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Manipulating Metal Spin States for Biomimetic, Catalytic and Molecular Materials Chemistry

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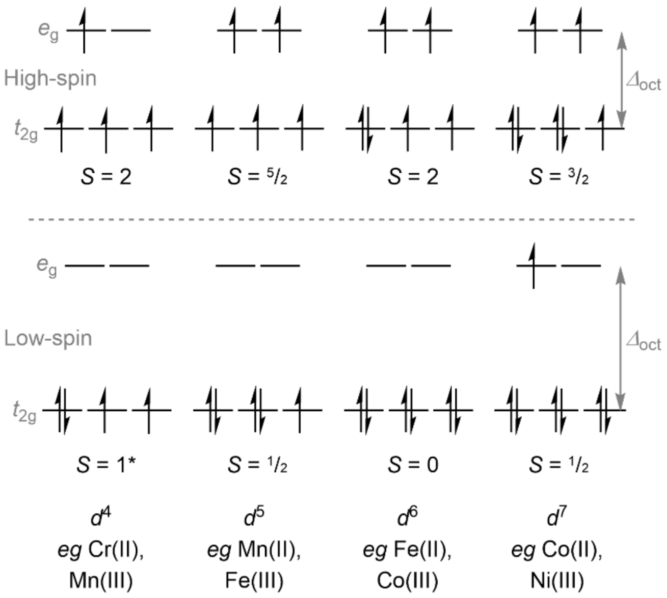
This article surveys the relationship between ligand type, coordination geometry and metal spin state in complexes of iron and other metal ions. Compounds and materials containing high-, intermediate- and low-spin metal ions differ in their molecular structures, their physical properties and their chemical reactivity. Implications and applications of these variations are summarised, including the use of base metals in light-harvesting dyes and in different forms of catalysis. Recent studies of the electronic influence of ligand substituents, or ligand conformational constraints, on metal ion spin states are described, which have revealed unexpected complexities.

Introduction

A number of first row transition metal ions can adopt more than one spin state in their compounds, depending on their electron counts and *d*-orbital splittings.[1] Best known are the high-spin and low-spin forms of octahedral complexes with d^4-d^7 electron counts, which respectively contain the maximum and minimum number of unpaired electrons that is possible within the Aufbau principle (Scheme 1). The dichotomy arises when the *d*-orbital splitting in such compounds is small enough, that their ground state configuration predicted by the Aufbau principle is ambiguous. If the split *d*-orbitals continue to behave as one orbital manifold within the ligand field, Hund's rule disfavours pairing of the *d* electrons and a high-spin configuration results. On the other hand, if each split *d*-orbital is considered as a separate energy level, the Pauli exclusion principle favours electron pairing resulting in a low-spin state.

In practise, this balance is governed by two unfavourable energy terms: the electrostatic repulsion between two electrons in the same *d*-orbital (the pairing energy, *P*); and the energy gap between the individual *d*-orbitals, which is a function of the ligand field splitting parameter Δ. When $\Delta < P$ it is less unfavourable to promote an electron to a different *d*-orbital than to pair it with another electron, resulting in a high-spin molecule, while a low-spin compound is formed when $\Delta > P$. The magnitude of *P* reflects an atom's electron configuration and effective nuclear charge, which is modulated by metal–ligand covalency (expressed by the spectroscopic nephelauxetic parameter β).[2,3] Values of Δ show much greater variation according to the number, type, strength and disposition of the metal–ligand bonds.[3] Hence, the spin state adopted by a metal ion depends predominantly on Δ. When Δ and *P* are sufficiently similar a compound can undergo a thermal spin-crossover equilibrium between high-spin and low-spin forms.[4] Several compounds cited as examples in this article have that property, and lie on the cusp between two spin states.[5]



Scheme 1 High-spin and low-spin configurations of octahedral metal ions (*the *S* = 1 configuration for d^4 ions is an intermediate spin state for that electron count).[6]

Generalisations about complex spin states are often made at undergraduate level. One, that compounds of second and third row transition ions are always low-spin because of their stronger, more covalent ligand fields, is still essentially true. The only caveat is that low→high spin equilibria occasionally occur between metal–metal bond orbitals in heavy metal cluster compounds.[7] Other common generalisations that tetrahedral complexes are high-spin and square planar complexes low-spin, are less secure. Tetrahedral metal centres in high oxidation states[8-10] and/or with strong-field ligands[10,11] are sometimes low-spin. Conversely high-spin configurations occur in square-planar chromium(II) complexes[12] and some manganese(II)

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tetrapyrroles.[13] They can also be found for later transition ions in an anionic or strongly π-donating ligand field;[14-16] a high-spin, square planar nickel(II) oxide was even reported last year.[16] Spin-crossover equilibria are also sometimes found in strong-field tetrahedral[17,18] or weak-field square-planar systems.[19]

In addition to high-spin (S = 5/2 or 2, Scheme 1) or low-spin (S = 1/2 or 0), intermediate-spin (S = 3/2 or 1) forms of d^4, d^5 and d^6 metal ions are also accessible. These cannot exist in a d^5 and d^6 octahedral geometry without a substantial distortion from O_h symmetry.[20] However they sometimes occur in six-coordinate iron/porphyrin complexes, where deformation of the porphyrin macrocycle induces the necessary symmetry reduction.[21,22] An important example may be the oxy-haem centre in haemoglobin and myoglobin, which recent data have formulated as an intermediate-spin iron(II)/O_2 centre.[23] Intermediate-spin states are better-known in octahedral d^4 complexes, where an S = 0 low-spin form is similarly impossible in a degenerate t_{2g} subshell (Scheme 1);[6] and in some tetrahedral,[10] square-planar,[24,25] and five-coordinate[22,25,26] iron complexes.

The influence of metal ion spin state on its physical properties

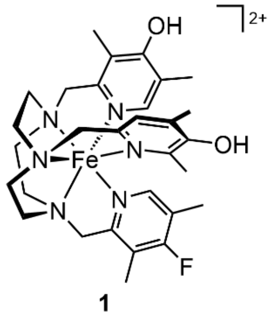
The spin state of a metal centre can strongly influence its physical properties and reactivity. The most obvious physical influence is on the magnetic moment of a compound, which is always larger in the high-spin form. This is most pronounced for d^6 metal ions like iron(II), which are diamagnetic in their low-spin state but strongly paramagnetic when high-spin (Scheme 1). Iron(II) compounds have been proposed as NMR or magnetic resonance imaging (MRI) probes, which are "switched on" by an externally triggered low→high-spin state change.[27] The CISSS molecular switches discussed below are an example, which are proof-of-principle photoswitchable MRI contrast agents.[28] Another is the spin-crossover compound **1**, whose ^{19}F NMR shift is a sensitive probe of pH in solution. That reflects deprotonation of its hydroxyl groups (pK_a 6.0) in basic media, which shifts the spin-state equilibrium towards the high-spin form of the compound thus increasing its magnetic moment.[29]

Alternatively, the different spin states of a metal ion can also be different colours. The changes are dominated by charge-transfer and low-spin d-d absorptions in the visible or near-UV,[3] which make low-spin compounds absorb up to 10x more strongly in this region.[30] In practise, this difference is more pronounced for some metal/ligand combinations than for others. However, it can afford a sufficient colorimetric response for chemosensor applications. Thus, hydrogen bonding of halides to the peripheral N–H groups of **2** results in a high→low spin-state change, which is clear to the naked eye as well as in its NMR spectrum.[31] Similarly, **3** gives a selective colorimetric response upon binding of barbiturate.[32] Vapochromic metal/organic materials[33] undergoing spin-state changes on absorption or desorption of water,[34] organic vapours[35-37] or other gaseous analytes[37,38] are also well known.

Other colorimetric applications depend on avoiding ambiguous or switchable spin states. Thus, low-spin iron complexes are only useful dyes for photocatalysis or solar cell applications, if their ligand field is so strong as to make their high-spin excited configurations energetically inaccessible.[39,40] That prevents relaxation of their charge-separated photoexcitation by intersystem crossing to high-spin energy states, leading to the extended nanosecond charge-separation lifetimes required for light-harvesting applications. An example is **4**,[40] whose strongly σ-donating carbene donors are aligned almost perfectly on the cartesian axes, increasing the e_g d-orbital energies and maximising Δ_{oct} (Scheme 1).[41]

Spin state changes lead to significant structural changes in the solid state, which can perturb the macroscopic properties of a material. This includes its volume and mechanical properties,[42] since high-spin metal centres are generally larger than their low-spin counterparts reflecting their extra, metal–ligand antibonding e_g d-electrons (Scheme 1). Switchable dielectric properties,[43] fluorescence[44] and/or conductivity[45] are also well-known in spin-crossover materials exhibiting those phenomena. There is great interest in exploiting these phenomena in switchable nano- and macro-scale devices.[46]

Many chemical processes at transition metal compounds involve a spin state change. Most simply a change in coordination geometry, with or without the gain or loss of a ligand, changes the ligand field and rearranges the d-orbitals. A textbook example is the square-planar (diamagnetic)/ octahedral (paramagnetic) equilibrium shown by a number of nickel(II) complexes in donor solvents.[47] More sophisticated molecules using the same principle have been termed Coordination-Induced Spin State Switches (CISSSs), which change spin state *via* triggered ligand (de)coordination reactions. Examples are metalloporphyrins related to those in Scheme 2, which have been developed as light-activated MRI contrast agents[28] or as switchable surface monolayers in an STM probe.[48] CISSS switching has also been generated by controlled, reversible coordination of exogenous ligands to a square planar metal centre;[49] and by protonation-induced cleavage of a metal–ligand bond in an octahedral complex.[50]



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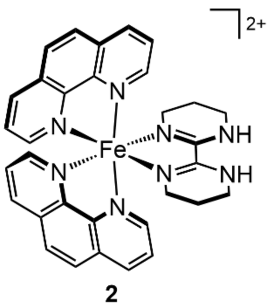

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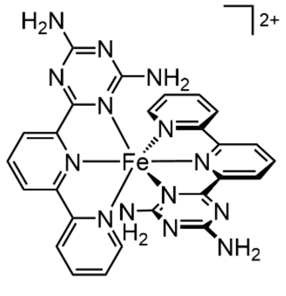

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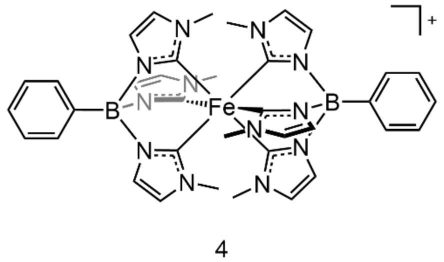

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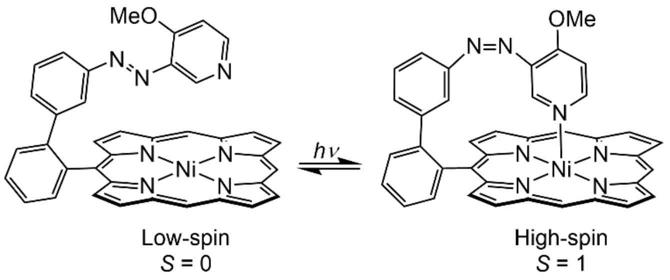
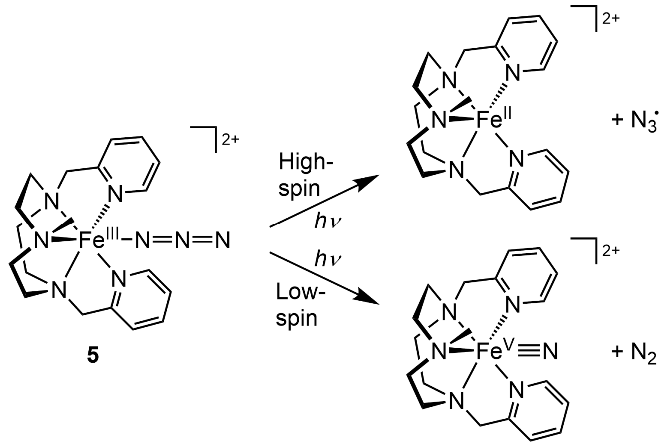


Scheme 2 A CISSS molecular switch for photochemically activated MRI applications. Coordination of the apical pyridyl donor is driven by light-induced *cis*/*trans* isomerisation of the azo linker. The porphyrin is decorated with C_6F_5 groups (not shown).[28]

The effect of metal ion spin state on its chemical reactivity

Their longer metal–ligand bonds and more flexible coordination geometries make high-spin metal ions inherently more labile than their low-spin congeners. For example, the water-exchange reaction of high-spin d^6 $[Fe(OH_2)_6]^{2+}$ is 10^7 times faster than for low-spin d^6 $[Co(OH_2)_6]^{3+}$.[51] High-spin metal centres are also prone to radical reactions and one-electron chemistry, whereas low-spin compounds favour two-electron processes. An example here is **5**, which exhibits a thermal spin-crossover equilibrium. Its high-spin (S = 2) form undergoes one-electron reduction upon UV photolysis, generating $N_3^{\bullet}$ radical as a byproduct. Conversely, the low-spin (S = 0) molecule undergoes two-electron oxidation under the same conditions, generating an iron(V) nitride with elimination of N_2 (Scheme 3).[52]



Scheme 3 Photochemical reactivity of two spin states of an iron/azide complex.[51]

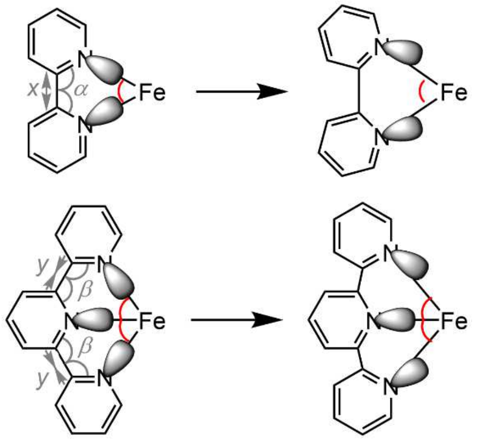
These considerations are important in catalytic oxidation reactions, which proceed by a radical rebound mechanism. This is initiated by H atom abstraction from the substrate molecule, often by a high-valent metal-oxo intermediate.[53] In iron chemistry, iron(IV) Fe=O species (ferryls) adopt intermediate-spin (S = 1) or high-spin (S = 2) configurations depending on the ligands employed.[54] High-spin ferryls occur in non-haem iron enzymes, and are more active towards H atom transfer (HAT) processes when chemically similar examples are compared.[55,56] The most reactive intermediate-spin ferryls can approach the HAT rates found in some high-spin cases, however.[57] Computational studies imply that some intermediate spin ferryls form high-spin intermediates during the radical rebound process, thus increasing their reaction rate *via* a "two state reactivity" pathway.[53] Such considerations are less obviously applicable to manganese(IV) Mn=O oxidation intermediates which, as d^3 species, always adopt the same S = 3/2 spin state.

Spin states also impact the development of first-row "base" metals as replacements for expensive platinum metal catalysts.[58] For example hydrogenation and other catalytic double bond reductions proceed in two-electron oxidative addition/reductive elimination steps.[59] These processes are favoured for low-spin catalysts[60] or, rarely, for high-spin species that can access a spin-paired reaction pathway through two-state reactivity.[61] Alternatively, some base metal catalysts circumvent the requirement for two-electron metal redox with a non-innocent supporting ligand, which acts as an H atom acceptor during the catalytic cycle.[62] In contrast, transmetallation steps during cross-coupling reactions proceed in one-electron steps at base metal centres.[63] This is favoured by high-spin iron catalysts, or by nickel(II) catalysts that are activated to radical chemistry by a square-planar (S = 0)→tetrahedral (S = 1) rearrangement which is another form of two-state reactivity.[64] Although they have been less studied, catalyst spin states can also impact the performance of iron-catalysed polymerisation reactions.[65]

Controlling spin states by ligand design

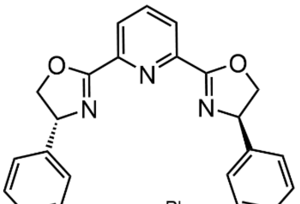
The spin state of a metal ion is ultimately governed by the number, geometry and character of its metal–ligand bonds. Like most aspects of chemistry, this can be controlled by both steric and electronic factors.[5] Steric influences reflect that metal–ligand bond lengths to high-spin metal ions are longer than to the same compound in a low-spin state. Thus, bulky ligand substituents that inhibit contraction of the metal–ligand bonds will favour a high-spin compound, and *vice versa*.[5,66,67] Polydentate ligands with six-membered (or larger) chelate rings also favour high-spin complexes, other things being equal. The longer metal–ligand bonds in the high-spin state reduce conformational strain in larger chelate ligand backbones.[5]

Conformational constraints that promote or inhibit overlap of the ligand lone pairs and metal orbitals also perturb the ligand field. For example, changes in ligand bite angle in five-membered chelate ligands have subtle, but measurable effects. Specifically, the high-spin state is favoured by larger ligand bite angles in $[Fe(NN)_3]^{2+}$,[68] but by smaller bite angles in $[Fe(NNN)_2]^{2+}$ (where NN and NNN are bidentate and linear tridentate N-donor ligands with five-membered chelate rings).[69] Increasing the bite angle of bidentate ligands, whose centroid lies between cartesian orbital axes, is accomplished through larger internal angles (α) or a lengthened backbone (x) within the chelate ring (Scheme 4). Conversely, increasing the β angles or shortening y both *decrease* the bite angle of a tridentate ligand, where the alignment of the central metal–ligand bond is fixed along an orbital axis. Both changes tend to misalign the ligand lone pair orbitals with the metal–ligand vectors, thus weakening those bonds and favouring a high-spin complex. These differences manifest when comparing N-donor ligands containing different heterocyclic or acyclic N-donor atoms, or with heteroatoms within their chelate backbone (which shorten x or y).[68,69]

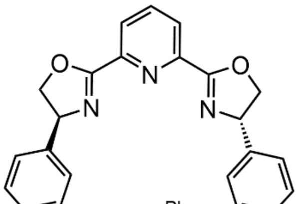


Scheme 4 The effect of widening the bite angle of bidentate ligands (top), or narrowing the bite angle of meridional tridentate ligands (bottom), on metal–ligand orbital overlap.

Because of their weaker ligand field, high-spin metal ions are also more prone than low-spin ions to geometric distortions of their coordination sphere.[70] Hence intramolecular or (in the solid state) intermolecular steric clashes, which induce a distortion away from an idealised coordination geometry, will also favour a high-spin compound.[5,71,72] A subtle example is found in two diastereomers of iron/pyridine-*bis*-oxazoline (PyBox) complexes $[Fe(L^{Ph})_2]^{2+}$. Both isomers exhibit spin-crossover equilibria in solution, occurring at 34 K lower temperature in homochiral $[Fe((R)\text{-}L^{Ph})_2]^{2+}$ than in heterochiral $[Fe((R)\text{-}L^{Ph})((S)\text{-}L^{Ph})]^{2+}$.[72] The high-spin state allows the L^{Ph} ligands to twist away from perpendicular, relieving a steric clash between phenyl substituents in $[Fe((R)\text{-}L^{Ph})_2]^{2+}$ which isn't present in the heterochiral isomer. That gives a small additional stabilisation to the high-spin form of the homochiral complex.[73]



$(R)\text{-}L^{Ph}$



$(S)\text{-}L^{Ph}$

In the first instance, the design of ligands to form high-spin or low-spin compounds can be based on the spectrochemical series and the above steric criteria.[5] Fine tuning metal spin state energies with electron-donating or -withdrawing ligand substituents involves more subtle considerations, however. This is exemplified by **6**, where X and Y substituents respectively exhibit positive and negative linear free-energy relationships with its solution-phase spin-crossover equilibrium temperature $T_{\frac{1}{2}}$. That is, electron-withdrawing substituents stabilise the low-spin form of **6**, but electron-withdrawing Y substituents favour its high-spin form (Figure 1).[74,75]

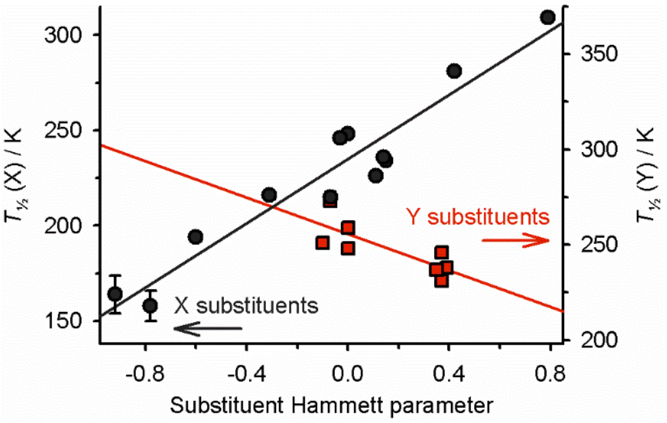
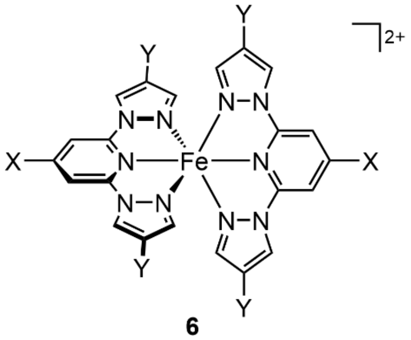


Figure 1 The different electronic influences of X (black circle) and Y (red square) ligand substituents on the spin state of **6**.[74] A higher $T_{\frac{1}{2}}$ value corresponds to stabilization of the low-spin state and *vice versa*.

The difference arises because the σ and π components of the Fe–N bonds have opposing influences on the ligand field in **6**. The X substituents, being *para* to the pyridyl N-donor atom, can directly conjugate with those Fe–N bonds. Electron-withdrawing X substituents enhance metal→ligand π-back-bonding to the pyridyl rings, thus strengthening the ligand field and favouring the low-spin state. Electron-deficient X substituents also inductively weaken the metal→ligand σ-bond, but that effect is smaller because the substituent is remote from the N donor atom. Hence, the π-bonding influence dominates in this case. In contrast Y substituents, being *meta* to the pyrazolyl N-donors, cannot conjugate to those Fe–N bonds and have no effect on their π-component. However, being closer to the N-donor atoms, Y substituents have a stronger inductive effect on the basicity of the pyrazolyl donors and the strength of the metal–ligand σ-bond. Hence, electron-withdrawing Y groups weaken those Fe–N σ-bonds, reducing the ligand field splitting and resulting in high-spin complexes.[75,76]

The trend for electron-withdrawing *para* substituents to favour low-spin states (and *vice versa*) has also been seen in other iron(II) spin-crossover systems of pyridyl ligands.[77] A comparable effect is also found when introducing additional heteroatoms into a heterocyclic ligand; more π-basic ligand



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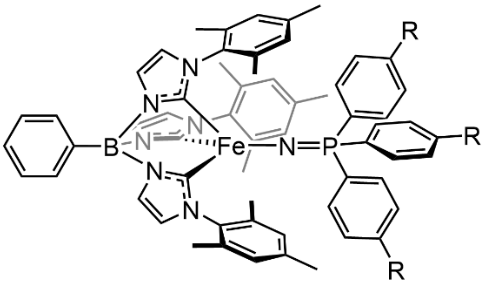

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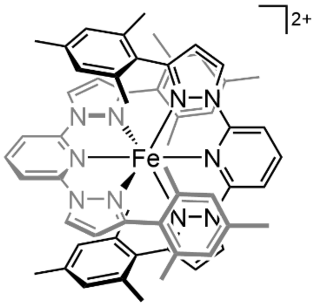

8

donors (*eg* pyrazinyl) stabilise the low-spin state compared to their pyridyl ligand analogues.[5,78] The trend for electron-withdrawing *meta* substituents to promote high-spin states has been less studied, but is apparent in NMR data from a family of iron(II) podand complexes.[79] Interestingly, two families of iron(III) 5-substituted salicyl Schiff base complexes apparently show different behaviours, which either replicate[5,80] or oppose[81] the above trend observed for pyridyl ligand donors. That inconsistency has not been explained at the time of writing. Investigations of cobalt(II) pyridyl complexes have also been less conclusive,[82] perhaps because their spin-equilibria span a wider temperature range in solution.[83]

A very different example is provided by two sets of tetrahedral iron(II) spin-crossover complexes bearing phosphoramidate ligands, including **7**. Despite their *para* disposition, more electron-withdrawing R groups lower $T_{½}$ in **7**, corresponding to a negative linear free energy relationship between those parameters.[18] This can be rationalised because the sp^3-hybridised P atom prevents the phenyl substituents from conjugating with the P=N donor group. Thus, R groups have only a σ-inductive effect on the ligand field in this case.

Finally, attractive interactions between ligands sometimes influence metal spin states. An example is **8**, whose low-spin state is unexpected given the steric influence of its distal mesityl ligand substituents. Its phenyl-substituted analogue is indeed high-spin, as expected.[84] A computational study attributed this to attractive dispersion interactions involving the mesityl methyl groups, which sandwich the pyridyl ring of the other ligand in the complex. That is sufficient to stabilise the shorter Fe–N bonds in the low-spin molecule, which bring those substituents closer together.[85] A low-spin stabilisation in a stereochemically similar complex with distal 2,6-dichlorophenyl substituents may have a similar explanation.[86]

Conclusion

Many applications of base metal compounds depend on control of their spin state. On one hand, catalytic reactions[54,59,61,63] and light-harvesting dyes[41] both require compounds in the correct spin state for the mechanistic pathway or optical properties required by those applications. Alternatively, use of spin-state switching in chemosensor or materials applications requires a fine control of spin-crossover properties.[46] Spin-crossover compounds are a sensitive probe of the relationship between ligand design and metal spin state,[5] and recent work from our group and elsewhere has shed new light on these questions.

Notwithstanding a recent unexplained counter-example,[81] the concept that ligand substituents influence metal spin state depending on whether they can conjugate with the metal–ligand bonds seems to be widely applicable.[18,75-80] The effects are small energetically; the $T_{½}$ values in Figure 1 span a thermal energy range of *ca* 1.5 kJmol^{-1}. Therefore, it's unlikely an iron complex will be converted into a useful light-harvesting dye simply by decorating it with nitro groups.[41] However, a judicious choice of remote ligand substituents can tune the balance of spin state energies to optimise the charge-separation lifetime of a dye candidate;[41,66] shift the operating temperature of a switchable material;[87] or, moderate the reactivity or mechanism of a base metal catalyst.[53,61,65]

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 M. Weller, T. Overton, J. Rourke and F. Armstrong, *Inorganic Chemistry*, 7th Edn., Oxford University Press, Oxford, UK, 2018, p. 568-574 and 600-601.
2 C. K. Jørgensen, *Prog. Inorg. Chem.*, 1962, **4**, 73.
3 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, Amsterdam, 1984.
4 K. S. Kumar and M. Ruben, *Coord. Chem. Rev.*, 2017, **346**, 176; J. Zarembowitch, F. Varret, A. Hauser, J.-A. Real and K. Boukheddaden, *C. R. Chimie*, 2018, **21**, 1056; Z.-S. Yao, Z. Tang and J. Tao, *Chem. Commun.,* 2020, **56**, 2071.
5 M. A. Halcrow, *Crystals*, 2016, **6**, 58 and refs therein.
6 S. Amabilino and R. J. Deeth, *Inorg. Chem.*, 2017, **56**, 2602.
7 H. Imoto and A. Simon, *Inorg. Chem.*, 1982, **21***,* 308; P. Angaridis, F. A. Cotton, C. A. Murillo, D. Villagrán and X. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 5008.
8 E. K. Byrne, D. S. Richeson and K. H. Theopold, *J. Chem. Soc., Chem. Commun.*, 1986, 1491; D. Zanders, G. Bačić, D. Leckie, D. O. Odegbesan, J. Rawson, J. D. Masuda, A. Devi and S. T. Barry, *Angew. Chem., Int. Ed.*, doi: 10.1002/anie.202001518.
9 Q. Zhao, J.-H. Sim, Z. Zhang, H. Su, F. Han, Q. Zhang, B. Tian, Q. Xu, M.-J. Han, C.-G. Duan and J. F. Mitchell, *Phys. Rev. Mater.*, 2019, **3**, 063607.
10 L. Bucinsky, M. Breza, W.-T. Lee, A. K. Hickey, D. A. Dickie, I. Nieto, J. A. DeGayner, T. D. Harris, K. Meyer, J. Krzystek, A. Ozarowski, J. Nehrkorn, A. Schnegg, K. Holldack, R. H. Herber, J. Telser and J. M. Smith, *Inorg. Chem.*, 2017, **56**, 4751.
11 D. M. Jenkins, A. J. Di Bilio, M. J. Allen, T. A. Betley and J. C. Peters, *J. Am. Chem. Soc.*, 2002, **124**, 15336; P. Coburger, S. Demeshko, C. Rödl, E. Hey-Hawkins and R. Wolf, *Angew. Chem., Int. Ed.*, 2017, **56**, 15871.
12 See *eg* A. R. Hermes, R. J. Morris and G. S. Girolami, *Organometallics*, 1988, **7**, 237; D. M. Goedde, G. K. Windler and G. S. Girolami, *Inorg. Chem.*, 2007, **46**, 2814; Y.-F. Deng, T. Han, Z. Wang, Z. Ouyang, B. Yin, Z. Zheng, J. Krzystek and Y.-Z. Zheng, *Chem. Commun.*, 2015, **51**, 17688; C. H. Schiwek, V. Vasilenko, H. Wadepohl and L. H. Gade, *Chem. Commun.*, 2018, **54**, 9139.
13 See *eg* B. Gonzalez, J. Kouba, S. Yee, C. A. Reed, J. F. Kirner and W. R. Scheidt, *J. Am. Chem. Soc.* 1975, **97**, 3247; S. P. Sellers, B. J. Korte, J. P. Fitzgerald, W. M. Reiff and G. T. Yee, *J. Am. Chem. Soc.*, 1998, **120**, 466.
14 X. Wurzenberger, H. Piotrowski and P. Klüfers, *Angew. Chem., Int. Ed.*, 2011, **50**, 4974; S. A. Cantalupo, S. R. Fiedler, M. P. Shores, A. L. Rheingold and L. H. Doerrer, *Angew. Chem., Int. Ed.*, 2012, **51**, 1000; D. Pinkert, S. Demeshko, F. Schax, B. Braun, F. Meyer and C. Limberg, *Angew. Chem., Int. Ed.*, 2013, **52**, 5155; N. Manicke, S. Hoof, M. Keck, B. Braun-Cula, M. Feist and C. Limberg, *Inorg. Chem.*, 2017, **56**, 8554.
15 M. E. Pascualini, N. V. Di Russo, A. E. Thuijs, A. Ozarowski, S. A. Stoian, K. A. Abboud, G. Christou and A. S. Veige, *Chem. Sci.*,

2015, **6**, 608; M. E. Pascualini, A. Ozarowski, S. A. Stoian, N. V. Di Russo, A. E. Thuijs, K. A. Abboud, G. Christou and A. S. Veige, *Dalton Trans.*, 2015, **44**, 20207; B. M. Hakey, J. M. Darmon, Y. Zhang, J. L. Petersen and C. Milsmann, *Inorg. Chem.*, 2019, **58**, 1252.

16 Y. Matsumoto, T. Yamamoto, K. Nakano, H. Takatsu, T. Murakami, K. Hongo, R. Maezono, H. Ogino, D. Song, C. M. Brown, C. Tassel and H. Kageyama, *Angew. Chem., Int. Ed.*, 2019, **58**, 756.

17 D. M. Jenkins and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 7148; R. Travieso-Puente, J. O. P. Broekman, M.-C. Chang, S. Demeshko, F. Meyer and E. Otten, *J. Am. Chem. Soc.*, 2016, **138**, 5503.

18 H.-J. Lin, D. Siretanu, D. A. Dickie, D. Subedi, J. J. Scepaniak, D. Mitcov, R. Clérac and J. M. Smith, *J. Am. Chem. Soc.*, 2014, **136**, 13326; S. E. Creutz and J. C. Peters, *Inorg. Chem.*, 2016, **55**, 3894.

19 A. C. Bowman, C. Milsmann, E. Bill, Z. R. Turner, E. Lobkovsky, S. DeBeer, K. Wieghardt and P. J. Chirik, *J. Am. Chem. Soc.*, 2011, **133**, 17353.

20 K. V. Lamonova, E. S. Zhitlukhina, R. Yu. Babkin, S. M. Orel, S. G. Ovchinnikov and Y. G. Pashkevich, *J. Phys. Chem. A*, 2011, **115**, 13596.

21 T. Sakai, Y. Ohgo, T. Ikeue, M. Takahashi, M. Takeda and M. Nakamura, *J. Am. Chem. Soc.*, 2003, **125**, 13028; R.-J. Cheng, C.-W. Chao, Y.-P. Han, Y.-C. Chen and C.-H. Ting, *Chem. Commun.*, 2009, 2180.

22 Admixed high/intermediate spin states are sometimes invoked to explain the electronic and magnetic properties of iron porphyrin complexes. R. Weiss, A. Gold and J. Terner, *Chem. Rev.*, 2006, **106**, 2550.

23 N. Schuth, S. Mebs, D. Huwald, P. Wrzolek, M. Schwalbe, A. Hemschemeier and M. Haum, *Proc. Natl. Acad. Sci. USA*, 2017, **114**, 8556 and 2017, **114**, E8129 (correction).

24 See *eg* Y. Liu, L. Luo, J. Xiao, L. Wang, Y. Song, J. Qu, Y. Luo and L. Deng, *Inorg. Chem.*, 2015, **54**, 4752; C. V. Thompson, H. D. Arman and Z. J. J. Tonzetich, *Organometallics*, 2017, **36**, 1795; C. Ott, H. Wadepohl, M. Enders and L. H. Gade, *J. Am. Chem. Soc.*, 2018, **140**, 17413; C. V. Thompson, H. D. Arman and Z. J. J. Tonzetich, *Organometallics*, 2019, **38**, 2979.

25 S. Sproules and K. Wieghardt, *Coord. Chem. Rev.*, 2011, **255**, 837.

26 See *eg* T. Niwa and M. Nakada, *J. Am. Chem. Soc.*, 2012, **134**, 1353; J. S. Anderson, M.-E. Moret and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 534; A. C. Bowman, A. M. Tondreau, E. Lobkovsky, G. W. Margulieux and P. J. Chirik, *Inorg. Chem.*, 2018, **57**, 9634; L. Wang, M. Zlatar, F. Vlahovic, S. Demeshko, C. Philouze, F. Molton, M. Gennari, F. Meyer, C. Duboc and M. Gruden, *Chem. Eur. J.*, 2018, **24**, 5091; M. R. Anneser, G. R. Elpitiya, J. Townsend, E. J. Johnson, X. B. Powers, J. F. DeJesus, K. D. Vogiatzis and D. M. Jenkins, *Angew. Chem., Int. Ed.*, 2019, **58**, 8115.

27 J. Hasserodt, J. L. Kolanowski and F. Touti, *Angew. Chem., Int. Ed.*, 2014, **53**, 60; I.-R. Jeon, J. G. Park, C. R. Haney and T. D. Harris, *Chem. Sci.*, 2014, **5**, 2461.

28 M. Dommaschk, M. Peters, F. Gutzeit, C. Schütt, C. Näther, F. D. Sönnichsen, S. Tiwari, C. Riedel, S. Boretius and R. Herges, *J. Am. Chem. Soc.*, 2015, **137**, 7552.

29 A. I. Gaudette, A. E. Thorarinsdottir and T. D. Harris, *Chem. Commun.,* 2017, **53**, 12962.

30 J. S. Costa, *C. R. Chimie*, 2018, **21**, 1121; J. A. Wolny, V. Schünemann, Z. Németh and G. Vankó *C. R. Chimie*, 2018, **21**, 1152.

31 Z. Ni, A. M. McDaniel and M. P. Shores, *Chem. Sci.*, 2010, **1**, 615.

32 M. C. Young, E. Liew and R. J. Hooley, *Chem. Commun.,* 2014, **50**, 5043.

33 O. S. Wenger, *Chem. Rev.*, 2013, **113**, 3686; E. Li, K. Jie, M. Liu, X. Sheng, W. Zhu and F. Huang, *Chem. Soc. Rev.*, 2020, **49**, 1517.

34 See *eg* C. Bartual-Murgui, C. Codina, O. Roubeau and G. Aromí, *Chem. Eur. J.*, 2016, **22**, 12767; W.-B. Chen, Y.-C. Chen, M. Yang, M.-L. Tong and W. Dong, *Dalton Trans.*, 2018, **47**, 4307; A. Tissot, X. Kesse, S. Giannopoulou, I. Stenger, L. Binet, E. Rivière and C. Serre, *Chem. Commun.,* 2019, **55**, 194; K. Kagesawa, Y. Ichikawa, H. Iguchi, B. K. Breedlove, Z. Li, M. Yamashita, A. Okazawa, W. Kosaka and H. Miyasaka, *Chem. Lett.*, 2019, **48**, 1221.

35 See *eg* J. S. Costa, S. Rodríguez-Jiménez, G. A. Craig, B. Barth, C. M. Beavers, S. J. Teat and G. Aromí, *J. Am. Chem. Soc.*, 2014, **136**, 3869; D. Gentili, N. Demitri, B. Schäfer, F. Liscio, I. Bergenti, G. Ruani, M. Ruben and M. Cavallini, *J. Mater. Chem. C,* 2015, **3**, 7836; R. G. Miller and S. Brooker, *Chem. Sci.*, 2016, **7**, 2501; E. Resines-Urien, E. Burzurí, E. Fernandez-Bartolome, M. A. G. García-Tuñón, P. de la Presa, R. Poloni, S. J. Teat and J. S. Costa, *Chem. Sci.*, 2019, **10**, 6612.

36 Z.-P. Ni, J.-L. Liu, M. N. Hoque, W. Liu, J.-Y. Li, Y.-C. Chen and M.-L. Tong, *Coord. Chem. Rev.*, 2017, **335**, 28.

37 Y. Guo, S. Xue, M. M. Dîrtu and Y. Garcia, *J. Mater. Chem. C,* 2018, **6**, 3895.

38 D. A. Reed, B. K. Keitz, J. Oktawiec, J. A. Mason, T. Runčevski, D. J. Xiao, L. E. Darago, V. Crocellà, S. Bordiga and J. R. Long, *Nature*, 2017, **550**, 96; T. Shiga, R. Saiki, L. Akiyama, R. Kumai, D. Natke, F. Renz, J. M. Cameron, G. N. Newton and H. Oshio, *Angew. Chem., Int. Ed.*, 2019, **58**, 5658.

39 T. C. B. Harlang, Y. Liu, O. Gordivska, L. A. Fredin, C. S. Ponseca jr, P. Huang, P. Chábera, K. S. Kjaer, H. Mateos, J. Uhlig, R. Lomoth, R. Wallenberg, S. Styring, P. Persson, V. Sundström and K. Wärnmark, *Nature Chem.*, 2015, **7**, 883; J. D. Braun, I. B. Lozada, C. Kolodziej, C. Burda, K. M. E. Newman, J. van Lierop, R. L. Davis and D. E. Herbert, *Nature Chem.*, 2019, **11**, 1144.

40 K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K.-E. Bergquist, L. Häggström, T. Ericsson, L. Lindh, A. Yartsev, S. Styring, P. Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Lomoth and K. Wärnmark, *Science*, 2019, **363**, 249.

41 O. S. Wenger, *Chem. Eur. J.*, 2019, **25**, 6043; C. Förster and K. Heinze, *Chem. Soc. Rev.*, 2020, **49**, 1057.

42 M. Mikolasek, M. D. Manrique-Juarez, H. J. Shepherd, K. Ridier, 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; S. P. Vallone, A. N. Tantillo, A. M. dos Santos, J. Molaison, R. Kulmaczewski, A. Chapoy, P. Ahmadi, M. A. Halcrow and K. G. Sandeman, *Adv. Mater.*, 2019, **31**, 1807334.

43 V. Jornet-Mollá, Y. Duan, C. Giménez-Saiz, Y.-Y. Tang, P.-F. Li, F. M. Romero and R.-G. Xiong, *Angew. Chem., Int. Ed.*, 2017, **56**, 14052; R. Akiyoshi, Y. Hirota, D. Kosumi, M. Tsutsumi, M. Nakamura, L. F. Lindoy and S. Hayami, *Chem. Sci.*, 2019, **10**, 5843.

44 See *eg* C. Lochenie, K. Schötz, F. Panzer, H. Kurz, B. Maier, F. Puchtler, S. Agarwal, A. Köhler and B. Weber, *J. Am. Chem. Soc.*, 2018, **140**, 700; J.-L. Wang, Q. Liu, Y.-S. Meng, X. Liu, H. Zheng, Q. Shi, C.-Y. Duan and T. Liu, *Chem. Sci.*, 2018, **9**, 2892; J.-Y. Ge, Z. Chen, L. Zhang, X. Liang, J. Su, M. Kurmoo, and J.-L. Zuo, *Angew. Chem., Int. Ed.*, 2019, **58**, 8789.

45 See *eg* H. Phan, S. M. Benjamin, E. Steven, J. S. Brooks and M. Shatruk, *Angew. Chem., Int. Ed.*, 2015, **54**, 823; H.-Y. Wang, J.-Y. Ge, C. Hua, C.-Q. Jiao, Y. Wu, C. F. Leong, D. M. D'Alessandro, T. Liu and J.-L. Zuo*, Angew. Chem., Int. Ed.*, 2017, **56**, 5465; A. V. Kazakova, A. V. Tiunova, D. V. Korchagin, G. V. Shilov, E. B. Yagubskii, V. N. Zverev, S. C. Yang, J.-Y. Lin, J.-F. Lee, O. V. Maximova and A. N. Vasiliev, *Chem. Eur. J.*, 2019, **25**, 10204.

46 S. Rat, M. Piedrahita-Bello, L. Salmon, G. Molnár, P. Demont and A. Bousseksou, *Adv. Mater.*, 2018, **30**, 17003862.

47 L. Ben-Dor and Y. Marcus, *J. Chem. Educ.*, 1998, **75**, 1458.

48 A. Köbke, F. Gutzeit , F. Röhricht , A. Schlimm, J. Grunwald, F. Tuczek, M. Studniarek, D. Longo, F. Choueikani, E. Otero, P. Ohresser, S. Rohlf, S. Johannsen, F. Diekmann, K. Rossnagel, A. Weismann, T. Jasper-Toennies, C. Näther, R. Herges, R. Berndt and M. Gruber, *Nature Nanotech.*, 2020, **15**, 18.

49 See *eg* C. Schütt, G. Heitmann, T. Wendler, B. Krahwinkel and R. Herges, *J. Org. Chem.*, 2016, **81**, 1206; M. Klass, J. Krahmer, C. Näther and F. Tuczek, *Dalton Trans.*, 2018, **47**, 1261; H. Kurz, C. Lochenie, K. G. Wagner, S. Schneider, M. Karg and B. Weber, *Chem. Eur. J.*, 2018, **24**, 5100.

50 R. Nowak, E. A. Prasetyanto, L. De Cola, B. Bojer, R. Siegel, J. Senker, E. Rössler and B. Weber, *Chem. Commun.,* 2017, **53**, 971.

51 H. Ohtaki and T. Radnai, *Chem. Rev.*, 1993, **93**, 1157.

52 E. Andris, R. Navrátil, J. Jašík, G. Sabenya, M. Costas, M. Srnec and J. Roithová, *Angew. Chem., Int. Ed.*, 2017, **56**, 14057.

53 M. Guo, T. Corona, K. Ray and W. Nam, *ACS Cent. Sci.*, 2019, **5**, 13.

54 M. Puri and L. Que jr., *Acc. Chem. Res.*, 2015, **48**, 2443.

55 E. Andris, J. Jašík, L. Gómez, M. Costas and J. Roithová, *Angew. Chem. Int. Ed.*, 2016, **55**, 3637; T. Terencio, E. Andris, I. Gamba, M. Srnec, M. Costas and J. Roithová, *J. Am. Soc. Mass Spectrom.*, 2019, **30**, 1923.

56 N. Y. Lee, D. Mandal, S. H. Bae, M. S. Seo, Y.-M. Lee, S. Shaik, K.-B. Cho and W. Nam, *Chem. Sci.,* 2017, **8**, 5460; R. Singh, G. Ganguly, S. O. Malinkin, S. Demeshko, F. Meyer, E. Nordlander and T. K. Paine, *Inorg. Chem.*, 2019, **58**, 1862.

57 S. Banerjee, W. Rasheed, R. Fan, A. Draksharapu, W. N. Oloo, Y. Guo and L. Que jr., *Chem. Eur. J.*, 2019, **25**, 9608.

58 P. Chirik and R. Morris, *Acc. Chem. Res.*, 2015, **48**, 2495; M. Beller, *Chem. Rev.*, 2019, **119**, 2089.

59 G. A. Filonenko, R. van Putten, E. J. M. Hensen and E. A. Pidko, *Chem. Soc. Rev.,* 2018, **47**, 1459; D. Wei and C. Darcel, *Chem. Rev.*, 2019, **119**, 2550.

60 H. Nagashima, *Bull. Chem. Soc. Jpn*. 2017, **90**, 761.

61 P. L. Holland, *Acc. Chem. Res.*, 2015, **48**, 1696.

62 T. Zell and D. Milstein, *Acc. Chem. Res.*, 2015, **48**, 1979; A. Fürstner, *ACS Cent. Sci.*, 2016, **2**, 778.

63 M. L. Neidig, S. H. Carpenter, D. J. Curran, J. C. DeMuth, V. E. Fleischauer, T. E. Iannuzzi, P. G. N. Neate, J. D. Sears and N. J. Wolford, *Acc. Chem. Res.*, 2019, **52**, 140.

64 A. K. Vitek, A. K. Leone, A. J. McNeil and P. M. Zimmerman, *ACS Catal.*, 2018, **8**, 3655.

65 M. P. Shaver, L. E. N. Allan, H S. Rzepa and V. C. Gibson, *Angew. Chem., Int. Ed.*, 2006, **45**, 1241; B. Minaev, A. Baryshnikova and W.-H. Sun, *J. Organomet. Chem.*, 2016, **811**, 48; M. A. Ortuño, B. Dereli, K. R. Delle Chiaie, A. B. Biernesser, M. Qi, J. A. Byers and C. J. Cramer, *Inorg. Chem.*, 2018, **57**, 2064.

66 S. M. Fatur, S. G. Shepard, R. F. Higgins, M. P. Shores and N. H. Damrauer, *J. Am. Chem. Soc.*, 2017, **139**, 4493.

67 Other recent examples: C. Bartual-Murgui, S. Vela, O. Roubeau and G. Aromí, *Dalton Trans.*, 2016, **45**, 14058; C. Bartual-Murgui, S. Vela, M. Darawsheh, R. Diego, S. J. Teat, O. Roubeau and G. Aromí, *Inorg. Chem. Front.*, 2017, **4**, 1374; H. Petzold, P. Djomgoue, G. Hörner, S. Heider, C. Lochenie, B. Weber, T. Rüffer and D. Schaarschmidt, *Dalton Trans.*, 2017, **46**, 6218; Y. Nelyubina, A. Polezhaev, A. Pavlov, D. Aleshin, S. Savkina, N. Efimov, T. Aliev and V. Novikov, *Magnetochemistry*, 2018, **4**, 46.

68 H. Phan, J. J. Hrudka, D. Igimbayeva, L. M. L. Daku and M. Shatruk, *J. Am. Chem. Soc.*, 2017, **139**, 6437; J. J. Hrudka, H. Phan, J. Lengyel, A. Yu. Rogachev and M. Shatruk, *Inorg. Chem.*, 2018, **57**, 5183.

69 I. Capel Berdiell, R. Kulmaczewski and M. A. Halcrow, *Inorg. Chem.*, 2017, **56**, 8817; J. N. McPherson, T. E. Elton and S. B. Colbran, *Inorg. Chem.*, 2018, **57**, 12312.

70 S. Alvarez, *Chem. Rev.*, 2015, **115**, 13447.

71 M. A. Halcrow, *Chem. Soc. Rev.*, 2011, **40**, 4119; G. A. Craig, O. Roubeau and G. Aromí, *Coord. Chem. Rev.*, 2014, **269**, 13; L. J. Kershaw Cook, R. Mohammed, G. Sherborne, T. D. Roberts, S. Alvarez and M. A. Halcrow, *Coord. Chem. Rev.*, 2015, **289–290**, 2.

72 K. E. Burrows, S. E. McGrath, R. Kulmaczewski, O. Cespedes, S. A. Barrett and M. A. Halcrow, *Chem. Eur. J.*, 2017, **23**, 9067.

73 *Rac* and *meso* isomers of chiral iron complexes often exhibit different spin states in the solid state. However, since they cannot be isostructural, their differences are also influenced by their crystal packing. That complicates attempts to discern the effect of chirality on the molecular ligand field from solid state data. L.-F. Qin, C.-Y. Pang, W.-K. Han, F.-L. Zhang, L. Tian, Z.-G. Gu, X. Ren and Z. Li, *Dalton Trans.*, 2016, **45**, 7340; C. Bartual-Murgui, L. Piñeiro-López, F. J. Valverde-Muñoz, M. C. Muñoz, M. Seredyuk and J. A. Real, *Inorg. Chem.*, 2017, **56**, 13535; W.-Q. Gao, Y.-S. Meng, C.-H. Liu, Y. Pan, T. Liu and Y.-Y. Zhu, *Dalton Trans.*, 2019, **48**, 6323; T.-T. Ma, X.-P. Sun, Z.-S. Yao and J. Tao, *Inorg. Chem. Front.*, 2020, **7**, 1196.

74 As with the optically active crystals in the previous footnote, solution phase data are the best measure of the interplay between ligand design and spin states at the molecular level.[5]

75 L. J. Kershaw Cook, R. Kulmaczewski, R. Mohammed, S. Dudley, S. A. Barrett, M. A. Little, R. J. Deeth and M. A. Halcrow, *Angew. Chem., Int. Ed.*, 2016, **55**, 4327.

76 A. Kimura and T. Ishida, *ACS Omega*, 2018, **3**, 6737.

77 J.-F. Létard, C. Carbonera, J. A. Real, S. Kawata and S. Kaizaki, *Chem. Eur. J.*, 2009, **15**, 4146; I. Prat, A. Company, T. Corona, T. Parella, X. Ribas and M. Costas, *Inorg. Chem.*, 2013, **52**, 9229; A. Kimura and T. Ishida, *Inorganics*, 2017, **5**, 52; K. S. Kumar, S. Vela, B. Heinrich, N. Suryadevara, L. Karmazin, C. Bailly and M. Ruben, *Dalton Trans.*, 2020, **49**, 1022.

78 H. L. C. Feltham, M. G. Cowan, J. A. Kitchen, G. N. L. Jameson and S. Brooker, *Supramol. Chem.*, 2018, **30**, 296.

79 N. Struch, F. Topić, G. Schnakenburg, K. Rissanen and A. Lützen, *Inorg. Chem.*, 2018, **57**, 241.

80 M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, 1976, **98**, 4824; T. Zhu, C.-H. Su, D. Schaeper, B. K. Lemke, L. J. Wilson and K. M. Kadish, *Inorg. Chem.*, 1984, **23**, 4345.

81 B. Dey, A. Mondal and S. Konar, *Chem. Asian J.*, 2020, **15**, 1709. See also R. H. Petty, E. V. Dose, M. F. Tweedle and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 1064.

82 J. Chambers, B. Eaves, D. Parker, R. Claxton, P. S. Ray and S. J. Slattery, *Inorg. Chim. Acta*, 2006, **359**, 2400; J. N. McPherson, R. W. Hogue, F. S. Akogun, L. Bondì, E. T. Luis, J. R. Price, A. L. Garden, S. Brooker and S. B. Colbran, *Inorg. Chem.*, 2019, **58**, 2218.

83 M. G. Simmons and L. J. Wilson, *Inorg. Chem.*, 1977, **16**, 126; M. Enamullah, M. Hasegawa, Y. Fukuda, W. Linert and T. Hoshi, *Bull. Chem. Soc. Jpn.,* 2002, **75**, 2449; A. A. Pavlov, G. L. Denisov, M. A. Kiskin, Y. V. Nelyubina and V. V. Novikov, *Inorg. Chem.*, 2017, **56**, 14759.

84 J. M. Holland, S. A. Barrett, C. A. Kilner and M. A. Halcrow, *Inorg. Chem. Commun.*, 2002, **5**, 328.

85 R. J. Deeth, M. A. Halcrow, L. J. Kershaw Cook and P. R. Raithby, *Chem. Eur. J.*, 2018, **24**, 5204.

86 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.

87 M. A. Halcrow, I. Capel Berdiell, C. M. Pask and R. Kulmaczewski, *Inorg. Chem.*, 2019, **58**, 9811.