and (b) evidence of the SCO, by Mössbauer spectroscopy, from 80% HS at 300 K (top) to 46% HS at 4.2 K (bottom). Structure redrawn from CCDC data.<sup>127</sup> (b) Figure adapted, reproduced with permission, from ref. 127. Copyright 2000 John Wiley and Sons.

showed that there was indeed a SCO event, which was very gradual and incomplete over 300–30 K. The authors performed Mössbauer spectroscopy studies to yield further evidence of SCO (Fig. 36b) and were able to induce SCO by varying the pressure, and by the LIESST effect, making this a triply switchable SCO [ $2 \times 2$ ] grid.

Modifications to the bis-terdentate ligand, through substitution of peripheral groups at the pyrimidine or bipyridine groups, allowed for a family of closely related grids to be investigated. Substitution of the phenyl group at the pyrimidine-2-position for a methyl group (**L51**, Chart 11) accessed the second example of an Fe(II) SCO grid, whereas H or OH groups yielded diamagnetic

analogues.<sup>128</sup> Further SCO-active grids were obtained by either the attachment of peripheral groups at the pyrimidine or bipyridine groups (X or Y, **L52–L55**, Chart 11)<sup>128,129</sup> or the use of bipyridine-like groups (**L56**, Chart 11).<sup>128</sup> Lehn and co-workers have since produced several more SCO-active Fe(II) grids of related pyrimidine ligands. In fact they have produced more than half of the known SCO-active Fe(II) grids in the literature. The other ligands used by them are also based on the pyrimidine bridging unit, but these ligands contain functionalised bis-hydrazone side arms and either pyridine<sup>130,131</sup> [**L57**<sup>−</sup> and **L58–L62**, Chart 11] or imidazole/thiazole<sup>132</sup> (**L63** and **L64**, Chart 11) rings, and various substitutions thereof, to complete the terdentate binding pockets. In each case where SCO was observed the transition was very gradual and incomplete across a wide thermal range.

In 2013 Kou and co-workers reported two SCO-active  $[\text{Fe}_4(\text{L65})_4]\text{X}_4$  grid complexes based on a bis-terdentate Schiff base ligand [**L65**<sup>−</sup>, Chart 11].<sup>135</sup> Similar to the ligands employed by Lehn and co-workers, the ligand scaffold also features a central pyrimidine bridging moiety. The SCO for the X = Cl<sup>−</sup> grid is incomplete, with the transition taking place above room temperature between (approximately) the [2HS–2LS] and [HS–3LS] states (Fig. 37, black data points). The transition is noticeably more abrupt than the pyrimidine based grids of Lehn and co-workers, and that of the X = BF<sub>4</sub><sup>−</sup> grid is even more abrupt again and appears to be centred at about 400 K, the high temperature limit of the measurement (Fig. 37, red data points). Interestingly, the analogous grid with less bulky methyl groups in place of the bromine atoms on the ligand scaffold is fully LS to high temperature.

Whilst nearly all of the SCO-active Fe(II) [ $2 \times 2$ ] grids reported in the literature to date have iron(II) ions with an N<sub>6</sub> coordination sphere, there is one exception, the N<sub>4</sub>O<sub>2</sub> coordinated grid from Sato and co-workers.<sup>134</sup> Here (**L66**<sup>−</sup> (Chart 11) features two terdentate pockets which share one bridging oxygen atom, and the corresponding O-bridged  $[\text{Fe}_4(\text{L66})_4](\text{BF}_4)_4$  grid



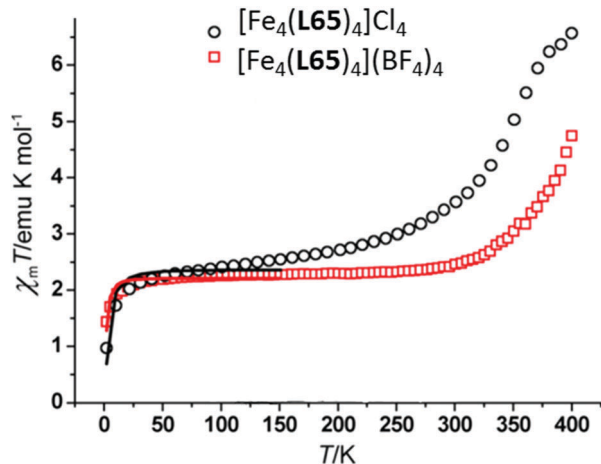


Fig. 37  $\chi_m T$  vs.  $T$  for the  $[2 \times 2]$  grids of  $[\text{Fe}_4(\text{L65})_4]\text{Cl}_4 \cdot 9\text{H}_2\text{O}$  (black circles) and  $[\text{Fe}_4(\text{L65})_4](\text{BF}_4)_4 \cdot 6\text{H}_2\text{O}$  (red squares).<sup>135</sup> Figure adapted, reproduced with permission, from ref. 135. Copyright 2013 ACS.

complex undergoes an abrupt SCO from [4HS] to [2HS–2LS] centred around 175 K.

Another bis-terdentate bridging ligand family which has provided a wealth of  $\text{Fe}_4\text{L}_4 [2 \times 2]$  grids are the bis-bipyridine pyrazolate family (Chart 11) from the group of Meyer. In 2010 they reported the synthesis of the  $[\text{Fe}_4(\text{L67})_4](\text{BF}_4)_4 [2 \times 2]$  grid (Fig. 38a) of the simple 3,5-bis{6(2,2'-dipyridyl)}pyrazolate ligand  $[(\text{L67})^-]$ , Chart 11.<sup>39</sup>

At room temperature both magnetic measurements and structural analysis indicate a fully HS state. Upon cooling to 133 K the structure is consistent with one LS Fe(II) and three HS Fe(II) ions in the grid complex and this is confirmed by a

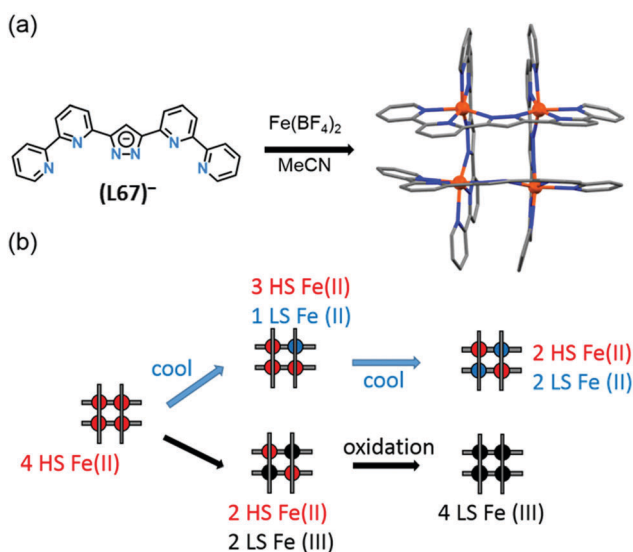


Fig. 38 (a) Synthesis of the  $[\text{Fe}_4(\text{L67})_4](\text{BF}_4)_4 [2 \times 2]$  grid from 3,5-bis(6(2,2'-dipyridyl))pyrazolate  $(\text{L67})^-$  and iron(II) tetrafluoroborate in MeCN. (b) Overview of the physical (SCO) and chemical (redox) transformations of the grid complex  $[\text{Fe}_4(\text{L67})_4](\text{BF}_4)_4$ . Structure redrawn from CCDC data.<sup>39</sup> Figure adapted, reproduced with permission, from ref. 39. Copyright 2010 John Wiley and Sons.

[3HS–LS] plateau in the  $\chi_M T$  vs.  $T$  data. Cooling even further allows for the beginning of a second SCO event to be observed, the SCO of a second Fe(II) to the LS state, thus the complex almost reaches [2HS–2LS] at 50 K. Cyclic voltammetry revealed two separate Fe(II)/Fe(III) redox events, meaning the complex is doubly switchable, by SCO or redox, with multistep events observed for both phenomena (Fig. 38b). By stoichiometric control, Meyer and co-workers have been able to access the ‘‘corner’’ unit of their  $[\text{Fe}_4(\text{L67})_4]^{4+}$  grids, *i.e.*  $[\text{Fe}(\text{HL67})_2]^{2+}$  which crystallises as hydrogen-bonded dimers.<sup>139</sup>

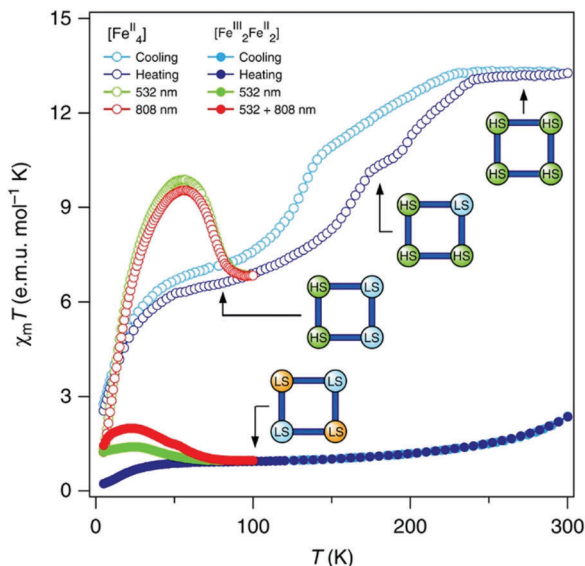
Here the Fe(II) ion of each  $\text{FeL}_2$  unit of the dimer is in the LS state, as evidenced by the short Fe–N bond lengths and regular octahedral geometry ( $\Sigma = 85.24^\circ$ ) as well as by Mössbauer spectroscopy. The LS  $[\text{Fe}(\text{HL67})_2]^{2+}$  complex suggests that the bipyridine-pyrazole binding pocket of HL67 is strong field and not suited to SCO. However, when the ligand is pyrazolate and bridging two Fe(II) ions, in addition to the steric constraints of four rigid ligands holding four Fe(II) ions in a  $[2 \times 2]$  grid, the binding environment facilitates SCO in the tetranuclear  $[\text{Fe}_4(\text{L67})_4]^{4+}$  complex.

Meyer and co-workers have since introduced a bromo substituent to the  $\text{C}^4$  position of the pyrazolate ring, *i.e.*  $(\text{L68})^-$  (Chart 11), and subsequently synthesised the corresponding  $[\text{Fe}_4(\text{L68})_4]\text{X}_4$  grids.<sup>133</sup> Variation of the counteranion ( $\text{X} = \text{PF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{Br}^-$ ) gave access to a variety of stable spin states, from [4HS] to [3HS–LS] to [2HS–2LS], with gradual thermal SCO between the states seen for some of the grids. The analogous grid of the  $\text{C}^4$ -methyl-substituted pyrazolate bis-bipyridine ligand is SCO inactive and persists in the [2HS–2LS] state up to 350 K; however, the authors note that the observed stability of the mixed spin state is favourable for potential use as a component for quantum cellular automata.<sup>38</sup> Finally, whilst technically not a  $[2 \times 2]$  grid, the controlled formation of a trinuclear defect grid  $[\text{Fe}_3(\text{HL67})_2(\text{L67})_2](\text{BF}_4)_4 \cdot \text{MeCN}$  is nevertheless highly relevant work.<sup>138</sup> It exists in the [HS–2LS] state at room temperature, but after loss of the lattice solvent MeCN it can undergo thermal SCO to the [2HS–LS] state above room temperature.

Another prominent example of a SCO-active Fe(II) grid was reported by Oshio and co-workers, using a bis-(pyrazole-pyridyl) ligand with a central bridging imidazolate,  $(\text{L69})^-$  (Chart 11).<sup>136</sup> Here, a two-step hysteretic SCO occurs for the Fe(II) grid,  $[\text{Fe}_4(\text{L69})_4](\text{BF}_4)_4$ , from the [4HS] state *via* the [3HS–LS] state to the [2HS–2LS] state (Fig. 39). At low temperatures, the [3HS–LS] state was also accessible by the LIESST effect, meaning the tri-stable  $[2 \times 2]$  grid is doubly switchable by thermal variation and light irradiation. The corresponding mixed valent  $[\text{Fe}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L69})_4](\text{BF}_4)_6$  grid is fully LS at low temperatures and only undergoes an incomplete gradual SCO upon warming at one of the Fe(III) centres (Fig. 39).

An interesting case of two tauto-conformer Fe(II)  $[2 \times 2]$  grids, where only one is SCO-active, was reported by Ruben and co-workers.<sup>137</sup> Here the bis-terdentate ligand L70 (Chart 11) consists of a benzo-diimidazole bridge, with two imidazole-pyridyl side-arms. The central bridging unit can undergo tautomerisation which, along with rotation of the single bonds



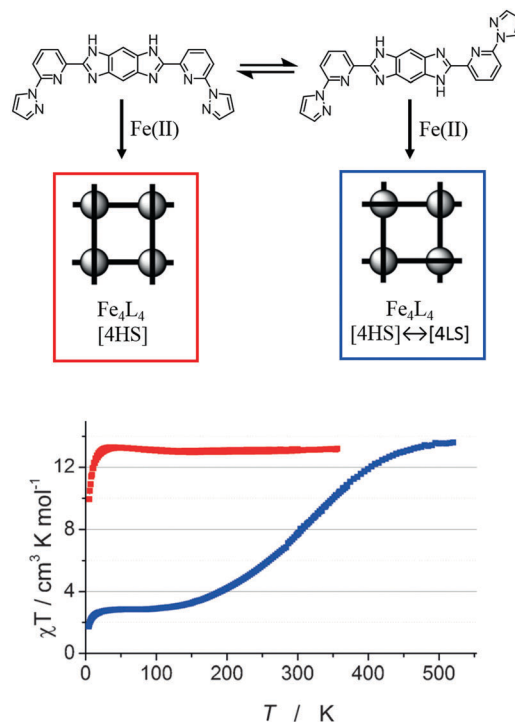


**Fig. 39**  $\chi_m T$  vs.  $T$  for the two  $[2 \times 2]$  grids of the imidazolate-bridging ligand **L69**.  $[\text{Fe}_4(\text{L69})_4](\text{BF}_4)_4 \cdot 2\text{MeCN}$  undergoes multistep hysteretic SCO,  $[4\text{HS}]$  to  $[2\text{HS}-2\text{LS}]$ , and also LIESST at low temperature.  $[\text{Fe}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{L69})_4](\text{BF}_4)_6$  shows incomplete gradual  $\text{Fe}(\text{III})$  SCO and modest LIESST effects. Figure reproduced with permission from ref. 136. Copyright 2014 Springer Nature.

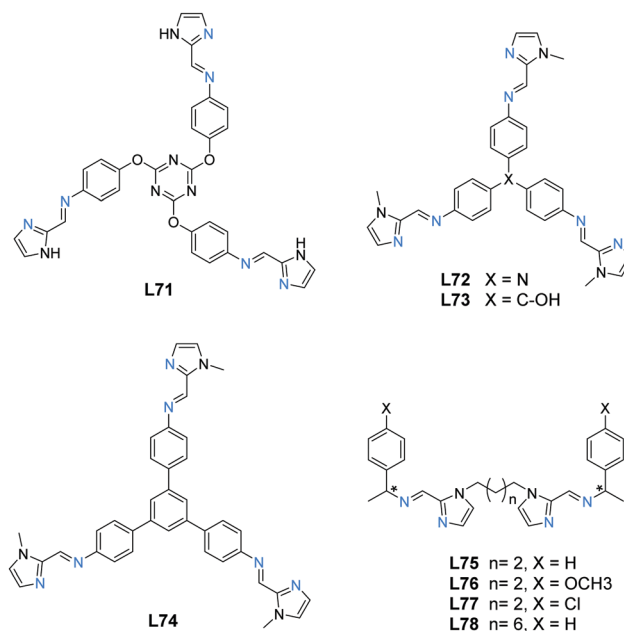
between aromatic side-arm groups, results in the two terdentate pockets being in either a *cis* or *trans* arrangement (Fig. 40). This gives rise to the parallel formation of two isomeric grid complexes  $[\text{Fe}_4(\text{L70})_4](\text{CF}_3\text{SO}_3)_8$ , which can be separated by fractional crystallisation – only one of which undergoes SCO. This is the direct result of the impact of the ligand conformations on the octahedral geometries at the  $\text{Fe}(\text{II})$  centres: the *cis* conformation gives a highly distorted octahedral geometry ( $\Sigma = 160^\circ$ ) which locks the  $\text{Fe}(\text{II})$  ions in the HS state, while the *trans* conformation reduces the octahedral distortion ( $\Sigma = 86^\circ$ ) and facilitates SCO to the LS state. This highlights that the geometric strain imposed by highly chelating ligands can have a larger influence on the spin state of the bound metal ions than the donor atoms alone.

#### Tetranuclear tetrahedral cage $\text{Fe}_4\text{L}_4$ and $\text{Fe}_4\text{L}_6$ complexes

In 2013, tetrametallic SCO-active architectures were expanded from  $[2 \times 2]$  grids and squares to include  $\text{Fe}_4$  tetrahedral cages (Fig. 2, **4C**).<sup>140–144</sup> The SCO-active  $\text{Fe}_4$  cage architectures have been mostly prepared *via* self-assembly of  $\text{Fe}(\text{II})$  with tritopic bidentate ligands which define the four faces of the  $\text{Fe}_4\text{L}_4$  tetrahedral (Td) cages, *i.e.* four face-capping ligands (**L71–L74**, Chart 12), but examples of ditopic bidentate ligands which define the six edges of  $\text{Fe}_4\text{L}_6$  Td cages are also known (**L75–L78**, Chart 12). In all cases, all of the donors to the bound  $\text{Fe}(\text{II})$  centres are provided by the ligands. But, as these are bidentate, and quite long, they are reasonably flexible, so the  $\text{Fe}(\text{II})$  octahedral distortion parameters  $\Sigma$  are smaller for these cages (42–121°, Tables 10 and 11) than for the tetranuclear grids (84–176°, Tables 8 and 9). The advent of these SCO-active 3D cages has also led to increased interest in studying SCO in solution,<sup>14,16,145</sup> in particular due to the possibility of guest recognition by the cage interior modifying the SCO-response.



**Fig. 40** (top) Tautomerisation of ligand **L70** gives rise to parallel formation of a HS grid (red box) where the ligands bind two metals in a *cis* mode, and a SCO-active grid (blue box) where ligands bind in a *trans* mode, and (bottom)  $\chi_m T$  vs.  $T$  for the HS *cis*-grid (red) and SCO *trans*-grid (blue). Figure adapted, reproduced with permission, from ref. 137. Copyright 2016 John Wiley and Sons.



**Chart 12** The eight ligands reported in the literature to form SCO-active  $\text{Fe}_4$  tetrahedral cages. Four are tri-topic (face bridging, to give  $[\text{Fe}_4(\text{L}_4)]^{8+}$ ) and other four are di-topic (edge bridging to give  $[\text{Fe}_4(\text{L}_6)]^{8+}$ ). All provide  $\text{N}_6$  donor sets to the octahedral  $\text{Fe}(\text{II})$  metal ions through the binding of three sets of bidentate binding pockets. For **L75–L77** both the (*R,R*) and (*S,S*) configurations at the chiral (\*) centre have been used to form cages.



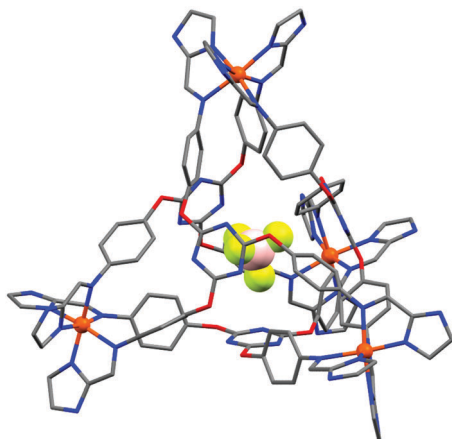


Fig. 41 Structure of the complex cation of  $[\text{Fe}_4(\text{L71})_4](\text{BF}_4)_8$  showing the encapsulated  $\text{BF}_4^-$  counteranion in spacefill.<sup>140</sup> Structure redrawn from CCDC data.

The first example of an SCO-active Td cage was reported by Kruger, Clérac and co-workers in 2013, with a face-capping ligand that was assembled from a triamine with a substituted triazine central moiety and 2-imidazolecarboxaldehyde (L71, Chart 12).<sup>140</sup> Coordination to Fe(II) resulted in a  $[\text{Fe}_4(\text{L71})_4](\text{BF}_4)_8$  tetrahedral cage (Fig. 41), which exhibits SCO in both the solid state and acetone solution.

Also in 2013, Nitschke, Brooker and co-workers reported a pair of self-assembled cages,  $[\text{Fe}_4(\text{L72})_4](\text{OTf})_8$  and  $[\text{Fe}_4(\text{L73})_4](\text{OTf})_8$  (Fig. 42), featuring smaller face-capping ligands (Chart 12).<sup>141</sup> While only  $[\text{Fe}_4(\text{L72})_4](\text{OTf})_8$  was SCO-active in the solid state (approximately [4HS] to [HS-3LS] transition), both were SCO-active in nitromethane solution. Furthermore, the solution SCO properties were able to be tuned by encapsulation of  $\text{Br}^-$  or  $\text{CS}_2$ , with the  $T_{1/2}$  lowering from 336 K for the empty cage  $[\text{Fe}_4(\text{L73})_4](\text{OTf})_8$  to 328 K for  $\text{Br}^-$  or 324 K for  $\text{CS}_2$ , thus highlighting the exciting possibilities of synergistic host-guest chemistry and magnetic properties that arise when SCO is extended to such large architectures.

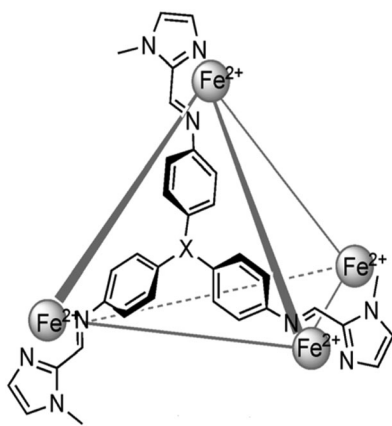


Fig. 42 Representation of the molecular structure of  $[\text{Fe}_4(\text{L72})_4](\text{OTf})_8$  and  $[\text{Fe}_4(\text{L73})_4](\text{OTf})_8$ . Figure adapted, reproduced with permission, from ref. 141. Copyright 2013 John Wiley and Sons.

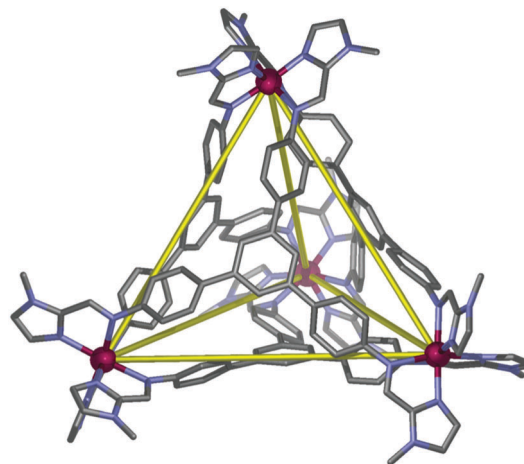


Fig. 43 Complex cation structure of  $[\text{Fe}_4(\text{L74})_4](\text{BF}_4)_8$ . Figure reproduced, with permission, from ref. 142. Copyright 2015 RSC.

A third face-capped SCO-active  $[\text{Fe}_4(\text{L74})_4](\text{BF}_4)_8$  tetrahedral cage (Fig. 43), also self-assembled from an imidazole carboxaldehyde and a triamine (Chart 12), was reported by Li and co-workers in 2015.<sup>142</sup> It exhibits a very gradual SCO from fully HS at 300 K to approximately 75% HS at 50 K in the solid state.

An Fe(II) tetrahedral cage system which instead involves di-topic Schiff base bidentate ligands (L75–L77, Chart 12) that define the six edges of the tetrahedron, giving  $[\text{Fe}_4(\text{L})_6]^{8+}$  cages, was reported by Gu and co-workers in 2015 (Fig. 44).<sup>143</sup> Here the intrinsic at-metal chirality of the tetrahedral cage architecture is exploited to produce enantiopure homochiral cages by self-assembly involving either the (*R*) or (*S*) optical isomer of the amine. The enantiomers, of course, exhibit identical magnetic properties. R group variation (H,  $\text{OCH}_3$ , Cl) on the ligand, as well as solvent desorption, subtly affecting the (gradual and incomplete) SCO behaviour observed in the solid state. Specifically, below 200 K the cages are 3–18% HS when solvated

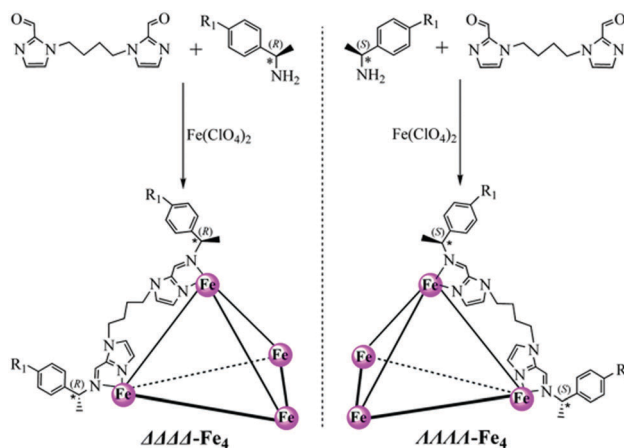


Fig. 44 Synthesis of enantiopure chiral tetrahedral  $[\text{Fe}_4\text{L}_6]^{8+}$  cages, where L is L75–L77, by use of either (*R*)- or (*S*)-phenylethylamine. Figure reproduced with permission from ref. 143. Copyright 2015 RSC.



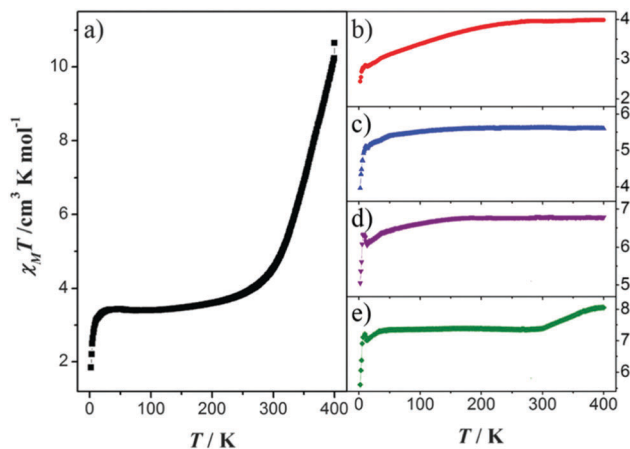


Fig. 45  $\chi_m T$  vs.  $T$  plots for cage  $[\text{Fe}_4\text{L786}](\text{BF}_4)_8$  (a)  $\text{Fe}^{\text{II}}$  cage (b)  $\text{Ni}^{\text{II}}$  cage (c) 20%  $\text{Fe}^{\text{II}}$  into  $\text{Ni}^{\text{II}}$  cage (d) 33%  $\text{Fe}^{\text{II}}$  content into  $\text{Ni}^{\text{II}}$  cage (e) 50%  $\text{Fe}^{\text{II}}$  content in  $\text{Ni}^{\text{II}}$  cage. Figure adapted, reproduced with permission from ref. 144. Copyright 2016 RSC.

or 17–37% HS when desolvated, and transition to 74–87% HS at 400 K (desolvated), with the LS state best stabilised when  $R = \text{Cl}$ .

The same group reported a  $\text{Fe}_4^{\text{II}}\text{L786}$  (Chart 12) cage exhibiting gradual and incomplete SCO. The  $\chi_m T$  value at 400 K was  $10.64 \text{ cm}^3 \text{ K mol}^{-1}$  which indicated about 88.7% of  $\text{Fe}(\text{II})$  were HS. The SCO curve falls abruptly from 400 K to 300 K, then gradually from 300 to 10 K (Fig. 45a). They have also studied the effect of varying the  $\text{Fe}(\text{II})$  content of a  $\text{Ni}_4^{\text{II}}\text{L6}$  cage on the SCO behaviour. Through SCSC transformations, they successfully manipulated the  $\text{Fe}(\text{II})$  proportion in a colourless  $\text{Ni}(\text{II})_4$  cage from 20% (yellow) to 33% (red) and 50% (dark purple), which was confirmed *via* atomic absorption spectroscopy. The former two did not show any SCO, but at 50%  $\text{Fe}(\text{II})$ , the  $\text{Ni}_2\text{Fe}_2$  cage showed a gradual transition at 300 K (Fig. 45e).<sup>144</sup>

### Penta-, hexa- and octa-nuclear complexes

SCO has rarely been seen in  $\text{Fe}(\text{II})$  supramolecular architectures with more than four metal centres, but this is an active area of research, and since 2009 this has been achieved in an  $\text{Fe}_6$  “nanoball”,<sup>146</sup> then in an  $\text{Fe}_5$  “helical cluster” with a planar  $[\text{Fe}_3(\mu_3\text{-O})]^{4+}$  core,<sup>147</sup> and in 2017 in a pair of  $\text{Fe}_8$  cubes<sup>45</sup> (Fig. 2, 6A, 5A and 8A, respectively), using the ligands shown in Chart 13.

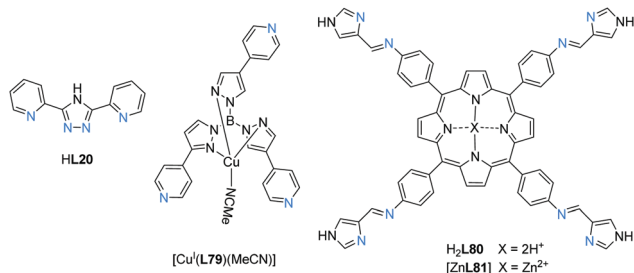


Chart 13 Ligands used in penta-, hexa- and octa-nuclear SCO- $\text{Fe}(\text{II})$  complexes (Fig. 2, 5A, 6A and 8A).

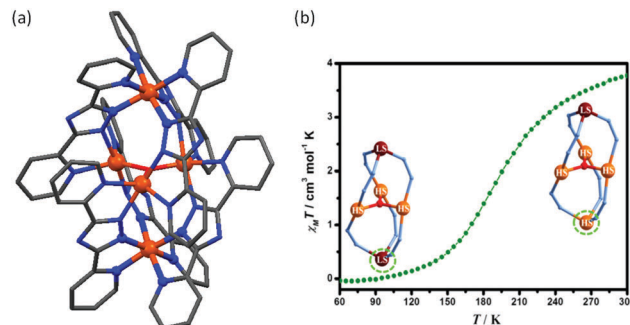


Fig. 46 (a) Structure of  $[\{\text{Fe}^{\text{II}}(\mu\text{-L20})_3\}_2\text{Fe}_3^{\text{II}}(\mu_3\text{-O})]$ . (b)  $\chi_m T$  plot for the single SCO-active site ( $\text{Fe}_2$ , at the bottom in these images) in the pentanuclear cluster complex,  $[\{\text{Fe}^{\text{II}}(\mu\text{-L20})_3\}_2\text{Fe}_3^{\text{II}}(\mu_3\text{-O})][\text{Fe}_2^{\text{II}}(\mu\text{-Cl})(\mu\text{-L20})(\text{NCS})_4(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ , after subtraction from the contribution of  $[\text{Fe}_3^{\text{II}}(\mu_3\text{-O})]^{4+}$  core, LS  $[\text{FeL}_3]^-$  and dinuclear counteranion. (b) Reproduced from reference with permission.<sup>147</sup> Copyright 2016 ACS.

The first SCO-active cluster helicate,  $[\{\text{Fe}^{\text{II}}(\mu\text{-L20})_3\}_2\text{Fe}_3^{\text{II}}(\mu_3\text{-O})][\text{Fe}_2^{\text{II}}(\mu\text{-Cl})(\mu\text{-L20})(\text{NCS})_4(\text{H}_2\text{O})]$  (HL20, Chart 13), was reported by Tong and Ni and co-workers in 2016 (Fig. 46a).<sup>147</sup> Closely related cationic cluster helicates had already been reported by Kawata and Kaizaki and co-workers in 2006, where two LS triple stranded  $[\text{FeL}_3]^-$  units wrapped a planar HS  $[\text{Fe}_3(\mu_3\text{-O})]^{4+}$  core, but with different counter anion,  $\text{NCS}^-$ ,<sup>148</sup> and in 2010 Oshio and co-workers varied the anions: the two apical  $[\text{FeL}_3]^-$  units were LS in the case of  $\text{NCS}^-$ ,  $\text{ClO}_4^-$ ,  $\text{I}^-$  and HS in the case of  $\text{Fe}_2^{\text{III}}(\mu\text{-O})\text{Cl}_6^{2-}$ . But no SCO behaviour was observed with any of these complexes.<sup>149</sup>

Tong and Ni and co-workers instead crystallised this cationic pentanuclear cluster helicate by use of a complex dinuclear dianion,  $[\text{Fe}_2^{\text{II}}(\mu\text{-Cl})(\mu\text{-L20})(\text{NCS})_4(\text{H}_2\text{O})]^{2-}$ , to induce SCO behaviour. In this modified cluster helicate, which again features a planar HS  $[\text{Fe}_3^{\text{II}}(\mu_3\text{-O})]^{4+}$  core, the average Fe–N bond lengths (and  $\Sigma$  values), at 150 and 293 K, clearly showed that one of the two apical  $[\text{FeL}_3]^-$  moieties was SCO-active ( $\text{Fe}_2$ ) whilst the other ( $\text{Fe}_1$ ) remained LS up to 300 K (Fig. 46b). All other  $\text{Fe}(\text{II})$  centres, in the cluster and in the anion, remained HS. The  $\Sigma$  for two apical  $[\text{FeL}_3]^-$  moieties,  $\text{Fe}_1$  changed from  $60.9$  to  $63.7^\circ$  and  $\text{Fe}_2$  changed from  $65.8$  to  $93.7^\circ$ , at 150 and 293 K respectively.

In 2009, Batten and co-workers reported the first SCO-active  $\text{Fe}_6$  supramolecular architecture. The six  $\text{Fe}(\text{II})$  centres are bridged by eight neutral tritopic tris-monodentate  $\text{Cu}(\text{I})$  metalloligands,  $\{\text{Cu}^{\text{I}}\text{L79}(\text{MeCN})\}$  (Chart 13), forming a  $\text{Fe}_6\text{L}_8$  cluster which they termed a “nanoball”,  $[\text{Fe}_6^{\text{II}}(\text{NCS})_{28/3}(\text{MeCN})_{8/3}\{\text{Cu}^{\text{I}}\text{L79}(\text{MeCN})\}_8][\text{ClO}_4]_{8/3}$ .<sup>146</sup> The equatorial plane of each of the octahedral  $\text{N}_6$ -coordinated  $\text{Fe}(\text{II})$  centres comprises four 4-pyridyl groups from four  $\text{Cu}(\text{I})$  metalloligands, and the axial sites are occupied by either  $\text{NCS}$  or  $\text{NCMe}$ . The six  $\text{Fe}(\text{II})$  ions are arranged octahedrally, so, along with the cubic arrangement of the eight  $\text{Cu}(\text{I})$  ions, this forms a distorted rhombic dodecahedron with a diameter of *ca.* 3 nm (Fig. 47). The as-synthesised complex undergoes approximately a 50% HS to LS SCO in the solid state, which is switched off, reversibly, by  $\text{MeCN}$  solvent loss. Owing to the poor lattice packing of the nanoball, large voids between



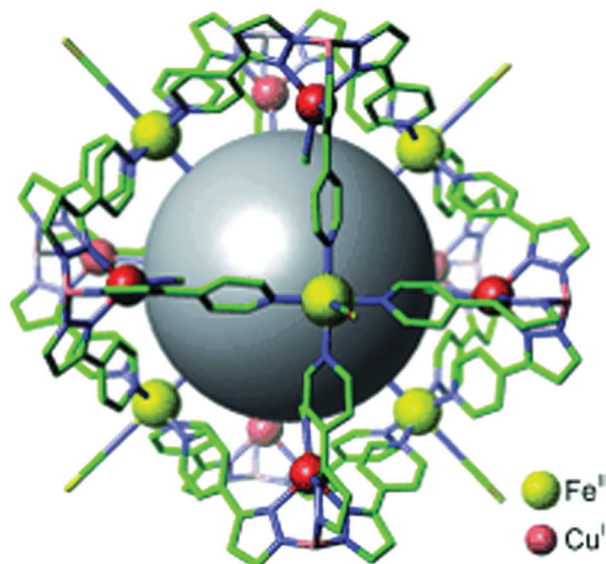


Fig. 47  $\text{Fe}_6[\text{CuL79}(\text{MeCN})_8]$  shell of nanoball structure featuring eight  $\text{Cu}(\text{I})$  metalloligands. Figure reproduced with permission from ref. 146. Stick colours: blue = nitrogen, green = carbon, yellow = sulphur, pink = boron. Copyright 2009 John Wiley and Sons.

complex cations were exploited for guest solvent molecule sorption/desorption, and this was found to tune the SCO properties. The same group went on to report the analogues with different anions,  $\text{NCE}^-$  ( $\text{E} = \text{Se}, \text{BH}_3$ ) in 2012, *i.e.*  $[\text{Fe}_6^{\text{II}}(\text{NCSe})_{28/3}(\text{MeCN})_{8/3}\{\text{CuL79}(\text{MeCN})\}_8][\text{ClO}_4]_{8/3}$  and  $[\text{Fe}_6^{\text{II}}(\text{NCBH}_3)_{28/3}(\text{MeCN})_{8/3}\{\text{CuL79}(\text{MeCN})\}_8][\text{ClO}_4]_{8/3}$ .<sup>150</sup> These new family members, with  $\text{NCSe}^-$  and  $\text{NCBH}_3^-$  co-ligands, which provide stronger field strengths than  $\text{NCS}^-$ , did not change the geometry significantly but, as expected, increased the  $T_{1/2}$  from 124 ( $\text{NCS}$ ) to 162 ( $\text{NCSe}$ ) to 173 K ( $\text{NCBH}_3$ ). The authors also studied the LIESST effect on all three nanoballs and correlated the  $T_{1/2}$  with  $T_{\text{LIESST}}$ . These nanoballs held the record for the largest nuclearity discrete  $\text{Fe}(\text{II})$  complex to undergo SCO until 2017.

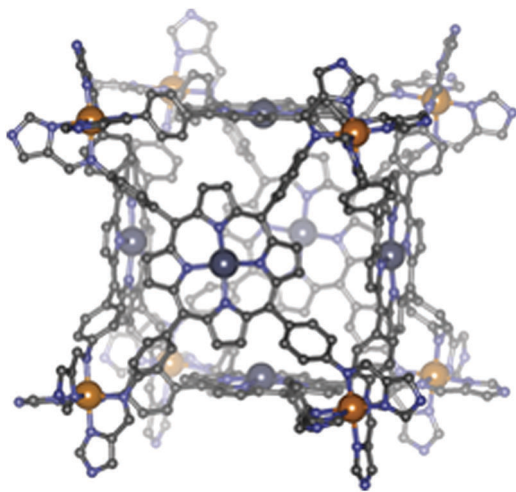


Fig. 48  $[\text{Fe}_8(\text{ZnL81})_6]^{16+}$  cube structure featuring six face capping  $\text{Zn}(\text{II})$  porphyrin metalloligands. Figure reproduced with permission from ref. 45. Copyright 2017 John Wiley and Sons.

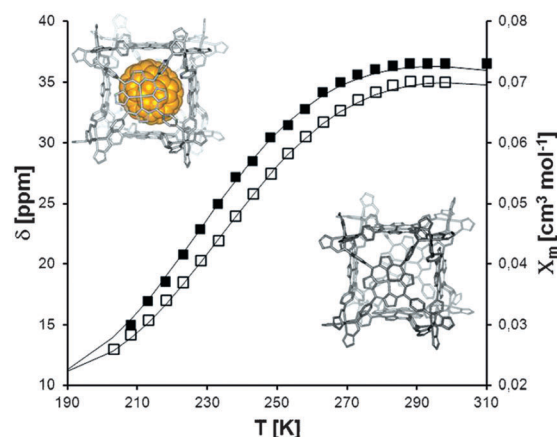


Fig. 49 VT- $^1\text{H}$  NMR in  $[\text{D}_4]$  MeOH, empty squares:  $[\text{Fe}_8(\text{ZnL81})_6]^{16+}$  cube; filled square  $\text{C70}@[\text{Fe}_8(\text{ZnL81})_6]^{16+}$ ; black line calculated molar susceptibility  $\chi_m$  based on the ideal solution model. Figure reproduced with permission from ref. 45. Copyright 2017 John Wiley and Sons.

In 2017, Lützen and co-workers reported two  $[\text{Fe}_8\text{L}_6]^{16+}$  cubes,  $[\text{Fe}_8(\text{H}_2\text{L80})_6][\text{CF}_3\text{SO}_3]_{16}$  and  $[\text{Fe}_8(\text{ZnL81})_6][\text{CF}_3\text{SO}_3]_{16}$  which exhibit SCO in methanol solution.<sup>45</sup> The eight  $\text{Fe}(\text{II})$  centres define the corners of the supramolecular cube, and six tetra-topic porphyrin ligands (Chart 13), where the porphyrins are all either uncoordinated ( $\text{H}_2\text{L80}$ ) or bound to  $\text{Zn}(\text{II})$  ( $\text{ZnL81}$ ), act as face-capping units (Fig. 48).  $\text{Zn}(\text{II})$  coordination to the porphyrin faces of the  $\text{Fe}_8$  cube appears to very slightly stabilise the HS state. Evans method studies from 298–203 K in deuterated-methanol solution revealed that the Zn-coordinated cube transitions from  $\sim 85\%$  HS to  $\sim 30\%$  HS (Fig. 49), while the cube without  $\text{Zn}(\text{II})$  transitions from  $\sim 80\%$  HS to  $\sim 15\%$  HS. In a nice example of guest influence on SCO, encapsulation of  $\text{C}_{70}$ , facilitated by the appropriately sized internal cavity, was found to stabilise the HS state and lowered the  $T_{1/2}$  of the solution based SCO by 15 K and 20 K for the Zn and Zn-free  $\text{Fe}_8$  cubes respectively.

## Summary

We have reviewed all 79 of the new discrete polynuclear SCO-active  $\text{Fe}(\text{II})$  complexes reported between 2012 to February 2018, as well as selected examples from before then, which brings the total to 127 complexes. Of these 127 complexes, 54% are dinuclear, 10% trinuclear, 31% tetranuclear, and the remaining 5% are penta, hexa and octanuclear (Fig. 50 and 51).

For the design of  $\text{Fe}(\text{II})$  SCO-active complexes, the first and foremost consideration is providing the right ligand field strength through careful choice of donor groups, and this also applies when constructing polynuclear architectures. As for mononuclear  $\text{Fe}(\text{II})$  SCO-active materials, most commonly a  $\text{N}_6$  coordination sphere is targeted, by the use of exclusively N-donor ligands. Of the 93 ligand and 8 bridging anion designs featured here, only 11 of them provide anything other than purely N-donors: three **PSRT** ligands ( $\text{N}_4\text{S}_2$  coordination sphere), ligand **L66** $^-$  ( $\text{N}_4\text{O}_2$ ), ligand **HL22** ( $\text{N}_5\text{P}$ ) and anions **A2–A5** ( $\text{N}_5\text{O}$ , Chart 7),  $\mu\text{-NCS}$  ( $\text{N}_5\text{S}$ ), and  $\mu\text{-CN}^-$  ( $\text{N}_4\text{C}_2$ ) feature



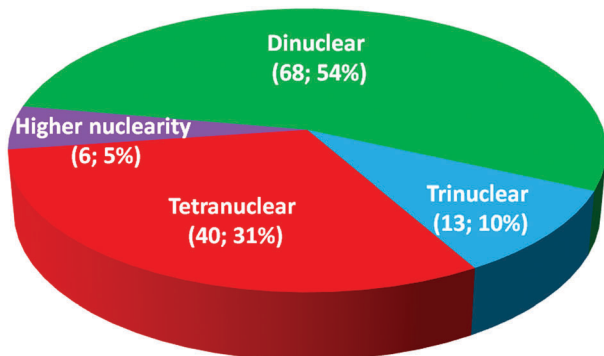


Fig. 50 Distribution of the 127 discrete polynuclear Fe(II) SCO-active complexes reviewed herein, as a function of nuclearity.

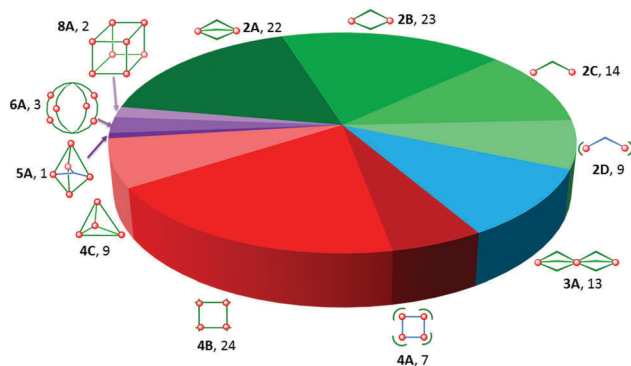


Fig. 51 The distribution of the 127 SCO complexes studied in this review across the different categories from dinuclear (**2A** triply bridged, **2B** doubly bridged, **2C** single bridged, **2D** anion bridged), to trinuclear (**3A** triply triazole bridged), to tetranuclear (**4A** squares, **4B** grids, **4C** tetrahedral cages), to pentanuclear (**5A**), to hexanuclear (**6A** 'nanoball') to octanuclear cube (**8A**).

some S, O, P, or C donor atoms. Amongst the types of N-donor moieties, azoles feature strongly across a range of architectures, with them being incorporated into 60 of the 93 designer ligands, including those that generated the numerous examples of simple triply-triazole-bridged dinuclear and trinuclear SCO-active Fe(II) complexes (Charts 1 and 9).

Of the 93 designer ligands presented here, 55 provide all of the donor atoms to the Fe(II) centres (no co-ligands are coordinated) in the polynuclear architectures. These ligands are constructed to have a particular number of bi- or tri-dentate binding pockets that are arranged carefully relative to each other to predictably result in the self-assembly of the desired architecture (Fig. 52). Specific examples include ditopic ligands with bidentate pockets (bis-bidentate), with a central linker which directs the angle of the two pockets (**L8–L16**), to give dinuclear Fe<sub>2</sub>L<sub>3</sub> helicates (Fig. 52a). When the linker is flexible (**L75–L78**), such ligands can instead generate edge-bridged tetranuclear Fe<sub>4</sub>L<sub>6</sub> tetrahedral cages (Fig. 52b). Carefully designed ditopic-tridentate ligands (Fig. 52c) result in either (a) dinuclear Fe<sub>2</sub>L<sub>2</sub> complexes, in the case of flexible facially coordinating pockets (**PMRT** and **PSRT** families, **PMTD**, **PMOD**, **L17**, **L18**), or (b) tetranuclear Fe<sub>4</sub>L<sub>4</sub> grids, all but one (**L66**<sup>−</sup>, O<sup>−</sup> bridge)

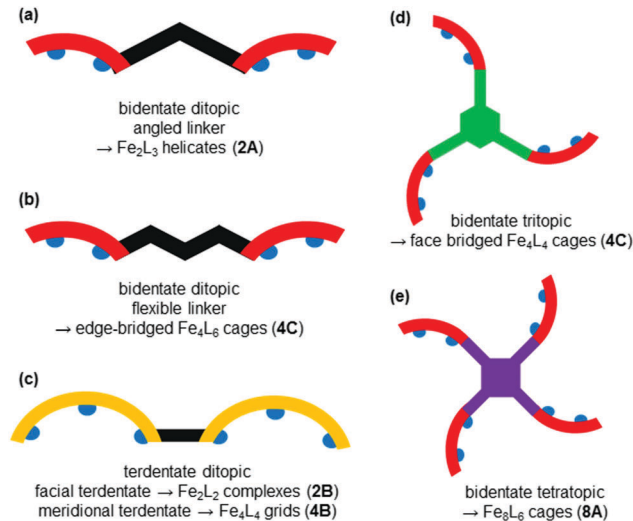


Fig. 52 Examples of ligand designs which provide the right number and topology of binding pockets, each with appropriate denticity, for the controlled self-assembly of discrete polynuclear Fe(II) complexes.

featuring heterocycle-bridged, meridionally coordinated, binding pockets (**L50–L70**). Moving up another level of complexity, tritopic-bidentate (tris-bidentate) ligands (**L71–L74**) can be used to generate face-capped tetranuclear Fe<sub>4</sub>L<sub>4</sub> tetrahedral cages (Fig. 52d). Finally, taking this to the maximum level of complexity reported to date, the first examples of octanuclear SCO-active complexes were generated using designer tetratopic-bidentate ligands (**H<sub>2</sub>L80**, **ZnL81**) to form face-bridged Fe<sub>8</sub>L<sub>6</sub> cubes (Fig. 52e).

It is worth noting that amongst these 55 designer ligands, that the 19 which provide bidentate pockets all generate 5-membered chelate rings, and comprise either azole-imine (17 ligands; 22 complexes) or azole-pyridine (2 ligands; 5 complexes) moieties (Fig. 53) – so clearly the combination of three such azole-imine/pyridine pockets around Fe(II) is a winner for providing about the right ligand field to support SCO.

Similarly, out of these 55 designer ligands, 35 provide tridentate pockets, all of which generate a pair of fused 5-membered chelate rings (Fig. 54). These 35 poly-tridentate ligands all comprise either (a) azole-amine-pyridine (9 ligands) or azole-thioether-pyridine (3 ligands) binding facially (Fig. 54a) to give dinuclear **PMRT**-like complexes, or (b), with the exception of oxygen-bridging **L66**<sup>−</sup>, a combination of three conjugated azines and/or azoles (11 ligands) or two azines or azine/azole joined by a conjugated central imine (12 ligands), all of which bind meridionally to give Fe<sub>4</sub>L<sub>4</sub> grids (Fig. 54b). So clearly the coordination of two such pockets, heterocycle-imine/amine/thioether/pyridine-heterocycle, provides about the right ligand field to support SCO at Fe(II).

The remaining ligand of this group of 55 designer ligands is the unique **L25** (Chart 6), which is bis-hexadentate and provides all 12 N-donor atoms to two Fe(II) centres in an Fe<sub>2</sub>L complex.

On the other hand, of the 38 ligands designed to work in conjunction with co-ligands, 28 of the resulting complexes involve NCE anions (NCS, NCSe, NCBH<sub>3</sub>, **dca**<sup>−</sup>) completing



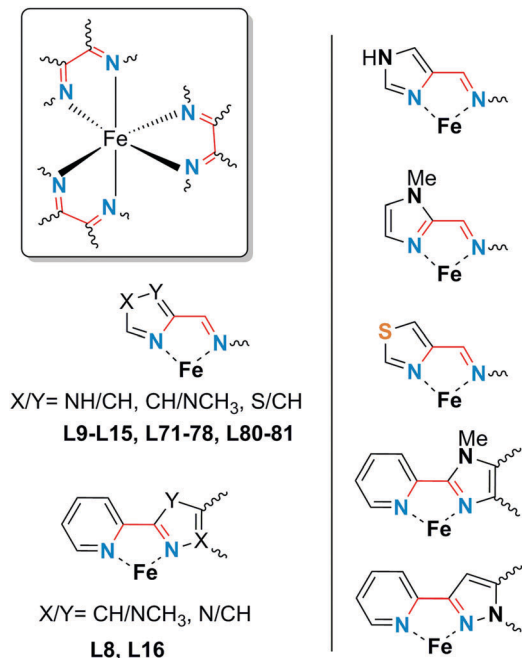


Fig. 53 Binding motifs common to the 19 bidentate ligands out of the 55 designer ligands that provide all of the donors to the SCO-active octahedral Fe(II) centres (no co-ligands bound) – by binding of three identical bidentate pockets (box). Right: The 5 specific binding moieties employed in all 19 of these polytopic ligands.

the coordination sphere and helping to provide the right overall field strength for SCO at Fe(II). Overall, 22% of the 127 complexes reviewed herein contain  $\text{NCE}^-$  anions as co-ligands, so it is clear that the use of NCE co-ligands remains another key way to obtain ligand fields that are in the right ballpark to promote the formation of SCO-active Fe(II) complexes.

Another factor that must be taken into consideration is the degree of distortion of the Fe(II) centres away from perfect octahedral geometry, as this also modifies the ligand field. There are a number of ways to probe and quantify this distortion. Here we focus on the octahedral distortion parameter  $\Sigma$ , the sum of the deviations from  $90^\circ$  of the 12 *cis* angles, and the SchM,<sup>151–154</sup> the continuous shape measure of the degree of distortion from an ideal geometry, here octahedral (Tables 1–11 and Fig. 55–59; see also the ESI†). As expected, in general the Fe(II) centres are less distorted when in the LS state than when in the HS state. Another key finding from this analysis of the structurally characterised discrete polynuclear complexes reviewed herein is that for the 55 designer ligands which provide all of the donors to the Fe(II) centres, the octahedral distortion is generally higher than for the 38 ligands which are designed to work in conjunction with co-ligands. This is perhaps not surprising, as the latter systems will have greater flexibility due to involving a mixture of ligands, often including some monodentate ligands. Clearly the same arguments, regarding the degree of distortion away from octahedral being to some extent a function of whether the metal ion is coordinated by (a) only polydentate ligands or (b) a mixture of ligands including monodentate, also apply to non SCO-active complexes – of iron(II) or indeed other metal ions.

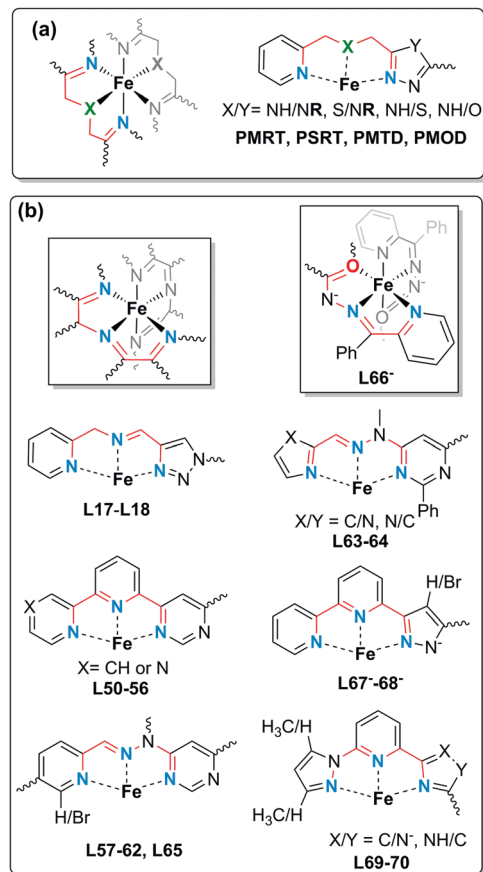


Fig. 54 Binding motifs common to the 35 tridentate ligands, out of the 55 designer ligands that provide all of the donors to the SCO-active octahedral Fe(II) centres (no co-ligands bound) by binding of two identical tri-dentate pockets in either (a) facial or (b) meridional binding mode.

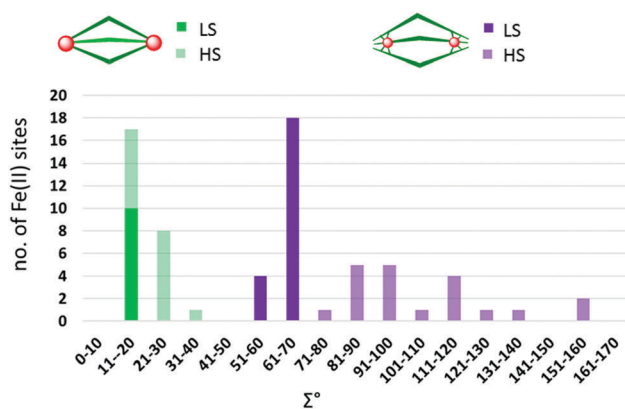


Fig. 55 Distribution of octahedral distortion parameter,  $\Sigma$  (°), for the Fe(II) centres in dinuclear complexes of type **2A** (Fig. 2): triply triazole bridged  $[\text{Fe}_2\text{L}_5(\text{NCE})_4]$  (green) and triple helicates  $[\text{Fe}_2\text{L}_3]$  (violet). Dark colour = LS; light colour = HS.

Examples of this variation, within SCO active iron(II) complexes, of the octahedral distortion as a function of complex type, are clearly seen in comparing the triply bridged dinuclear complexes (**2A**), which fall into two distinct categories: triply-triazole bridged with co-ligands  $[\text{Fe}_2\text{L}_5(\text{NCE})_4]$  (Fig. 3 and Chart 1) for



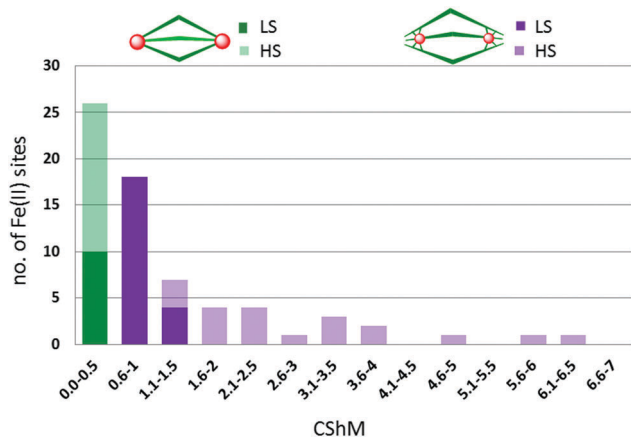


Fig. 56 Distribution of continuous shape measured value, CShM, of octahedral distortion, for the Fe(II) centres in dinuclear complexes of type **2A** (Fig. 2): triply triazole bridged  $[\text{Fe}_2\text{L}_5(\text{NCE})_4]$  (green) and triple helicates  $[\text{Fe}_2\text{L}_3]$  (violet). Dark colour = LS; light colour = HS.

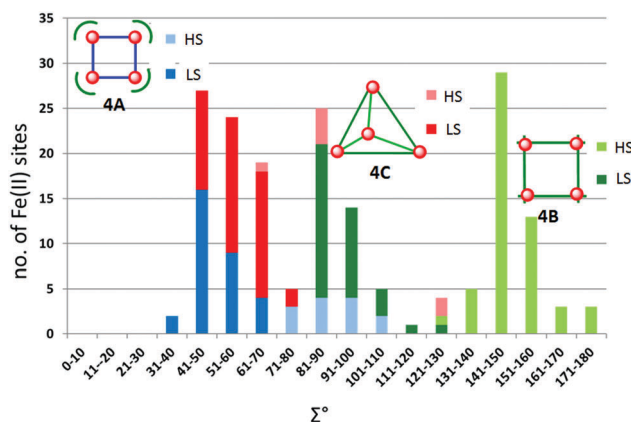


Fig. 57 Distribution of octahedral distortion parameter,  $\Sigma$  ( $^\circ$ ), for the Fe(II) centres in tetranuclear complexes: types **4A** squares (blue), **4B** grids (green) and **4C** tetrahedral cages (red) (Fig. 2).

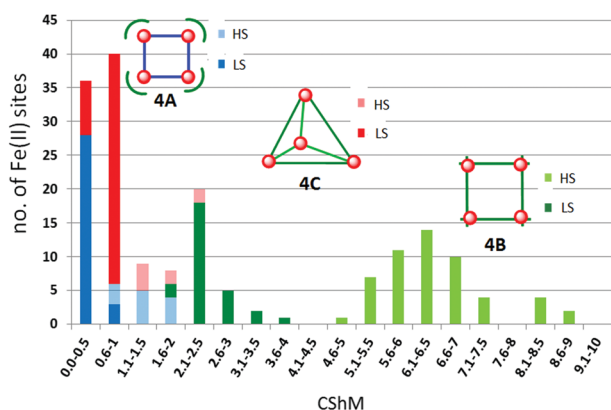


Fig. 58 Distribution of continuous shape measured value, CShM, of octahedral distortion, for the Fe(II) centres in tetranuclear complexes: types **4A** squares (blue), **4B** grids (green) and **4C** tetrahedral cages (red) (Fig. 2).

which  $\Sigma$  is consistently lower (Table 1) than it is for the triple helicates  $[\text{Fe}_2\text{L}_3]$  (Fig. 6–9, Chart 2 and Tables 2–4), as is

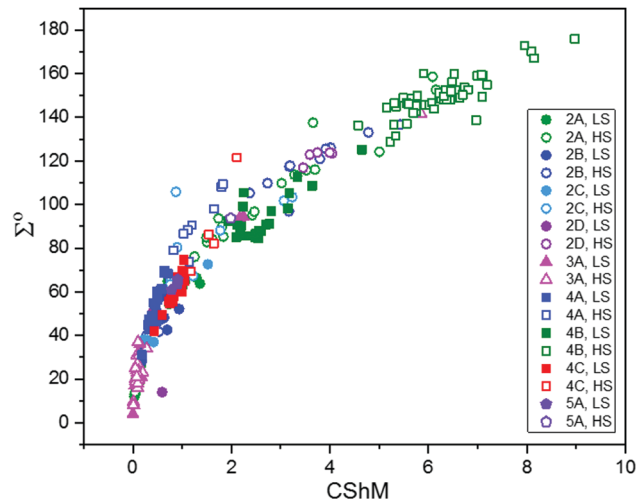


Fig. 59 Comparison of two measures of octahedral distortion,  $\Sigma$  ( $^\circ$ ) and CShM, for structurally characterised discrete polynuclear SCO-active Fe(II) complexes reviewed herein (see also ESI,† Table S1).

illustrated in Fig. 55. Indeed the  $\Sigma$  values for the Fe(II) centres in the triply-triazole bridged complexes (Fig. 55, green) are in the range  $11\text{--}20^\circ$  for LS and  $11\text{--}40^\circ$  for HS, with the octahedral geometry close to ideal in both cases (CShM < 0.5, Fig. 56, green). In contrast, for  $\text{Fe}_2\text{L}_3$  helicates, the  $\Sigma$  values are far higher, at  $51\text{--}70^\circ$  for LS *versus*  $71\text{--}160^\circ$  for HS (Fig. 55, violet), with correspondingly high CShM values (LS = 0.6–1.5, HS = 1.1–6.5; Fig. 56, purple).

Similarly, the Fe(II) centres in tetranuclear squares with co-ligands (Fig. 2, **4A**) have smaller  $\Sigma$  values (Fig. 57, blue) than those in grids (Fig. 2, **4B**, Fig. 57 green), as the latter systems comprise just four ligands that provide all of the 24 donors to the four Fe(II) centres. Interestingly, the tetranuclear tetrahedral cages (Fig. 2, **4C**, Fig. 57 red) also comprise a single type of ligand which provides all of the donors, and yet the distortions are smaller than in the grids, falling in a similar range to those seen for the squares (Fig. 57 blue). Specifically, in the LS state, the Fe(II) centres in the squares and cages have consistently much lower  $\Sigma$  ( $31\text{--}70^\circ$  and  $43\text{--}75^\circ$  respectively, Fig. 57 dark blue and red) and CShM (0.183–0.826 and 0.433–1.035 respectively, Fig. 58 dark blue and red) values, than in the grids ( $\Sigma = 84\text{--}125^\circ$ , Fig. 57 dark green; CShM = 1.935–5.686; Fig. 58, dark green). Indeed the  $\Sigma$  values for the LS grids (Fig. 57, dark green) are in the same range as for the HS squares ( $\Sigma = 79\text{--}109^\circ$ , Fig. 57 light blue).

The highly constrained coordination environment imposed by the four bis-terdentate ligands in the  $\text{Fe}_4\text{L}_4$  grids, as evidenced by large  $\Sigma$  and CShM values, may be providing a barrier to complete SCO to the [4LS] state, with a regular octahedral LS coordination environment for all four of the Fe(II) centres perhaps geometrically impossible in some cases. In most of the grids reviewed here, the fully LS state is inaccessible, with only the grids of **L54**, **L65**, and **L70** (only the *trans* isomer, which is unique among the grids reviewed here) being structurally characterised in the [4LS] state. On the other hand, all of the square complexes, which contain co-ligands and hence a more



readily accessible regular octahedral geometry, have been structurally characterised as [4LS]. For the tetrahedral cages, all but two complexes,  $[\text{Fe}_4^{\text{II}}(\text{L74})_4](\text{BF}_4)_4 \cdot 16\text{CH}_3\text{CN}$  and  $[\text{Fe}_4^{\text{II}}(\text{L71})_4](\text{BF}_4)_8 \cdot 14.75\text{CH}_3\text{CN} \cdot 4.5\text{C}_6\text{H}_6 \cdot 3\text{H}_2\text{O}$ , have been observed in the [4LS] state by X-ray crystallography, despite having all donors to the Fe(II) centres provided by just the one type of ligand. The key difference, however, for the tetrahedral cages is that the octahedral environment at the Fe(II) centres is completed by three bidentate donors, unlike in the grid complexes where just two terdentate donors coordinate to each Fe(II) centre.

Unsurprisingly a positive, but not linear, correlation is observed between these two measures of distortion,  $\Sigma$  and CShM (Fig. 59 and Table S1, ESI<sup>†</sup>). It is interesting to note that when the distortion away from octahedral is relatively small,  $\Sigma$  is perhaps a more informative measure than the CShM. Indeed it is pertinent to note that a CShM value of just 2 corresponds to a  $\Sigma$  value of approximately  $90^\circ$ . Finally, as expected, regardless of the measure used,  $\Sigma$  or CShM, lower distortion parameters are observed for the LS Fe(II) centres (Fig. 59, solid points) than for the HS Fe(II) centres (Fig. 59, hollow points).

Generally, the Fe...Fe distances in the helicates vary from 9–12 Å, except in case of L14 and L15 (Chart 2), where distance is far lower,  $\sim 4$  Å, because of the short NN bridge between them and the resultant twist of the ligand to bind, which also leads to a very high distortion  $\Sigma$  and CShM for the Fe(II) centres ( $158.5^\circ$  and 6.084, respectively, Table S1, ESI<sup>†</sup>). The Fe<sub>4</sub> grids have a very rigid geometry around the metal centres and their Fe...Fe distances (4–7 Å) are much lower than those seen in the Fe<sub>4</sub> tetrahedral cages (with face capping ligands, 11–15 Å; edge capping ligands 9–11 Å). This is mostly because the bisterdentate ligands of the grids also provide a short bridge (*e.g.* pyrimidine-bridge) between the two binding pockets and hence Fe(II) centres, whereas for the cages, longer, non-coordinating linkers (*e.g.* 1,3,5-triphenylbenzene) are utilised.

An important feature of many of the SCO-active polynuclear architectures reviewed here is the presence of a guest-accessible internal cavity which may be exploited for SCO tuning and/or guest sensing. The effects on SCO of guest inclusion into the cavity in Fe<sub>2</sub>L<sub>3</sub> helicates, Fe<sub>4</sub>L<sub>4</sub> cages, and Fe<sub>8</sub>L<sub>6</sub> cubes have been probed in a handful of studies. The largest of the internal cavities to date occur in the Fe<sub>8</sub>L<sub>6</sub> cubes, where the uptake of the large C<sub>70</sub> into the 1300 Å<sup>3</sup> cavity tuned the SCO  $T_{1/2}$  by 15–20 K in the solution phase. For the face-capped Fe<sub>4</sub>L<sub>4</sub> cages, smaller internal cavities of 61–183 Å<sup>3</sup> are reported, and in the case of  $[\text{Fe}_4(\text{L73})_4](\text{OTf})_8$  inclusion of the small guests Br<sup>−</sup> and CS<sub>2</sub> tuned the SCO  $T_{1/2}$  by 8–12 K in the solution phase. Interestingly, the smallest of the cavities probed for guest tuning of SCO, the 28–33 Å<sup>3</sup> cavities in the  $\{X@[\text{Fe}_2(\text{L16})_3]\}X(\text{PF}_6)_2$  ( $X = \text{Cl}^-$  or Br<sup>−</sup>) helicates, had the largest observed shift in  $T_{1/2}$ . Upon changing the encapsulated Cl<sup>−</sup> to the larger Br<sup>−</sup> anion, the  $T_{1/2}$  in the solid state was decreased by 40 K. Furthermore, the position of the halide inside the small cavity was seen to greatly affect the nature of the SCO, with half *vs.* full SCO observed when the halide is positioned closer to one Fe(II) centre *vs.* equidistant to both Fe(II) centres. Clearly, large, easily observable effects on the SCO properties of these complexes can be induced by the

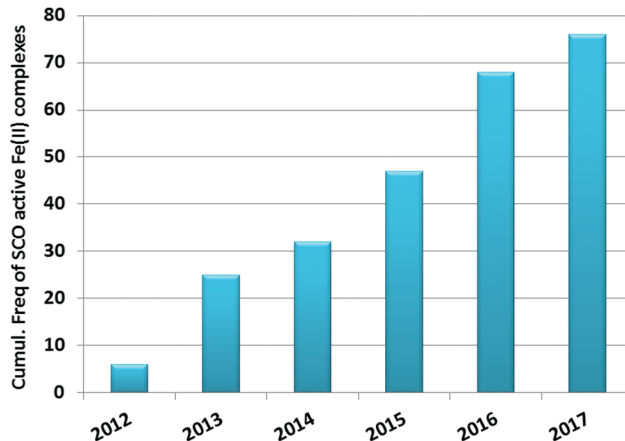


Fig. 60 Increasing number of discrete di- to poly-nuclear SCO-active Fe(II) complexes reported in the period from 2012 to 2017 (76 in total). Our previous review<sup>35</sup> covered the 68 examples reported 2004–2011.

encapsulation of various guests, and as more examples of large cage-like SCO-active complexes are developed one can anticipate a wealth of host–guest chemistry, including sensing applications, being reported in the near future.

Finally, the number of discrete polynuclear SCO-active Fe(II) complexes has increased significantly over the period from 2012 to 2017 (Fig. 60): the 76 new examples reported more than doubles the number reported in the literature, 68, over the period 2004–2011 covered by our previous review.<sup>35</sup>

## Concluding remarks

By applying supramolecular self-assembly strategies,<sup>43,58,155–158</sup> and linking multiple donor pockets of the right ligand field strength and denticity into carefully structured ligands (Fig. 52), chemists have created a wealth of SCO-active discrete polynuclear Fe(II) complexes, ranging to date from dinuclear to octanuclear. The development of such complexes is a flourishing field, as illustrated by the fact that the 8 years from 2004–2011, 68 complexes were reported, and in the 7 subsequent years another 76 were reported. The architectural diversity of these complexes has also expanded considerably since 2011, with the first examples of SCO-active tetranuclear cages reported in 2013, and then a new record nuclearity for a discrete SCO complex was set in 2017 when the first examples of SCO-active octanuclear cube cages were reported. These trends are likely to continue, with many more reports of SCO-active discrete supramolecular architectures anticipated.

Covalently linking Fe(II) centres into polynuclear architectures has led to access to multistep SCO with stable intermediate spin states, *e.g.* [HS–LS], which opens up the possibility of multi-state molecular switches. In some cases linking SCO-appropriate binding pockets has led to more abrupt and even hysteretic SCO being observed in comparison to mononuclear analogues of the same immediate coordination environment. In many cases, the polynuclear architectures are highly strained, with steric and intermolecular crystal packing or solvent interactions often



dominating the SCO properties. In other cases, less strained ligands in same family induced different SCO behaviour through very small modification in ligand or counter-anion/solvent molecules.

Whilst a number of winning ligand design features for inducing SCO at Fe(II) are identified in the previous section (e.g. Fig. 53 and 54), it remains very difficult to predictably fine-tune or control SCO behaviour (including  $T_{1/2}$  or hysteresis) in advance of synthesis and characterisation.<sup>159–163</sup> The effects of intermolecular crystal packing and/or counter anion/solvent interactions can dominate, over ligand field effects, the SCO properties in the solid state.

Solution state studies<sup>13–16,145</sup> are of increasing prevalence and promise to facilitate the development of more detailed understanding of the ligand field effects, as packing effects no longer apply. Solution studies are also of key importance in the case of SCO-active systems that can recognise guests, such as cages, as modifications in the SCO behaviour could facilitate guest sensing. But solution studies warrant two notes of caution: (a) the potential for speciation to be an issue must be addressed, otherwise it could confound such studies, and (b) the influence of solvent choice on the SCO should also be explored.<sup>164</sup> Nevertheless, the solution stability of many of these supramolecular assemblies is such that exploiting the internal cavities of SCO-active helicates, cages and new types of discrete supramolecules for guest sensing applications is another rapidly evolving area of interest in this field.

## Conflicts of interest

There are no conflicts to declare.

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