COMMUNICATION www.rsc.org/chemcomm | ChemComm

Iron(II) complexes with a terpyridine embrace packing motif show remarkably consistent cooperative spin-transitions†

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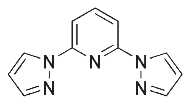
Received (in Cambridge, UK) 15th September 2006, Accepted 26th October 2006
First published as an Advance Article on the web 14th November 2006
DOI: 10.1039/b613402e

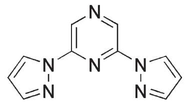
Six structurally related iron(II) complexes show remarkably similar abrupt thermal spin-transitions.

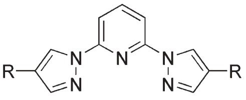
Metal–organic spin-crossover materials are of great current interest,[1] owing to their potential applications in displays, or optical or dielectric memory devices.[2] Most of these applications require materials showing spin-transitions that occur abruptly with a hysteresis loop, centred about room temperature.[3] The cooperativity of a thermal spin-transition (that is, whether it occurs gradually or abruptly, and with or without hysteresis) is a function of the geometry and strength of intermolecular contacts between spin centres in the material.[4] The *de novo* design of such materials is therefore a question of crystal engineering. This is a field still in its early development,[5] and recent studies have concluded that correlation of structure with function in molecular spin-crossover compounds is not presently feasible.[6] We describe here a series of six complex salts showing similar, but non-identical, crystal packing and whose spin-transitions are remarkably consistent in form. Crystal engineering of cooperativity into functional molecular solids with this structure type is a real possibility.

We have been studying the spin-transitions of iron(II) complexes of 2,6-di(pyrazol-1-yl)pyridine (L^1), 2,6-di(pyrazol-1-yl)pyrazine (L^2), and their derivatives substituted at the pyrazole or pyridine rings.[7] As a continuation of this work, we have investigated the iron complexes of derivatives of L^1 halogenated at the 4-positions.[8] Variable temperature magnetic measurements from ground polycrystalline samples of $[Fe(L^3)_2][BF_4]_2$ and $[Fe(L^4)_2][BF_4]_2$‡ showed that each undergoes an abrupt thermal spin-transition upon cooling (Fig. 1). For $[Fe(L^3)_2][BF_4]_2$, this takes place at 202 K, with a narrow but reproducible hysteresis loop of 3 K, and proceeds to completeness. For $[Fe(L^4)_2][BF_4]_2$, the transition takes place at 253 K with a 2 K hysteresis loop. This transition was only 85% complete at 250 K, with the remaining iron content converting slowly as the temperature was lowered further.

Single crystals of $[Fe(L^3)_2][BF_4]_2$ and $[Fe(L^4)_2][BF_4]_2$ adopt the tetragonal space group $P\bar{4}2_1c$ at 300 K, in which the complex molecule has crystallographic S_4 symmetry and the unique anion site is disordered about a C_2 axis (Fig. 2).§ Cooling $[Fe(L^3)_2][BF_4]_2$ to 204 ± 1 K resulted in a colour change from yellow to brown, consistent with a high → low-spin transition[9–12] and in agreement with the magnetic data. Additional structure determinations at 220 and 202 K showed that $[Fe(L^3)_2][BF_4]_2$ undergoes a crystallographic phase change during spin-crossover, to the monoclinic space group $P2_1$. In this phase all the internal symmetry of the dication and disordered anions is lost. Crystals of $[Fe(L^4)_2][BF_4]_2$ also remain in the tetragonal space group until undergoing spin-crossover at 255 ± 1 K. Crystal decomposition prevented a full data collection of the low-spin form of $[Fe(L^4)_2][BF_4]_2$, but its unit cell implies that it also adopts the $P2_1$ structure [a = 9.803(11), b = 9.822(18), c = 16.41(2) Å, β = 90.26(13)°, V = 1580(2) Å^3 at 250 K]. The Fe–N bond lengths in all the crystal structures referred to above are consistent with the iron centres being purely in the expected high-spin or low-spin state (ESI†).[13]


L^1


L^2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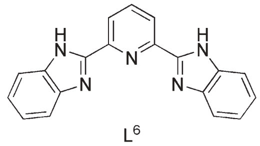
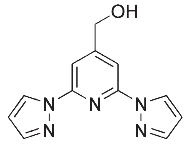
R = CH_3, L^5


L^6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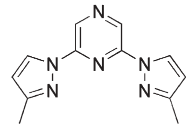
L^8

The similarity of the spin-transitions in $[Fe(L^3)_2][BF_4]_2$ and $[Fe(L^4)_2][BF_4]_2$ to those of four other compounds we have previously published is striking (Fig. 1). Although the temperatures of the transitions vary, all six compounds show highly abrupt thermal spin-crossover with a small hysteresis width of 2 or 3 K. Notably, all these compounds crystallise in the series of three different space groups listed in Table 1. Their packing is dominated by face-to-face π–π interactions, and edge-to-face C–H···π or C–X···π (X = Cl or Br) contacts, between pyrazole groups of neighbouring molecules. These interactions lead to four-fold layers of complex dications parallel to the (001) crystal plane, with adjacent layers associating weakly through van der Waals contacts (Fig. 3). This structure type is common in metal terpyridyl complexes, and has been dubbed a "terpyridine embrace".[14] Different versions of this structure have been discussed, which differ according to the internal symmetry within the layers, and the symmetry relating adjacent layers stacked along the

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† Electronic supplementary information (ESI) available: Selected bond lengths and angles, and additional figures for the crystal structures in this work. See DOI: 10.1039/b613402e

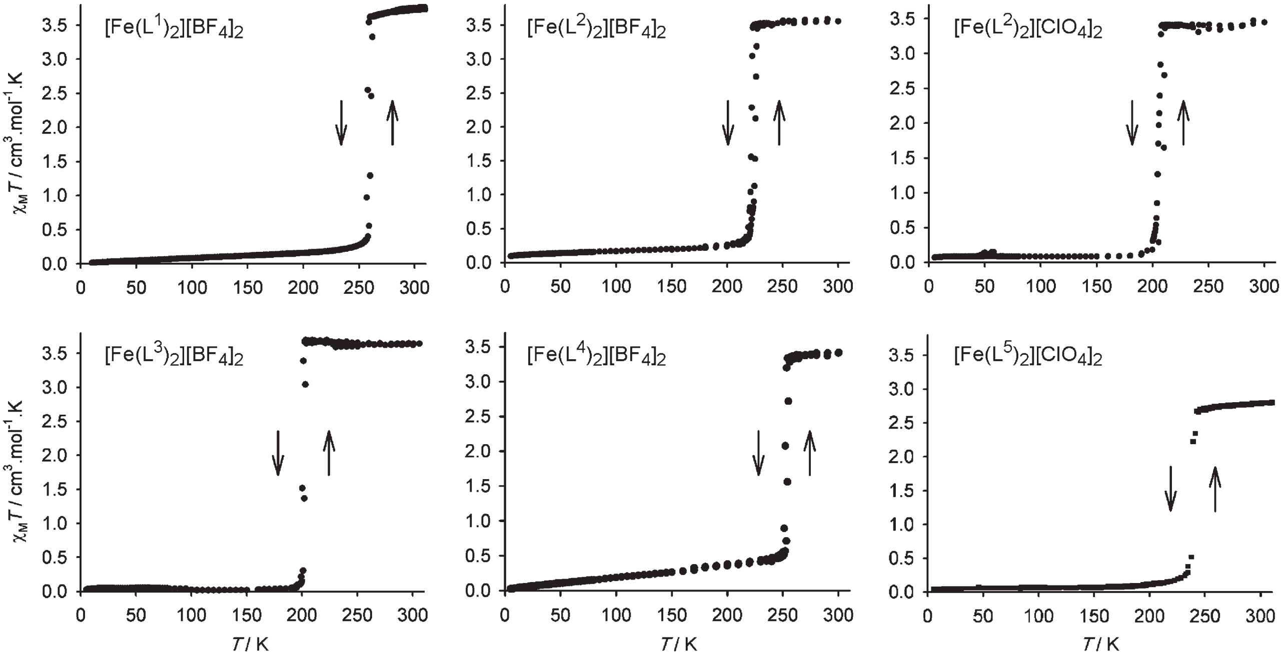

Fig. 1 Variable temperature magnetic behaviour of the compounds discussed in this work. The low high-temperature value of $\chi_M T$ for $[Fe(L^5)_2][ClO_4]_2$ reflects the presence of a minor low-spin contaminant phase in this material.[12]

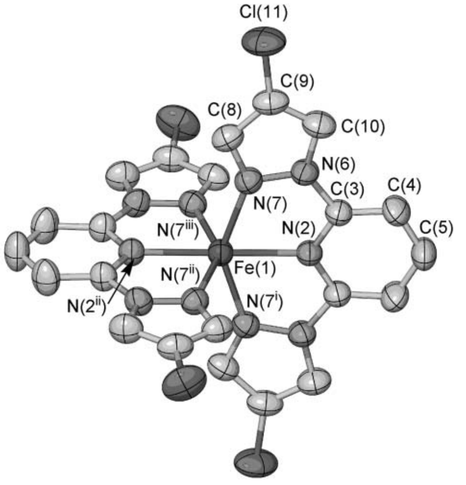

Fig. 2 View of the complex dication in the tetragonal phase of $[Fe(L^3)_2][BF_4]_2$ at 300 K. All H atoms have been removed for clarity, and thermal ellipsoids are at the 50% probability level. Symmetry codes: (i) $-x, 2-y, z$; (ii) $-1+y, 1-x, 2-z$; (iii) $1-y, 1+x, 2-z$.

crystallographic *c* direction.[15] In the compounds in Table 1, neighbouring cation layers are related by 2_1 symmetry.

Despite their similarities, the structural chemistry of spin-crossover in most of the compounds in Fig. 1 is different. High-spin $[Fe(L^1)_2][BF_4]_2$[9] and $[Fe(L^2)_2][ClO_4]_2$[10,11] adopt the $P2_1$ space group, with one molecule in their asymmetric unit (*i.e.* $Z = 2$). While the first of these compounds retains this structure following spin-crossover, $[Fe(L^2)_2][ClO_4]_2$ exhibits the same space-group in its low-spin form but with a doubled unit-cell ($Z = 4$).[11] High-spin $[Fe(L^2)_2][BF_4]_2$ is isostructural with low-spin $[Fe(L^2)_2][ClO_4]_2$, but undergoes another crystallographic phase-change in its low-spin state, possibly involving a further unit cell expansion.[10] The final three compounds in Table 1 all adopt the $P\bar{4}2_1c$ space-group in their high-spin state, and undergo crystallographic phase changes to either $P2_1$ or $P2_12_12_1$[12] in their low-spin structures. Comparison of Fig. 1 and Table 1 shows that the different space groups exhibited by these compounds, and the presence or absence of a crystallographic phase change, has no effect on the form of their thermal spin-crossover.

Table 1 Spin-transition temperatures and associated structural changes for the compounds in this work

	$T_{1/2}\downarrow$/K	$T_{1/2}\uparrow$/K	HS space group	LS space group
$[Fe(L^1)_2][BF_4]_2$[a]	258	261	$P2_1$ ($Z = 2$)	$P2_1$ ($Z = 2$)
$[Fe(L^2)_2][BF_4]_2$[b]	218	221	$P2_1$ ($Z = 4$)	$P2_1$ ($Z = 6$)[d]
$[Fe(L^2)_2][ClO_4]_2$[b]	203	206	$P2_1$ ($Z = 2$)	$P2_1$ ($Z = 4$)
$[Fe(L^3)_2][BF_4]_2$	200	203	$P\bar{4}2_1c$	$P2_1$ ($Z = 2$)
$[Fe(L^4)_2][BF_4]_2$	252	254	$P\bar{4}2_1c$	$P2_1$ ($Z = 2$)[d]
$[Fe(L^5)_2][ClO_4]_2$[c]	231	234	$P\bar{4}2_1c$	$P2_12_12_1$

[a] Ref. 9. [b] Ref. 10 and 11. [c] Ref. 12. [d] Tentative—from a preliminary unit-cell measurement only. See text for details.

The are four other series of complexes of tris-heterocyclic N-donor ligands, that adopt terpyridine embrace structures and undergo thermal spin-crossover. First is $[Fe(L^6)_2][ClO_4]_2\cdot \frac{1}{4}H_2O$, whose spin-transition occurs abruptly about 403 K with a 12 K hysteresis loop.[16] The larger hysteresis in its spin-crossover may reflect the more extensive π–π stacking within its four-fold layers mediated by the large benzimidazole arms. Second, is $[Fe(L^7)_2]X_2$ ($X^- = BF_4^-$ and ClO_4^-), whose spin-crossover is still relatively sharp but clearly less cooperative than those in Table 1.[12,17] Importantly, the cations and anions in these compounds are linked by strong O–H···Y (Y = O or F) hydrogen bonds, and spin-crossover is accompanied by a crystallographic ordering of both anions and ligand CH_2OH groups. It is reasonable that the coupling of structural changes in the cation and anion sites should perturb intermolecular cooperativity in these materials. Third, is

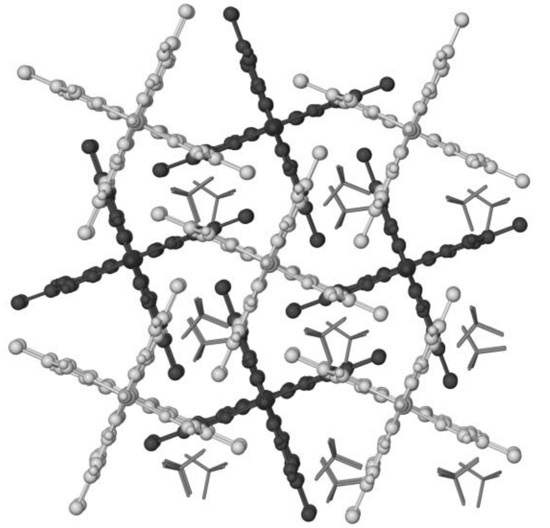

Fig. 3 Partial packing diagram of the tetragonal phase of $[Fe(L^3)_2][BF_4]_2$ at 300 K. All atoms have arbitrary radii, and alternating layers of π–π stacked molecules are shown in pale and dark coloration. Only one disorder orientation at each anion site is shown. The view is parallel to the (001) crystal plane, with the [110] vector vertical.

$[Fe(L^8)_2]X_2$ ($X^- = BF_4^-$ and ClO_4^-), whose spin-crossover shows a discontinuity at 50% conversion that is controlled by a change in anion disorder.[10,18] The packing geometry in these compounds resembles a known terpyridine embrace structure type. However, the steric bulk of the L^8 methyl groups pushes neighbouring molecules in the four-fold cation layers apart, so that no face-to-face π–π interactions can form.[18] Hence cooperativity between molecules in each terpyridine embrace layer is reduced, and anion-mediated cooperativity becomes dominant. Finally, several salts of $[Co(terpy)_2]^{2+}$ undergo thermal spin-transitions, that are much more gradual than the iron(II) complexes discussed here.[19] Poor cooperativity is typical of cobalt(II) spin-transition compounds, and reflects the smaller Co–N bond contraction associated with a $S = 3/2 \rightarrow 1/2$ spin-transition, compared to $S = 2 \rightarrow 0$ in iron(II) compounds. This leads to smaller structural rearrangements accompanying spin-crossover in cobalt(II).[13]

In conclusion, the compounds in Fig. 1 strongly imply that a terpyridine embrace packing motif reliably gives rise to a particular degree of cooperativity in iron(II) spin-crossover compounds, all other things being equal. Iron(II) complexes of L^6–L^8, and $[Co(terpy)_2]^{2+}$ salts, also adopt the terpyridine embrace and show different degrees of cooperativity in their spin-transitions. However, in every case those differences can be grossly correlated with particular elements of their structural chemistry (stronger or weaker intralayer π–π stacking, strong cation···anion hydrogen bonding, or smaller changes in cation size between the spin states). This robust structure type, which can form even in the presence of competing supramolecular functionality,[17,20] represents an ideal model system for quantification of the interplay between structure and cooperativity. It also has exciting potential for the rational engineering of bulk cooperativity into discrete molecular materials.

The authors thank Dr H. J. Blythe (University of Sheffield) for the magnetic susceptibility data, and the EPSRC for funding.

Notes and references

‡ Analytical data. For $[Fe(L^3)_2][BF_4]_2$. Found: C, 34.0; H, 1.80; N, 17.5%. Calcd for $C_{22}H_{14}B_2Cl_4F_8FeN_{10}$: C, 33.5; H, 1.79; N, 17.7%. For $[Fe(L^4)_2][BF_4]_2$. Found: C, 27.3; H, 1.50; N, 14.6%. Calcd for $C_{22}H_{14}B_2Br_4F_8FeN_{10}$: C, 27.3; H, 1.46; N, 14.5%.

§ Crystal data for $[Fe(L^3)_2][BF_4]_2$, $C_{22}H_{14}B_2Cl_4F_8FeN_{10}$, $M_r = 789.70$. At 300 K: tetragonal, $P\bar{4}2_1c$, $a = 9.5613(1)$, $c = 17.3177(3)$ Å, $V = 1583.16(4)$ Å^3, $Z = 2$, μ(Mo-Kα) = 0.895 mm^{-1}, 24687 measured reflections, 1824 independent, $R_{int} = 0.043$; $R(F) = 0.042$, $wR(F^2) = 0.121$, Flack parameter 0.00(3). At 220 K: tetragonal, $P\bar{4}2_1c$, $a = 9.5410(3)$, $c = 17.1024(6)$ Å, $V = 1556.84(9)$ Å^3, $Z = 2$, μ(Mo-Kα) = 0.910 mm^{-1}, 23329 measured reflections, 1814 independent, $R_{int} = 0.108$; $R(F) = 0.057$, $wR(F^2) = 0.161$, Flack parameter 0.03(5). At 202 K: monoclinic, $P2_1$, $a = 9.6268(3)$, $b = 9.6508(3)$, $c = 16.5051(5)$ Å, $\beta = 90.7285(12)°$, $V = 1533.30(8)$ Å^3, $Z = 2$, μ(Mo-Kα) = 0.924 mm^{-1}, 21495 measured reflections, 6726 independent, $R_{int} = 0.068$; $R(F) = 0.074$, $wR(F^2) = 0.207$, Flack parameter 0.13(3). Different crystals were used for these three data sets. The crystal used at 202 K was a racemic twin, while the other two were optically pure but of opposite handedness. The asymmetric unit at 300 and 220 K contains ¼ of a complex dication, with Fe(1) occupying the S_4 site [0, 1, 1] and N(2) and C(5) lying on the C_2 axis [0, 1, z]; and, half a BF_4^- anion that is disordered about the C_2 axis [0, ½, z] and was refined over two environments. At 202 K the asymmetric unit contains one complex dication and two anions, all on general positions. Both anions were disordered over three sites. Refined restraints were applied to the B–F and F···F distances in each partial anion site at all temperatures.

Crystal data for $[Fe(L^4)_2][BF_4]_2$, $C_{22}H_{14}B_2Br_4F_8FeN_{10}$, $M_r = 967.54$. At 300 K: tetragonal, $P\bar{4}2_1c$, $a = 9.7615(1)$, $c = 17.2273(3)$ Å, $V = 1641.54(4)$ Å^3, $Z = 2$, μ(Mo-Kα) = 5.406 mm^{-1}, 35262 measured reflections, 1884 independent, $R_{int} = 0.104$; $R(F) = 0.036$, $wR(F^2) = 0.092$, Flack parameter 0.199(18). The crystal was a racemic twin. This compound is isostructural with the high-spin form of $[Fe(L^3)_2][BF_4]_2$, shows the same anion disorder and was refined in the same way.

CCDC 614634–614637. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613402e

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