Correlations between ligand field $\Delta_o$, spin crossover $T_{1/2}$ and redox potential $E_{pa}$ in a family of five dinuclear helicates†

Sandhya Singh and Sally Brooker*†

A family of five new bis-bidentate azole–triazole Rat ligands (1.3-bis(5-(azole)-4-isobutyl-4H-1,2,4-triazol-3-yl)benzene), varying in choice of azole (2-imidazole, 4-imidazole, 1-methyl-4-imidazole, 4-oxazole and 4-thiazole), and the corresponding family of spin-crossover (SCO) and redox active triply bridged dinuclear helicates, $[\text{Fe}_2L_3]^{4+}$, has been prepared and characterised. X-ray crystal structures show all five Fe(ii) helicates are low spin at 100 K. Importantly, DOSY NMR confirms the intactness of these SCO-active dinuclear helicates in D$_2$-MeCN solution, regardless of HS fraction: $\gamma_{HS}(298 K) = 0.81$. Variable temperature $^1$H NMR Evans and UV-vis studies reveal that the helicates are SCO-active in MeCN solution. Indeed, the choice of azole in the Rat ligand used in $[\text{Fe}_2L_3]^{4+}$ tunes: (a) solution SCO $T_{1/2}$ from 247 to 471 K, and (b) reversible redox potential, $E_{pa}(\text{Fe}^{II/III})$, from 0.25 to 0.67 V for four helicates, whilst one has an irreversible redox process, $E_{pa} = 0.78$ V, vs. 0.01 M AgNO$_3$/Ag. For the four reversible redox systems, a strong correlation ($R^2 = 0.99$) is observed between $T_{1/2}$ and $E_{pa}$; $\Delta_o$. Finally, the analogous Ni(ii) helicates have been prepared to obtain $\Delta_o$, establishing: (a) the ligand field strength order of the ligands: 4-imidazole (11 420) $\sim$ 1-methyl-4-imidazole (11 430) $< 2$-imidazole (11 505) $\sim$ 4-oxazole (11 516) $< 4$-thiazole (11 804 cm$^{-1}$), (b) that $\Delta_o$ ($\text{Ni}^{II}_2L_3^{4+}$) strongly correlates ($R^2 = 0.87$) with $T_{1/2}$ ($[\text{Fe}_2L_3]^{4+}$), and (c) interestingly that $\Delta_o$ strongly correlates ($R^2 = 0.98$) with $E_{pa}$ for the four helicates with reversible redox, so the stronger the ligand field strength, the harder it is to oxidise the Fe(ii) to Fe(iii).

Introduction

Spin crossover (SCO) is a phenomenon seen in 3d$^4$–3d$^7$ octahedral metal complexes when the ligand field is ‘just right’ so that the application of an external stimulus, including temperature, pressure, light irradiation and guest molecules, causes a reversible switch of spin state, from HS to LS.$^1$–$^3$ This conversion is accompanied by a pronounced change in colour, volume, mechanical, electrical and magnetic properties of the materials; which gives rise to a multitude of potential applications, in sensing, data storage, actuators, thermometers and display devices.$^4$–$^5$

The study of self-assembled coordination complex architectures$^6$ (metallosupramolecular chemistry)$^7$ has become very popular in the last few decades, not least because of interesting host–guest chemistry, catalysis and sensing ability.$^8$–$^{10}$ Discrete polynuclear iron(ii) supramolecular architectures are particularly interesting for SCO,$^{11}$–$^{13}$ as (a) intramolecular interactions, electronic and steric, between the metal centres can influence the SCO, amongst other things enhancing the potential for polynary rather than binary information storage through multistep SCO,$^{4,13}$ and (b) host–guest interactions can influence the SCO.$^{5,13}$ Nevertheless, prior to this study, only 12 ligands (Fig. S1.1, ESI,† L1–L12), comprising either azole–pyridine or azole–amine coordinating pockets (Fig. 1), had been employed to form SCO-active dinuclear iron(ii) helicates.$^{14}$–$^{16}$ The first example of an SCO-active dinuclear helicate, $[\text{Fe}_2L_1]^{4+}$ (Fig. S1.1, ESI†) was reported by Williams and co-workers in 1998.$^{17}$ Since then this field has been expanded on by various authors, including Hannon,$^{18}$ Li,$^{19,20}$ Kruger and Clérac,$^{21}$–$^{23}$ Sunatsuki,$^{24,25}$ and Aromi.$^{26}$

Despite considerable interest in redox properties, especially of iron complexes due to potential relevance to understanding the function of heme-based metalloproteins, in which spin state changes are also crucial,$^{27}$–$^{29}$ studies of SCO and redox in families of complexes are rare.$^{24}$–$^{26}$–$^{30}$–$^{35}$ Drago,$^{30}$ Kadish$^{32,33}$ and Kuroda-Sowa$^{34}$ studied mononuclear complexes, whilst Sunatsuki and co-workers have reported the only examples involving dinuclear iron(ii) helicates$^{34}$ (or tetranuclear cages$^{28}$). Of these, only the Drago$^{30}$ and Kadish$^{32,33}$ studies (Fig. S1.2, ESI†) involved
solution SCO, which is the most relevant for comparison with the redox potential, also determined in solution.

In the solid state, crystal packing, co-crystallised solvent and intermolecular cooperativity can obscure the electronic modifications imposed by variation of the ligand. In contrast, solution SCO opens the door to investigating the electronic effect arising from ligand modification,\textsuperscript{37-40} including from a ‘tail’,\textsuperscript{41-43} as well as the effects of solvent polarity,\textsuperscript{44} concentration\textsuperscript{41} and pH.\textsuperscript{45}

1,2,4-Triazole ligands, which can be substituted at the C\textsuperscript{2}, N\textsuperscript{4} and/or C\textsuperscript{5} positions on the triazole ring (Fig. 2), provide an appropriate ligand field strength for generating Fe(II) spin crossover materials.\textsuperscript{46-48}

Such ligands have included (Fig. 2): mono- and bis-dentate Rdpt,\textsuperscript{48} bis-terdentate PMRT/PSRT,\textsuperscript{31,49-51} and the related PMTD/PMOD,\textsuperscript{52-54} or TMTD\textsuperscript{55} all of which have been reported in the literature to form SCO active Fe(II) complexes. Recently, we reported that our general synthetic strategy for accessing Rdpt ligands,\textsuperscript{56} could be extended to access the first examples of ditopic azine-triazole analogues\textsuperscript{57} and of azole–triazole monotopic Rat ligands.\textsuperscript{58} The first four ditopic azine-triazole ligands prepared, L\textsubscript{npm-meta} and L\textsubscript{npm-para} (Fig. 2),\textsuperscript{57} featured n-pyrimidine-triazole binding sites linked by either meta- (for helicates) or para- (for tetrahedral cages) substituted phenylene linkers. All four of the structurally characterised iron(II) complexes, both helicates and cages, of these first ditopic Rat ligand systems were found to be LS.\textsuperscript{57} Clearly, the ligand field of these new robust ditopic Rat ligands needs to be reduced in order to enable SCO. With this goal in mind, very recently, we reported the first examples of monotopic azole–triazole L\textsuperscript{4NMe/SIm} ligands (Fig. 2), which, as expected, imposed a weaker ligand field: [Fe(L\textsuperscript{4NMe/SIm})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2} is HS whereas [Fe(L\textsuperscript{4SIm})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2} is SCO-active in both the solid state and in MeCN solution.\textsuperscript{58}

The focus herein is on the development of a new family of robust yet easily modified ligands for the assembly of SCO-active triply bridged iron(II) dinuclear helicates. Hence the ditopic versions of these weaker fields azole–triazole ligands (L\textsuperscript{4NMe/SIm}) are prepared, using a meta-phenylene linker, to enable access to a new class of SCO-active [Fe\textsuperscript{2+}L\textsubscript{4}]\textsuperscript{4+} dinuclear helicates. Specifically we report the synthesis of five new ditopic Rat ligands (Lazole-meta, Fig. 2, violet box) and the synthesis, structural, spectroscopic, solid and solution spin crossover and redox characterisation of the corresponding triply bridged dinuclear helicates, [Fe\textsuperscript{2+}(Lazole-meta)\textsubscript{3}][BF\textsubscript{4}]\textsubscript{2}. Furthermore, to determine the ligand field strengths of these new Rat ligands, the corresponding Ni(II) helicates are also synthesised, two are structurally characterised and all five are studied by UV-vis spectroscopy.

This study of five helicates provides a rare demonstration of the expected, often said but seldom shown, correlation between the SCO switching temperature (T\textsubscript{1/2}) and the ligand field splitting energy (Δ\textsubscript{fs}) for a family of complexes. Somewhat less intuitive is that a connection is also established between these spin crossover properties (Δ\textsubscript{fs}, T\textsubscript{1/2}) and the oxidation potentials (E\textsubscript{pa}), a combination of properties not often studied together (see above).

### Results and discussion

#### Synthesis

In contrast to the previously published azine-triazole dinuclear helicates featuring a 1,3-phenylene linker ligand, both of which...
were LS,\textsuperscript{37} herein the ligand field induced by the ditopic ligands is reduced. So, whilst the same linker is used, both bidentate ligand binding sites are changed from featuring azine-triazole to azole-triazole binding pockets. The five new ditopic ligands of azole–triazole, 2-imidazole L\textsuperscript{2NHIm-meta}, 4-imidazole L\textsuperscript{4NHIm-meta}, 1-methyl-4-imidazole L\textsuperscript{4NMeIm-meta}, 4-oxazole L\textsuperscript{4OIm-meta} and 4-thiazole L\textsuperscript{4SIm-meta}, were synthesised by refluxing the previously reported ethylated bis-thioamide\textsuperscript{37} and appropriate azole carbohydrazide in n-butanol for three days, and were obtained as analytically pure powders in 31–56% yield (Scheme S1, ESI\textsuperscript{†}).

Next, the dinuclear Fe(u) helicates were prepared by a one-pot synthesis at room temperature, reacting a 2:3 ratio of Fe(BF\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O and the appropriate ligand L\textsuperscript{2NHIm-meta} or L\textsuperscript{4NHIm-meta} (X = NH, NMe, O and S), in acetonitrile except for L\textsuperscript{4SIm-meta} where nitromethane was used. In addition, nitromethane was used to obtain a solvatomorph of [Fe\textsubscript{2}L\textsubscript{4OIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4} (crystal structure determined at 100 and 253 K, see below). Similarly, the five [Ni\textsubscript{2}L\textsubscript{4NHIm-meta}]BF\textsubscript{4}\textsubscript{4} helicates were obtained, in order to determine Δ\textsubscript{d} from the UV-vis spectra, by using Ni(BF\textsubscript{4})\textsubscript{2}•6H\textsubscript{2}O and acetonitrile as the solvent.

All five [Fe\textsubscript{2}L\textsubscript{4NHIm-meta}]BF\textsubscript{4}\textsubscript{4} complexes were obtained as single crystals suitable for X-ray crystallography (Fig. S4, ESI\textsuperscript{†}), by slow vapour diffusion of diethyl ether into the reaction solutions: dark orange blocks of [Fe\textsubscript{2}L\textsubscript{4NHIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4}•2CH\textsubscript{3}CN•solvent (1-solvents), light brown plates of [Fe\textsubscript{2}L\textsubscript{4NHIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4}•2solvent (2-solvent), light orange-yellow irregular blocks of [Fe\textsubscript{2}L\textsubscript{4SIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4}•6CH\textsubscript{3}CN•C\textsubscript{6}H\textsubscript{10}O (3-6CH\textsubscript{3}CN•C\textsubscript{6}H\textsubscript{10}O), violet-pink needles of [Fe\textsubscript{2}L\textsubscript{4OIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4}•6CH\textsubscript{3}CN•solvent (4-solvents), and dark orange blocks of [Fe\textsubscript{2}L\textsubscript{4SIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4}•solvent (5-solvents). After air drying, compounds 1–5 were obtained, as analytically pure powders (Fig. S6, ESI\textsuperscript{†}), as the following solvatomorphs, all hydrates, in 30–87% yield: 1•4H\textsubscript{2}O (orange, 73%), 2•6H\textsubscript{2}O (brown, 30%), 3•5H\textsubscript{2}O (orange, 87%), 4•6H\textsubscript{2}O (grey, 37%) and 5•2.5H\textsubscript{2}O (orange, 87%).

In the same way, the analogous dinuclear Ni(u) helicates were prepared and isolated by vapour diffusion of diethyl ether into the MeCN reaction solutions. After air drying, 1\textsuperscript{Ni}, 2\textsuperscript{Ni} were obtained, as analytically pure pale violet/pink powders (Fig. S9, ESI\textsuperscript{†}), as the following solvatomorphs, all hydrates, in 50–96% yield: 1\textsuperscript{Ni}•6H\textsubscript{2}O (62%), 2\textsuperscript{Ni}•4H\textsubscript{2}O (50%), 3\textsuperscript{Ni}•5H\textsubscript{2}O (92%), 4\textsuperscript{Ni}•2.5H\textsubscript{2}O (62%) and 5\textsuperscript{Ni}•3H\textsubscript{2}O (96%).

Crystal structure descriptions

Single crystal X-ray data for all five of the Fe(u) dinuclear helicates were collected at 100 K. In all but one case data collection at higher temperatures was not possible due to loss of crystallinity: the exception was 4•5NO\textsubscript{2}CH\textsubscript{3} which, on warming to 253 K appeared to lose about half a molecule of nitromethane of crystallisation, becoming 4•SNO\textsubscript{2}CH\textsubscript{3} for which data was able to be collected. Modelling of the disorder of some iso-butyl groups, and of some anions, is detailed in ESI\textsuperscript{†}. Due to solvent disorder that could not be modelled satisfactorily, the SQUEEZE\textsuperscript{39} routine in PLATON\textsuperscript{39} was applied to five of the datasets: 1-solvents, 2-solvents, 4-solvents 4•SNO\textsubscript{2}CH\textsubscript{3} and 5-solvents, (see ESI\textsuperscript{†} for details).

All of the dinuclear helicates (Fig. 3) crystallised in centrosymmetric space groups: 1-solvents (triclinic P\textsuperscript{1}), 2-solvents (orthorhombic P\textsubscript{b}ca), 3•6CH\textsubscript{3}CN•C\textsubscript{6}H\textsubscript{10}O (triclinic P\textsuperscript{1}), 4-solvents (triclinic P\textsuperscript{1}), 4•5•SNO\textsubscript{2}CH\textsubscript{3} (100 K, triclinic P\textsuperscript{1}), 4•5•SNO\textsubscript{2}CH\textsubscript{3} (253 K, triclinic P\textsuperscript{1}) and 5-solvents (monoclinic C\textsubscript{2h}). The entire helicate, [Fe\textsubscript{2}L\textsubscript{4NHIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4}•solvents, was present in the asymmetric unit for all of them, except 5-solvents in which half of the helicate, [Fe\textsubscript{1.5}L\textsubscript{4NHIm-meta}]\textsubscript{4}BF\textsubscript{4}\textsubscript{4}•solvents, was present with the other half generated by a 2-fold axis.

In all cases, the formation of the desired triply bridged dinuclear helicate is confirmed. The N\textsubscript{4} coordination sphere forms a distorted octahedral geometry at Fe(u) centre, and comprises the pair of donors from one end of each of the three

![Fig. 3 Molecular structure of the cation of the triply bridged dinuclear helicate, [Fe\textsubscript{2}L\textsubscript{4NHIm-meta}]•2CH\textsubscript{3}CN•solvent (1-solvents). The other four helicates are isostructural with this one (see Fig. S7, ESI\textsuperscript{†}). For clarity, the hydrogen atoms, counter-anions and iso-butyl groups are not shown. Colours: Fe orange; N blue; C grey.](image-url)
distinct bis-bidentate azole–triazole Rat ligands (Fig. 3 and S7, ESI†).

Excluding the nitromethane solvatomorphs of 4 (see later), at 100 K all of the Fe–Nazole/triazole distances fall in the range of 1.934–2.000 Å (Table S1, ESI†), which is consistent with LS Fe(II). The octahedral distortion parameters (sum of deviations of the 12 cis angles from 90°) of the Fe(u) centres in 1–5 lie in a narrow range, 56.8–62.0° (Tables 1 and S1, ESI†) that is close to those seen for the LS azine-triazole Fe(II) dinuclear helicates [Fe2L3]4+ (56.7°) and [Fe2L3]4+ (60.3°), and falls in the range seen for all of the SCO-active helicates reported in the literature (51–70°).11–17 The intraahelicate Fe–Fe distances in 1–5 lie between 9.971–10.323 Å (Table 1), which falls in the range of 9–12 Å reported for seven of the literature examples SCO-active Fe(n) helicates37,19–21,26,60 (exception ~ 4 Å (L7/L8),24,25 ~15 Å (L10/L11)13 and 19 Å (L12),16 Fig. S1.1, ESI†).

Only for the nitromethane solvates of the oxazole–triazole helicate could datasets be collected at two temperatures: 4:5.5NO2CH3 at 100 K and 4:5NO2CH3 at 253 K (some nitromethane lost on warming). The resulting parameters (Tables 1 and S1) are consistent with the helicate being in a [LS–mixedLS/HS] state at 100 K and a [LS–HS] state at 253 K (Fig. 4, Table 1). At 100 K, the [LS–mixedLS/HS] state is proposed as the average Fe–N bond distances and Σο are 1.967 Å and 62° for Fe1 (LS) and 2.058 Å and 77° for Fe2 (mixedLS/HS). The Σο value for mixedLS/HS Fe2 is higher than is usual for LS Fe(II) in FeL3 helicates (51–70°),13 and is close to that seen for mixedLS/HS [Fe5(L2)]8+ (76°).11,60 The average intraahelicate Fe–Ntriazole distances are 80.7 (LS) and 78.5°(mixedLS/HS). At 253 K, 4:5NO2CH3 is in the [LS–HS] state as the SCO at Fe2 is now complete, whilst Fe1 remains LS (Table 1), as shown by the Fe–N and Σο values 1.980 Å and 63.0° for Fe1 versus 2.181 Å and 95.3° for Fe2 (Table 1 and Fig. 4). On conversion to LS–HS, the average intraahelicate Fe–Ntriazole angles are 80.3 (LS) and 75.8° (HS, a reduction of ~3°; similar to 75.7° seen for the mononuclear HS 1-methyl-4-imidazole complex68 [FeL3](BF4)2, Table S1, ESI†). The Fe–Fe distance expands from 10.155(7) [LS-mixLS/HS] to 10.2281(9) Å [LS–HS].

The structures of two of the dinuclear Ni(n) helicate analogues, those of the 2- and 4-NH imidazole ligands L2NHIm- and L4NHIm-, were also obtained at 100 K. The Ni–N distances (2.069–2.103 Å)44 and octahedral distortion values (Σο = 69.7–75.2°) are in between those expected for HS and LS Fe(II). In both cases, the average intraligand N–Fe–Ntriazole angle (78.3/78.7 and 78.8°, Table S1, ESI†) falls in between those seen for HS and LS Fe(n), and an increase of 2–3% in M–M distance was observed on LS Fe(n) → Ni(n) (Table 1).

**ESI-MS and 1H DOSY NMR spectra**

The ESI-MS and 1H DOSY NMR spectra both showed the dinuclear helicates 1–5 are intact in acetonitrile solution (Fig. S67–S95 and S62–S66, ESI†), confirming the robust nature of these [Fe2L3]4+ helicates. Specifically, the ESI-MS spectra showed the presence of [Fe2L3]+, [Fe2L3](X)+ and [Fe2L3](X)2+ (X = F or BF4) species.

Diffusion ordered 1H NMR spectroscopy (DOSY) was initially developed for use in characterising aggregates such as micelles, protein fragments and coordination polymers.62–64 Further development led to its widespread use in determining the molecular weights65,66 and size of polymers65,66 and to study molecular interaction between frustrated Lewis acid–base pairs in solution.5,67 Indeed it is now the ‘go to’ technique in supramolecular chemistry for determining the molecular weight and hence n for large diamagnetic self-assembled architectures, as is exemplified by the huge Pd4L2n cages (n = 12, 24 and 30) cages assembled by Fujita and co-workers.64,65,71–73

Maury, Giraud and co-workers were the first to use DOSY to characterise paramagnetic lanthanide complexes.72 Later on, Byers and co-workers successfully extended the use of DOSY to the determination of molecular weights of paramagnetic 3d transition metal complexes.73 Building on that report, DOSY is used here to analyse the intactness of this family of five paramagnetic dinuclear helicates, 1–5, in MeCN solution at 298 K. The 1H DOSY signals

![Fig. 4](image-url) Overlay of the structures (all atoms fitted) of the nitromethane solvates, [LS–mixedLS/HS] 4:5.5NO2CH3 at 100 K (blue) and [LS–HS] 4:5NO2CH3 at 253 K (orange), emphasising the lengthening of the Fe2–N bond (in the black dashed ellipse) and increased distortion around the Fe2 > Fe1.

![Fig. 5](image-url) Correlation (dark blue line, R² = 0.93) of diffusion coefficient (D) with molecular weight (M) observed at 298 K for LS FeL3 helicates (blue circles) and FeL4 cages (blue squares).37 and the SCO-active FeL3 helicates reported here (violet circles). When the two mononuclear FeL3 complexes, one HS and one SCO, are included in the fit, the R² only drops to 0.93 (green line), despite them not being members of the Fe2L3 family.
revealed the same diffusion coefficients \((D \sim 6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1};\) range 6.4–6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1})\) for all five dinuclear helicates, regardless of the variation in HS fraction at 298 K (from 0 to 0.80, see next section). This confirms the ESI-MS finding that all five helicates are robust in MeCN solution.

Regardless of the spin state at 298 K, a plot of the diffusion coefficients vs. molecular weight (Fig. 5), for these five SCO active dinuclear helicates \(1–5\), along with the previously reported LS helicates \([\text{Fe}_2(\text{L}^{2/3\text{apym-meta}}_{\text{L}})]\text{BF}_4\)4 and cages \([\text{Fe}_2(\text{L}^{2/3\text{apym-para}}_{\text{L}})]\text{BF}_4\)4,77 gave an excellent correlation \((R^2 = 0.98,\) dark blue line). The results for the pair of mononuclear HS and SCO \(\text{[Fe}^{1\text{NMe/Im}^\text{L}]}\text{4} \times \text{[BF}_4\) complexes are also shown (stars, Fig. 5) for completeness. Whilst these are not expected to lie on this correlation line (dark blue line, Fig. 5), as they are not members of the \(\text{Fe}_2\text{L}_{2\text{meta}}\) family, including them in the correlation only drops the \(R^2\) to 0.93 (green line, Fig. 5).

Variable magnetic \(^1\text{H} \text{NMR Evans method}\)

The magnetic response in solution is not affected by crystal packing effects, intermolecular cooperativity or co-crystallised solvents. The absence of all of these effects in the solution enables the effect of ligand modifications on the ligand field strength imposed on the Fe(II) centres to be clearly seen.83,74,75 Hence, the spin state of the five new dinuclear helicates \(1–5\) is monitored in acetonitrile solution at variable temperatures using both the \(^1\text{H} \text{NMR Evans method}\) and by UV-vis spectroscopy (discussed in this and the following sections).

The Evans method was used to determine magnetic susceptibility of dinuclear helicates \(1–5\) in accurately prepared, approximately 6 mM CD\(_3\)CN solution in the temperature range 243–343 K (Fig. S36–S40, ESI†), expected error associated with \(T_{1/2}\) is 5–10% (Fig. S31–S35, ESI†). Four of the complexes, \(1\cdot\text{4H}_2\text{O}, 2\cdot\text{6H}_2\text{O}, 3\cdot\text{5H}_2\text{O}\) and \(4\cdot\text{6H}_2\text{O}\), undergo partial SCO whereas the fifth complex, \(5\cdot\text{2.5H}_2\text{O}\), remains mostly LS (Fig. 6).

Fitting the data to the regular solution model,76 as a one-step SCO (Fig. 6), gave \(T_{1/2}\) values of 331 K \((1\cdot\text{4H}_2\text{O}), 267 K \((2\cdot\text{6H}_2\text{O}), 247 K \((3\cdot\text{5H}_2\text{O}), 249 K \((4\cdot\text{6H}_2\text{O})\) and 471 K \((5\cdot\text{2.5H}_2\text{O})\).

For \(1\cdot\text{4H}_2\text{O}, \) the \(\chi_m T\) value (per Fe\(^{3+}\) ion) increased from 0.37 to 1.91 cm\(^3\) K mol\(^{-1}\) on increasing the temperature from 243 to 333 K (Fig. 6, black), which corresponds to an increase in high spin fraction \((\gamma_{\text{HS}}\) of 0.1 → 0.5, whilst for \(2\cdot\text{6H}_2\text{O}\) the \(\chi_m T\) (per Fe\(^{3+}\) ion) increased from 1.38 to 2.67 cm\(^3\) K mol\(^{-1}\) (Fig. 6, red), which corresponds to an increase in \(\gamma_{\text{HS}}\) of 0.37 → 0.72. The \(T_{1/2}\) of the 2-imidazole helicate \(1\cdot\text{4H}_2\text{O} \((T_{1/2} = 331 K)\) is higher than that of the 4-imidazole helicate \(2\cdot\text{6H}_2\text{O} \((T_{1/2} = 267 K)\) which implies that the ligand field imposed by 2-imidazole is stronger than that imposed by 4-imidazole, consistent with the Kruger’s \(\text{L}^{\text{110}}\) and \(\text{L}^{\text{111}}\) dinuclear helicates (Fig. S1.1, ESI†),31 and with the relative ligand field strengths calculated from the UV-vis of analogous Ni(II) helicates of \(\text{L}^{\text{2NHlm-meta}}\) and \(\text{L}^{\text{1NHlm-meta}}\) (see later). The \(\chi_m T\) value (per Fe\(^{3+}\) ion) for \(3\cdot\text{5H}_2\text{O}\) at 243 K of 1.73 cm\(^3\) K mol\(^{-1}\) increased to 3.36 cm\(^3\) K mol\(^{-1}\) at 343 K (Fig. 6, blue), which corresponds to an increase in \(\gamma_{\text{HS}}\) of 0.47 → 0.91.

The only difference between the ligands in \(2\cdot\text{6H}_2\text{O} \((T_{1/2} = 267 K)\) and those in \(3\) \((T_{1/2} = 247 K)\) is the methylation of the non-coordinated 4-imidazole NH to give the NMe, but this change significantly decreases the ligand field imposed in \(3\cdot\text{5H}_2\text{O}\). Halcrow previously commented on the hydrogen bonding by 4-imidazole, increasing the acidity of the –NH hydrogen which increases the electron-density of the coordinated N, strengthening the σ bond donation in the N–Fe bond and favouring the LS state, relative to the methylated analogue,40 and the present findings are consistent with this.

Almost identical behaviour to the 1-methyl-4-imidazole helicate \(3\cdot\text{5H}_2\text{O} \((T_{1/2} = 247 K)\) is observed for the 4-oxazole helicate \(4\cdot\text{6H}_2\text{O} \((T_{1/2} = 331 K)\) in CD\(_3\)CN solution, as determined by Evans method.77,78 The curves correspond to the best fit found for a complete one-step SCO using the regular solution model (see ESI† for details).51,76

Fig. 6 Plot of \(\chi_m T\) vs. \(T\) for \(1\cdot\text{4H}_2\text{O} \((\text{black})\), 2\cdot\text{6H}_2\text{O} \((\text{red})\), 3\cdot\text{5H}_2\text{O} \((\text{blue})\), 4\cdot\text{6H}_2\text{O} \((\text{green})\) and 5\cdot\text{2.5H}_2\text{O} \((\text{purple})\) in CD\(_3\)CN solution, as determined by Evans method.77,78 The curves correspond to the best fit found for a complete one-step SCO using the regular solution model (see ESI† for details).51,76

Variable temperature solid state magnetic measurements

In contrast to the above, the magnetic studies of the hydrates of these five helicates in the solid state (Fig. S142–146, ESI†)
showed that both the 2NH-imidazole $L^{2NH\text{-meta}}$ (1·4H$_2$O) and 4-thiazole $L^{4\text{-thiazole-meta}}$ (5·2.5H$_2$O) based helicates remain mostly LS, with only small fractions of HS above 300 K. The other three helicates, of the 4NH-imidazole $L^{4NH\text{-meta}}$ (2·6H$_2$O), 4-oxazole $L^{4\text{oxazole-meta}}$ (4·6H$_2$O) ligands and 4NMe-imidazole $L^{4\text{NMe-Im-meta}}$ (3·5H$_2$O), undergo incomplete SCO with $T_{1/2}$ values of 200, 230 and 280 K, respectively. These $T_{1/2}$ values place the helicates in a different order, 2·6H$_2$O < 3·5H$_2$O < 4·6H$_2$O < 1·4H$_2$O < 5·2.5H$_2$O, from the above solution studies, once again demonstrating the often confounding impact of lattice solvent and crystal packing on solid state SCO.

### Variable temperature UV-vis studies

UV-vis spectra of 1–5 in acetonitrile solution were obtained at variable temperatures in our cryostat, in 10 K steps from 253 to 303 K, to probe the SCO of each of these helicates (Fig. S41–S51, ESI†), and the data compared with the Evans NMR method data (Tables S9–S11, ESI†). The spectra of the four complexes at 253 K are shown in Fig. 7, with the Laporte forbidden, spin allowed d–d transition of the LS Fe(II) centres, $^4A_{1g} \rightarrow ^4T_{1g}$, clearly seen at approximately 540 nm in the case of 2·6H$_2$O, 3·5H$_2$O and 4·6H$_2$O, and at 524 nm for 5·2.5H$_2$O. In contrast, in the case of 1·4H$_2$O, a charge transfer transition (Fig. S41, ESI†), at room temperature 446 nm ($\epsilon = 5646$ L mol$^{-1}$ cm$^{-1}$) obscured this d–d transition, so this charge transfer transition was monitored instead, as such bands have also been used by others to monitor SCO.\(^{79}\)

For the four complexes that undergo a significant amount of SCO in this temperature range (all but 5·2.5H$_2$O, see later), the $\epsilon$ values obtained from the variable temperature UV-vis study were plotted against the $T_{1/2}$ values from the Evans method NMR analysis, enabling a calibration line to be fitted, and in turn conversion of the $\epsilon$ values into $T_{1/2}$ values (Table S11, ESI†). In turn, this enables the calculation of an estimated value for the true $\epsilon$ value for the fully LS complexes, $\epsilon_{\max}$ (Fig. S52 and S54, ESI†). With that value in hand, the $\epsilon$ vs. $T$ values can be fitted with the regular solution model,\(^{54,76}\) to a full SCO from [LS–LS] $\rightarrow$ [HS–HS], to obtain the $T_{1/2}$ values (Fig. S53 and S55, ESI†).

Considering the spectrum of 0.032 mM of the 2-imidazole complex 1·4H$_2$O in acetonitrile, the charge transfer transition band observed at $\lambda_{\max} = 446$ nm with extinction coefficient per Fe(II) ion of 8597 L mol$^{-1}$ cm$^{-1}$ at 253 K (Fig. S42, ESI†) which dropped to 4863 at 303 K, with $T_{1/2} = 306$ K. In contrast, d–d transition band were seen at $\lambda_{\max} = 524$ to 540 nm for the other four complexes (Fig. 7). In the case of the 4-imidazole complex 2·6H$_2$O, the temperature dependence band at 540 nm, $\epsilon$ (per Fe(II) ion) dropped from 174 → 107 L mol$^{-1}$ cm$^{-1}$ while heating from 253 K to 303 K, respectively, $T_{1/2} = 267$ K (Fig. S44, ESI†). Similarly, for 1-methyl-4-imidazole complex 3·5H$_2$O d–d band at 540 nm $\epsilon$ value per Fe(II) ion vary from 82 to 35 L mol$^{-1}$ cm$^{-1}$ ($T_{1/2}$ of 251 K) (Fig. S8). Further, monitoring of the 540 nm band of 4-oxazole complex (4·6H$_2$O), the $\epsilon$ value (per Fe(II) ion) of 102 L mol$^{-1}$ cm$^{-1}$ at 253 K decreased to 58 L mol$^{-1}$ cm$^{-1}$ at 303 K, $T_{1/2} = 265$ K (Fig. S47, ESI†).

In the 4-thiazole helicate 5·2.5H$_2$O (Fig. 7), the d–d transition occurs at slightly higher energy (524 nm) than for 2–4, and only a small change is observed in the $\epsilon$ value. The apparent $\epsilon$ (per Fe(II) ion) decreased from 225 to 198 L mol$^{-1}$ cm$^{-1}$ on warming from 253 K to 303 K (Fig. S51, ESI†). As this temperature range does not overlap with that of the Evans method data in the region where a non-zero $\Delta_T$ and hence $\chi_{mT}$ value was observed, this could not be analysed in the same way as for the other four complexes.

### Ligand field strengths of $L^\text{meta}$ ligands

The analogous Ni(n) helicates, $1^{\text{Ni}-5^{\text{Ni}}}$, have been prepared and characterised (see the experimental section, ESI-MS in Fig. S96–S115† and crystal structures of two in Fig. S10, ESI† for details) as analysis of the UV-vis spectra of them (Fig. S56, ESI†) enables the ligand field splitting energy, $J_0$ (10$Dq$), to be obtained, and compared with the $T_{1/2}$ values observed for the Fe(n) helicates.

![Fig. 7 UV-vis spectra at 253 K in acetonitrile solution, highlighting the d–d transition, of 2·6H$_2$O ($\lambda_{\max} = 540$ nm, $\epsilon = 174$, red), 3·5H$_2$O ($\lambda_{\max} = 540$ nm, $\epsilon = 82$, blue), 4·6H$_2$O ($\lambda_{\max} = 540$ nm, $\epsilon = 102$, green) and 5·2.5H$_2$O ($\epsilon = 225$, purple), and lack of a distinct d–d transition for 1·4H$_2$O (charge transfer band at 446 nm, $\epsilon = 5642$). Note: $\epsilon$ is calculated per Fe$^{II}$ ion.](image)
Octahedral Ni$^{2+}$ ($d^8$) has a $^3A_{2g}$ ground state, which gives rise to three spin allowed d-d transitions, $^{89}$ from highest to lowest energy: $^3A_{2g} \rightarrow ^3T_{2g}(P) = 400$–$310$ nm, $^3A_{2g} \rightarrow ^3T_{1g}(F) = 715$–$550$ nm, and $^3A_{2g} \rightarrow ^3T_{2g}(F) = 1000$–$800$ nm (near IR). This last band corresponds to $\Delta_a$, but it is often weak and broad, and sometimes the spin forbidden $^3A_{2g} \rightarrow ^1E_g$ transition (which gains some intensity through spin–orbit coupling with $^3T_{2g}$) can be seen as a shoulder on this band, further complicating the analysis.$^{88,89}$ Indeed, when $\Delta_a$ is close to 12 000 cm$^{-1}$, as it is herein, mixing of these two bands, $^3A_{2g} \rightarrow ^3T_{2g}(F)$ and $^3A_{2g} \rightarrow ^1E_g$, becomes more significant and it is not possible to correctly analyse them. To deal with this issue, Hart, Boeyens and Hancock$^{88}$ developed an empirical relationship:

$$10Dq \text{ (corrected)} = 10630 + 1370\epsilon_1/\epsilon_2$$

where $\epsilon_1/\epsilon_2$ is the ratio of the extinction coefficients of the lower to higher wavelength components of this near IR band.

Using this equation on the ratio of the extinction coefficients corresponding to the shoulder ($\epsilon_1$)/peak ($\epsilon_2$) in the near IR band observed in each of the spectra of $1^{\text{Ni}}$–$5^{\text{Ni}}$ (Fig. 9), the “corrected 10$Dq$” values, $\Delta_{o(corr.)}$, have been determined for these five helicates (Table S12, ESI).

In summary, the resulting $\Delta_{o(corr.)}$ values, in order of increasing ligand field strength, as follows (cm$^{-1}$):

$$L^{4\text{NM}-\text{meta}} \text{ (11 420)} \sim L^{4\text{NH}-\text{meta}} \text{ (11 430)} < L^{2\text{Ni}-\text{meta}} \text{ (11 505)} \sim L^{4\text{OIm-meta}} \text{ (11 516)} < L^{4\text{Im-meta}} \text{ (11 804)}$$

This analysis of the UV-vis spectra of the Ni(u) helicates shows that the effect of changing from –NH, –NMe and –O in the non-coordinating position of the azole moiety in the ligand leads to relatively minor changes in the field strength, whereas changing to –S provides a significant increase in the ligand field strength. The ligand field strengths of these five ligands $\Delta_{o(corr.)}$ are not entirely consistent with the $T_{1u}$ values of the corresponding Fe(u) complexes, but despite this there is a good linear correlation ($R^2 = 0.87$) between them (Fig. 10).

Electrochemical studies

The magnetic response of 1–5 varied considerably with small modifications to the ligand strands, clearly reflecting the effect of changing the heteroatom present in the azole rings of these Rat ligands on the Fe(u) centres, we also expected to see tuning of the Fe$^{II/III}$ redox potentials.

Cyclic voltammetry was performed on 1 mM MeCN solutions of 1–5, vs. 0.01 M Ag/AgNO$_3$. These solutions also contained 0.1 M TBAClO$_4$, except in the case of 4-thiazole helicate $5\cdot2.5$H$_2$O, which was insoluble in 0.1 M TBAClO$_4$ but was
soluble in 0.1 M TBAPF₆. Four of the five complexes, 1·4H₂O (Eₚₐ = 0.39 V), 2·6H₂O (Eₚₐ = 0.27 V), 3·5H₂O (Eₚₐ = 0.25 V) and 5·2.5H₂O (Eₚₐ = 0.67 V), showed a reversible Fe(II)/Fe(III) redox process. In the case of the 4-oxazole helicate 4·6H₂O, an irreversible oxidation event, at higher Eₚₐ = 0.78 V than the others, was observed (Fig. 11).

The five helicates, identified by ligand, in order of decreasing Eₚₐ, are as follows:

$$4\cdot6H_2O (E_{pa} = 0.78 V) \sim 5\cdot2.5H_2O (E_{pa} = 0.73 V) > 1\cdot4H_2O (E_{pa} = 0.44 V) > 2\cdot6H_2O (E_{pa} = 0.33 V) \sim 3\cdot5H_2O (E_{pa} = 0.30 V)$$

In general, the presence of an electron donating group pushes more electron density onto a metal centre making it easier to oxidise, and vice versa. Therefore, the oxidation potential (Eₚₐ) for 1-methyl-4-imidazole helicate 3·5H₂O (0.30 V) is lower than 4-imidazole helicate 2·6H₂O (0.33 V), which is attributed to the presence of the electron donating group -NMe in 3·5H₂O, making the Fe(II) centre easier to oxidise.³⁶,⁸²

**Correlations of SCO T₁/₂ versus Δₒ versus Eₚₐ**

Interestingly, the four helicates with the reversible redox events, 1·4H₂O, 2·6H₂O, 3·5H₂O and 5·2.5H₂O, show a strong linear correlations between the (a) oxidation potential Eₚₐ vs. the SCO T₁/₂ (R² = 0.99, Fig. 12a, red line), and (b) γ_HS (298 K) vs. Eₚₐ (R² = 0.91, Fig. 12b, red line). But when the helicate with the irreversible redox event, 4-oxazole helicate 4·6H₂O, included in the linear fit the R² drops to just 0.20 (Fig. 12a, green line) and 0.10 (Fig. 12b, green line). Given the above, unsurprisingly there is also a strong linear correlation (R² = 0.98) of Δₒ and Eₚₐ for the four reversible complexes (Fig. 12c, red line), which when 4·6H₂O is included again drops, to R² = 0.49 (Fig. 12c, green line), i.e. in all cases the inclusion of the 4-oxazole helicate 4·6H₂O which shows irreversible redox in these correlations leads to a big drop in R², to 0.10–0.49.

In summary, for the four complexes with reversible redox, Eₚₐ(Fe²⁺/³⁺) is strongly positively correlated with T₁/₂ and Δₒ (R² = 0.91–0.99), and strongly negatively correlated with the γ_HS fraction at 298 K. This shows that as the ligand field (Δₒ) and hence fraction LS increases, it gets harder to oxidise, i.e. Eₚₐ(Fe²⁺/³⁺) increases (Fig. 12 and Table 2).

As noted in the introduction, studies of both redox and SCO across a family of complexes are not common.²⁴,³⁰–³² In the 1980’s, in a family of nine solution SCO-active Fe(II) complexes, Kadish and co-workers observed the same trend as is seen here, the lower the γ_HS the easier it was to reduce (higher E₁/₂, Fig. S1.2, ESF†).²²,²³ On the other hand, in 1975 Drago and co-workers²⁸ had studied a family of four solution SCO-active mononuclear Fe(II) complexes of hexadentate ligands varying in number of ortho-methyl groups present, and showed the opposite: the complexes with the highest γ_HS, rather than those with least electron-donating methyl groups (perhaps due to steric factors), were the most difficult to oxidise.²⁸ Simplistically, SCO T₁/₂ values are expected to increase with increasing Δₒ whereas redox potentials E₁/₂ are expected to increase with decreasing HOMO energy level. So the observation of some correlations between these two distinct properties is intriguing and warrants further attention. Hence a collaborative study

### Table 2

Summary of cyclic voltammetry data obtained for dinuclear iron(II) helicates, 1–5, in MeCN (0.1 mol L⁻¹ TBAClO₄ unless indicated with * in which case, for solubility reasons, 0.1 M TBAPF₆ was used) versus 0.01 mol L⁻¹ Ag/AgNO₃ at 200 mV s⁻¹, along with the T₁/₂ and γ_HS(298 K) in MeCN solution, and the Δₒ for the nickel(II) analogues

| Complexes | Eₚₐ (V) | E_pc (V) | E_m (ΔE) (V) | T₁/₂ (K) | γ_HS 298 K | Δₒ (cm⁻¹) (Ni₂L₃⁻) |
|-----------|---------|---------|-------------|---------|-----------|---------------------|
| L²NHim-meta (1·4H₂O) | 0.44 | 0.34 | 0.39 (0.10) | 331 | 0.33 | 11 505 |
| L⁴NHm-meta (2·6H₂O) | 0.33 | 0.22 | 0.27 (0.11) | 267 | 0.61 | 11 420 |
| L⁴Mcm-meta (3·5H₂O) | 0.30 | 0.20 | 0.25 (0.10) | 247 | 0.81 | 11 430 |
| L⁴Oim-meta (4·6H₂O) | 0.78 | Irrev | Irrev | 249 | 0.81 | 11 516 |
| L⁴SIm-meta (5·2.5H₂O) | 0.73 | 0.61 | 0.67 (0.12) | 471 | 0 | 11 804 |

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probing this family of interesting helicates in detail, using a range of theoretical models, will be carried out in the future in order to better understand the basis of the correlations observed.

Conclusion

The previously reported ditopic Rat ligands consisted of a pair of pyrimidine-triazole pockets linked through meta-phenylene which resulted in Fe(n) dinuclear helicates that were trapped in the LS state. So herein, the strong ligand field pyrimidines (azines) were replaced by lower ligand field azoles. Five such ligands have been prepared (L \textsubscript{4oxazole-meta}, L \textsubscript{4NHIm-meta}, L \textsubscript{4NMeIm-meta}, L \textsubscript{4HIm-meta}, and L \textsubscript{4Im-meta}) along with the corresponding triply bridged dinuclear helicates [M\textsubscript{2}L\textsubscript{3}(BF\textsubscript{4})\textsubscript{4}] \textsuperscript{−}·solvents with M = Fe or Ni. Single crystal X-ray structures of the iron(n) helicates (1–5) confirmed that they are indeed helicates, and are in the [LS-LS] state at 100 K.

ESI-MS and \textsuperscript{1}H DOSY NMR spectroscopy studies confirmed the robustness of 1–5 in MeCN solution. Indeed, a strong linear correlation (R\textsuperscript{2} = 0.98) was seen between the diffusion coefficient and the molecular weight for the nine Fe\textsubscript{2}L\textsubscript{3} helicates (7) and Fe\textsubscript{4}L\textsubscript{6} cages (2) prepared to date, regardless of the \( \gamma_{HS} \) at 298 K ranging from 0 to 0.81.

VT-NMR Evans method studies of 1–5 in CD\textsubscript{3}CN solution (243–343 K) revealed that all of the complexes undergo incomplete SCO within this temperature range, with \( T_{1/2} \) values ranging from 247 to 471 K. The SCO was also followed by VT-UV-vis spectroscopy (253–303 K) in CH\textsubscript{3}CN solution, by monitoring changes in the absorbance of either the charge transfer band for 1, or of the d–d band for 2–5.

UV-vis spectra of the corresponding Ni(n) helicates revealed the ligand field splitting energy \( \Delta_{o(other)} \) for four of the L \textsubscript{4oxazole-meta} ligands falls in the range 11 420–11 516 cm\textsuperscript{−}1 (azole = 2-imidazo, 4-imidazo, 1-methyl-4-imidazo and 4-oxazo) whereas the fifth ligand imposes a significantly stronger ligand field, 11 804 cm\textsuperscript{−}1 (azole = 4-thiazo).

Cyclic voltammetry studies in acetonitrile solution showed a Fe(n)/Fe(n) redox process that was reversible for four of the complexes, but irreversible for the 4-oxazo helicate 4·6H\textsubscript{2}O. For the four reversible cases, excellent linear correlations of: \( E_{pa} \) with \( T_{1/2} \) (R\textsuperscript{2} = 0.99), \( E_{pa} \) with \( \gamma_{HS} \) (R\textsuperscript{2} = 0.91) and \( E_{pa} \) with \( \Delta_{o(other)} \) (R\textsuperscript{2} = 0.98) are observed.

This is a unique study, as it determines all three properties, ligand field splitting energy \( \Delta_{o} \), SCO \( T_{1/2} \) and oxidation potential \( E_{pa} \), across a family of complexes – here for a family of five robust triply bridged dinuclear helicates differing in the choice of non-coordinated diazole heteroatom. In doing so it provides a rare illustration of the textbook statement that the stronger the ligand field (\( \Delta_{o} \)) the more the LS state is stabilised over the HS state (\( T_{1/2} \); strong correlations, R\textsuperscript{2} > 0.87). Also, less intuitively, a connection is made between the SCO and redox properties of this family of helicates: for the four reversible systems the stronger the ligand field (\( \Delta_{o} \)) and higher the \( T_{1/2} \), the harder the Fe(n) helicate is to oxidise to Fe(II) (\( E_{pa} \)). Future studies will include collaborative theoretical studies to probe these interesting helicates in more detail.

Author contributions

S. S. carried out all of the experimental work. S. B. conceived and supervised the project. S. S. prepared the first draft of the manuscript and S. B. and S. S. refined it to publication standards.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the University of Otago for supporting this work (including a doctoral scholarship and publishing bursary to SS), and Mr Ian Stewart (Otago) for measuring the ESI-MS and NMR spectra.

Notes and references

1 M. A. Halcrow, Spin-Crossover Materials: Properties and Applications, John Wiley & Sons, Ltd, Chichester, 1st edn, 2013.
2 P. Gültlich and H. A. Goodwin, Spin Crossover in Transition Metal Compounds I–III, Top. Curr. Chem., 2004, 233–235.
3 P. Gültlich, Y. Garcia and T. Woike, Coord. Chem. Rev., 2001, 219–221, 839–879.
4 J.-F. Létard, P. Guionneau and L. Goux-Capes, Top. Curr. Chem., 2004, 235, 221–249.
5 M. Mikolasek, M. D. Manrique-Juarez, H. J. Shepherd, K. Rijlder, S. Rat, V. Shalabaeva, A.-C. Bas, I. E. Collings, F. Mathieu, J. Cacheux, T. Leichle, L. Nicu, W. Nicolazzi, L. Salmon, G. Molnár and A. Bousseksou, J. Am. Chem. Soc., 2018, 140, 8970–8979.
6 J.-M. Lehn, Supramolecular chemistry: concepts and perspectives, VCH, Weinheim, 1995.
7 E. C. Constable and A. M. W. Cargill Thompson, J. Chem. Soc., Dalton Trans., 1994, 1409–1418.
8 A. Lennartson, P. Souton, N. F. Sciortino, C. J. Kepert, C. Frandsen, S. Morup, S. Piligkos and C. J. McKenzie, Chem.– Eur. J., 2015, 21, 16066–16072.
9 F. Wang, C.-Y. Zhu, Y.-Q. Zhang, R.-Z. Liao, W. Xia, J.-C. Hu, J. Wu and H. Liu, Dalton Trans., 2018, 47, 13142–13150.
10 S. Rodriguez-Jiménez and S. Brooker, Inorg. Chem., 2019, 58, 8188–8197.
11 R. W. Hogue, S. Singh and S. Brooker, Chem. Soc. Rev., 2018, 47, 7303–7338 and inside front cover.
12 H. S. Scott, R. W. Staniland and P. E. Kruger, Coord. Chem. Rev., 2018, 362, 24–43.
13 A. J. McConnell, Supramol. Chem., 2018, 30, 858–868.
14 N. Struch, C. Bannwarth, T. K. Ronson, Y. Lorenz, B. Mienert, N. Wagner, M. Engeser, E. Bill, R. Puttreddy, K. Rissanan, J. Beck, S. Grimme, J. R. Nitschke and A. Lützen, Angew. Chem., Int. Ed., 2017, 56, 4930–4935.
15 R. A. Bilbeisi, S. Zarra, H. L. C. Feltham, G. N. L. Jameson, J. K. Clegg, S. Brooker and J. R. Nitschke, Chem.–Eur. J., 2013, 19, 8058–8062.
67 P. S. Pregosin, P. G. A. Kumar and I. Fernández, *Chem. Rev.*, 2005, **105**, 2977–2998.

68 H. Takezawa, T. Murase, G. Resnati, P. Metrangolo and M. Fujita, *Angew. Chem., Int. Ed.*, 2015, **54**, 8411–8414.

69 D. Fujita, Y. Ueda, S. Sato, H. Yokoyama, N. Mizuno, T. Kumasaka and M. Fujita, *Chem*, 2016, **1**, 91–101.

70 Q. F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi and M. Fujita, *Science*, 2010, **328**, 1144–1147.

71 M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Shakamoto, K. Yamaguchi and M. Fujita, *Angew. Chem., Int. Ed.*, 2004, **43**, 5621–5625.

72 S. Denis-Quanquin, F. Riobé, M.-A. Delsuc, O. Maury and N. Giraud, *Chem.–Eur. J.*, 2016, **22**, 18123–18131.

73 M. P. Crockett, H. Zhang, C. M. Thomas and J. A. Byers, *Chem. Commun.*, 2019, **55**, 14426–14429.

74 C. Bartual-Murgui, S. Vela, M. Darawsheh, R. Diego, S. J. Teat, O. Roubeau and G. Aromi, *Inorg. Chem. Front.*, 2017, **4**, 1374–1383.

75 B. Weber and F. A. Walker, *Inorg. Chem.*, 2007, **46**, 6794–6803.

76 O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., New York, 1993.

77 L. A. Yatsunyk and F. A. Walker, *Inorg. Chem.*, 2004, **43**, 757–777.

78 D. F. Evans, *J. Chem. Soc.*, 1959, 2003–2005.

79 I. Nikovskiy, A. Polezhaev, V. Novikov, D. Aleshin, A. Pavlov, E. Saffiulina, R. Aysin, P. Dorovatovskii, L. Nodaraki, F. Tuna and Y. Nelyubina, *Chem.–Eur. J.*, 2020, **26**, 5629–5638.

80 F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 6th edn, 1999.

81 S. M. Hart, J. C. A. Boeyens and R. D. Hancock, *Inorg. Chem.*, 1983, **22**, 982–986.

82 D. C. Ashley and E. Jakubikova, *Inorg. Chem.*, 2018, **57**, 9907–9917.