

The Influence of Ligand Conformation on the Thermal Spin Transitions in Iron(III) Saltrien Complexes

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Electronic Supplementary Information

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Table S4 Structural parameters for iron(III) complexes of hexadentate saltrien-type ligands.

Table S5 Structural changes during spin-crossover for iron(III) complexes of hexadentate saltrien-type ligands.

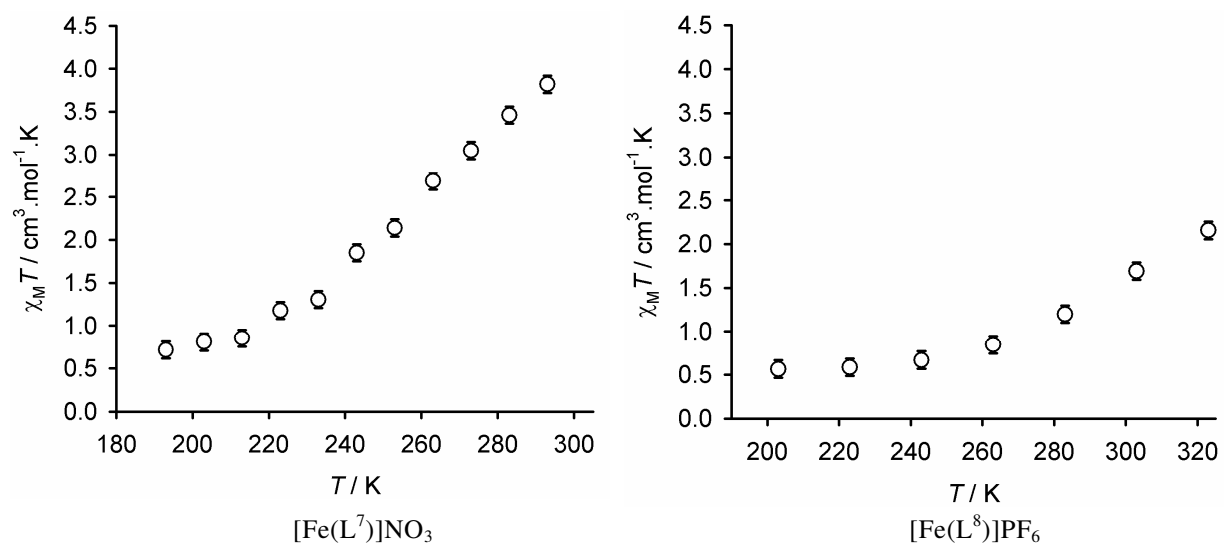


Figure S1 Variable temperature magnetic data for $[\text{Fe}(\text{L}^7)]\text{NO}_3$ and $[\text{Fe}(\text{L}^8)]\text{PF}_6$ in $(\text{CD}_3)_2\text{CO}$. The midpoint of the transitions $T_{1/2}$ was measured, or estimated, to be the temperature where $\chi_M T = 2.38 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$.

Table S1 Selected bond lengths and angles in the crystal structures of $[\text{Fe}(\text{L}^1)]\text{PF}_6$ (\AA , $^\circ$). Data at 140 K, given in the main paper, are quoted again for comparison.

	240 K		140 K	
	Molecule A	Molecule B	Molecule A	Molecule B
Fe(1)–N(2)	2.126(4)	2.133(4)	2.126(3)	2.131(4)
Fe(1)–N(5)	2.197(4)	2.197(4)	2.196(4)	2.203(4)
Fe(1)–N(8)	2.230(4)	2.236(4)	2.223(4)	2.225(3)
Fe(1)–N(11)	2.137(4)	2.138(4)	2.136(4)	2.133(3)
Fe(1)–O(19)	1.929(3)	1.923(3)	1.928(3)	1.922(3)
Fe(1)–O(27)	1.924(3)	1.934(3)	1.912(3)	1.931(3)
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N(2)–Fe(1)–N(5)	75.91(16)	77.39(17)	76.16(14)	77.57(14)
N(2)–Fe(1)–N(8)	95.25(16)	105.41(17)	94.14(14)	109.17(14)
N(2)–Fe(1)–N(11)	170.72(16)	175.32(16)	169.36(13)	171.32(14)
N(2)–Fe(1)–O(19)	86.86(13)	85.08(14)	86.86(12)	84.99(13)
N(2)–Fe(1)–O(27)	101.50(14)	92.94(16)	102.96(12)	89.89(13)
N(5)–Fe(1)–N(8)	78.60(18)	78.63(18)	78.44(14)	78.61(14)
N(5)–Fe(1)–N(11)	100.86(17)	107.10(16)	101.07(14)	109.90(13)
N(5)–Fe(1)–O(19)	160.15(15)	155.71(16)	160.82(13)	154.33(13)
N(5)–Fe(1)–O(27)	90.95(16)	91.28(17)	90.74(13)	91.46(13)
N(8)–Fe(1)–N(11)	75.52(17)	77.10(15)	75.22(14)	77.28(13)
N(8)–Fe(1)–O(19)	93.49(16)	90.18(15)	94.20(13)	89.71(13)
N(8)–Fe(1)–O(27)	157.51(14)	156.35(14)	157.01(13)	155.69(13)
N(11)–Fe(1)–O(19)	94.61(14)	91.00(13)	93.99(13)	89.30(12)
N(11)–Fe(1)–O(27)	87.17(14)	85.71(14)	87.26(12)	85.57(12)
O(19)–Fe(1)–O(27)	102.25(15)	106.43(15)	101.87(12)	107.36(13)

Table S2 Selected bond lengths and angles in the crystal structure of $[\text{Fe}(\text{L}^1)]\text{BPh}_4 \cdot \frac{1}{2}(\text{CH}_3)_2\text{CO}$ at 120 K (\AA , $^\circ$). Data for $[\text{Fe}(\text{L}^1)]\text{BPh}_4 \cdot \frac{1}{2}\text{C}_2\text{H}_4\text{Cl}_2$, given in the main paper, are quoted again for comparison.

	$(\text{CH}_3)_2\text{CO}$	$\text{C}_2\text{H}_4\text{Cl}_2$
Fe(1)–N(2)	2.1386(14)	2.148(2)
Fe(1)–N(5)	2.2094(14)	2.203(2)
Fe(1)–N(8)	2.2202(14)	2.220(2)
Fe(1)–N(11)	2.1349(14)	2.139(2)
Fe(1)–O(19)	1.9132(13)	1.923(2)
Fe(1)–O(27)	1.9343(12)	1.934(2)
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N(2)–Fe(1)–N(5)	76.81(6)	77.09(9)
N(2)–Fe(1)–N(8)	103.03(5)	102.64(9)
N(2)–Fe(1)–N(11)	173.48(6)	174.40(9)
N(2)–Fe(1)–O(19)	87.41(6)	86.93(9)
N(2)–Fe(1)–O(27)	93.39(5)	94.09(8)
N(5)–Fe(1)–N(8)	78.53(5)	78.46(9)
N(5)–Fe(1)–N(11)	96.67(5)	97.44(9)
N(5)–Fe(1)–O(19)	158.05(5)	158.64(9)
N(5)–Fe(1)–O(27)	90.06(5)	89.70(9)
N(8)–Fe(1)–N(11)	75.20(5)	74.79(9)
N(8)–Fe(1)–O(19)	90.52(6)	91.55(9)
N(8)–Fe(1)–O(27)	157.13(5)	156.63(8)
N(11)–Fe(1)–O(19)	98.84(5)	98.06(9)
N(11)–Fe(1)–O(27)	86.69(5)	87.04(8)
O(19)–Fe(1)–O(27)	106.22(6)	105.69(9)

Table S3 Metric parameters for the hydrogen bonds in the crystal structures in this work (Å, °).^a There are no hydrogen bonds in the two solvates of [Fe(L¹)]BPh₄.

	D–H	H...A	D...A	D–H...A
[Fe(L ⁵)]PF ₆				
N(5A)–H(5A)...F(32)	0.93	2.54	3.367(2)	148.9
N(5A)–H(5A)...F(35)	0.93	2.50	3.258(2)	139.4
N(8A)–H(8A)...F(33 ⁱ)	0.93	2.40	3.178(2)	141.1
N(8A)–H(8A)...F(34 ⁱ)	0.93	2.27	3.163(2)	161.3
N(5B)–H(5B)...F(40 ⁱ)	0.93	2.09	3.009(2)	171.6
N(5B)–H(5B)...F(41 ⁱ)	0.93	2.58	3.231(2)	127.8
N(8B)–H(8B)...F(38)	0.93	2.50	3.228(2)	135.4
N(8B)–H(8B)...F(39)	0.93	2.18	3.076(2)	162.3
[Fe(L ⁷)]NO ₃ ·C ₂ H ₄ Cl ₂				
N(5)–H(5)...O(37A)/O(37B) ^b	0.93	2.11/2.02	3.024(3)/2.886(8)	166.1/153.5
N(8)–H(8)...X ⁱⁱ [X = centroid of C(13)–C(18)]	0.93	2.72	3.61	159.0
[Fe(L ⁸)]PF ₆ ·(C ₂ H ₅) ₂ O				
N(5)–H(5)...F(39)	0.93	2.30	3.227(3)	171.4
N(8)–H(8)...X ^v [X = centroid of C(13)–C(18)+C(28)–C(31)]	0.93	2.73	3.66	177.7
[Fe(L ¹)]PF ₆ , 140 K				
N(5A)–H(5A)...F(38A)/F(38B)/F(38C) ^b	0.93	2.15/2.30/2.25	3.082(9)/3.007(12)/3.125(10)	176.1/132.4/157.0
N(5A)–H(5A)...F(39A)/F(39B)/F(39C) ^b	0.93	2.47/2.18/2.45	3.091(12)/3.063(8)/3.232(10)	124.2/157.3 /141.7
N(8A)–H(8A)...X [X = centroid of C(13B)–C(18B)]	0.93	2.85	3.71	155.0
N(5B)–H(5B)...F(31A)/F(31B)/F(31C) ^b	0.93	2.16/2.19/2.27	3.088(11)/3.096(11)/3.191(11)	172.0/163.3/170.2
N(5B)–H(5B)...F(35A)/F(35B)/F(35C) ^b	0.93	2.40/2.51/2.55	3.058(12)/3.216(17)/3.244(14)	127.6/132.4/132.1
N(8B)–H(8B)...F(34A ^{iv})/F(34B ^{iv})/F(34C ^{iv}) ^b	0.93	2.45/2.33/2.17	3.325(14)/3.220(15)/3.017(10)	156.2 /160.5/150.7
[Fe(L ¹)]ClO ₄				
N(5A)–H(5A)...O(32A)/O(32B) ^b	0.93	2.26/2.53	3.120(12)/3.345(14)	153.9/146.9
N(8A)–H(8A)...O(35A)/O(35B)/O(35C) ^b	0.93	2.37/2.58/2.47	3.133(14)/3.189(13)/3.345(17)	139.1/123.8/156.1
N(5B)–H(5B)...O(29A)/O(29B) ^b	0.93	2.04/2.32	2.871(11)/3.157(11)	147.2/149.3
N(8B)–H(8B)...O(39A ^{iv})/O(39B ^{iv}) ^b	0.93	2.26/2.15	3.187(14)/3.016(12)	172.8/155.1
N(5C)–H(5C)...O(30A) ^b	0.93	2.21	3.023(10)	145.5
N(5C)–H(5C)...O(31A) ^b	0.93	2.44	3.094(12)	127.8
N(8C)–H(8C)...O(42A) ^b	0.93	2.15	3.060(11)	167.3
N(5D)–H(5D)...O(30A) ^b	0.93	2.41	3.186(11)	141.2
N(5D)–H(5D)...O(31B) ^b	0.93	2.27	3.101(16)	148.4
N(8D)–H(8D)...O(42B) ^b	0.93	2.15	2.956(10)	144.8

^aSymmetry codes: (i) 1+x, y, z; (ii) x, 3/2–y, –1/2+z; (iv) x, 3/2–y, 1/2+z; (v) 2–x, –y, 1–z. ^bHydrogen bond to a disordered anion, whose parameters should be treated with caution.

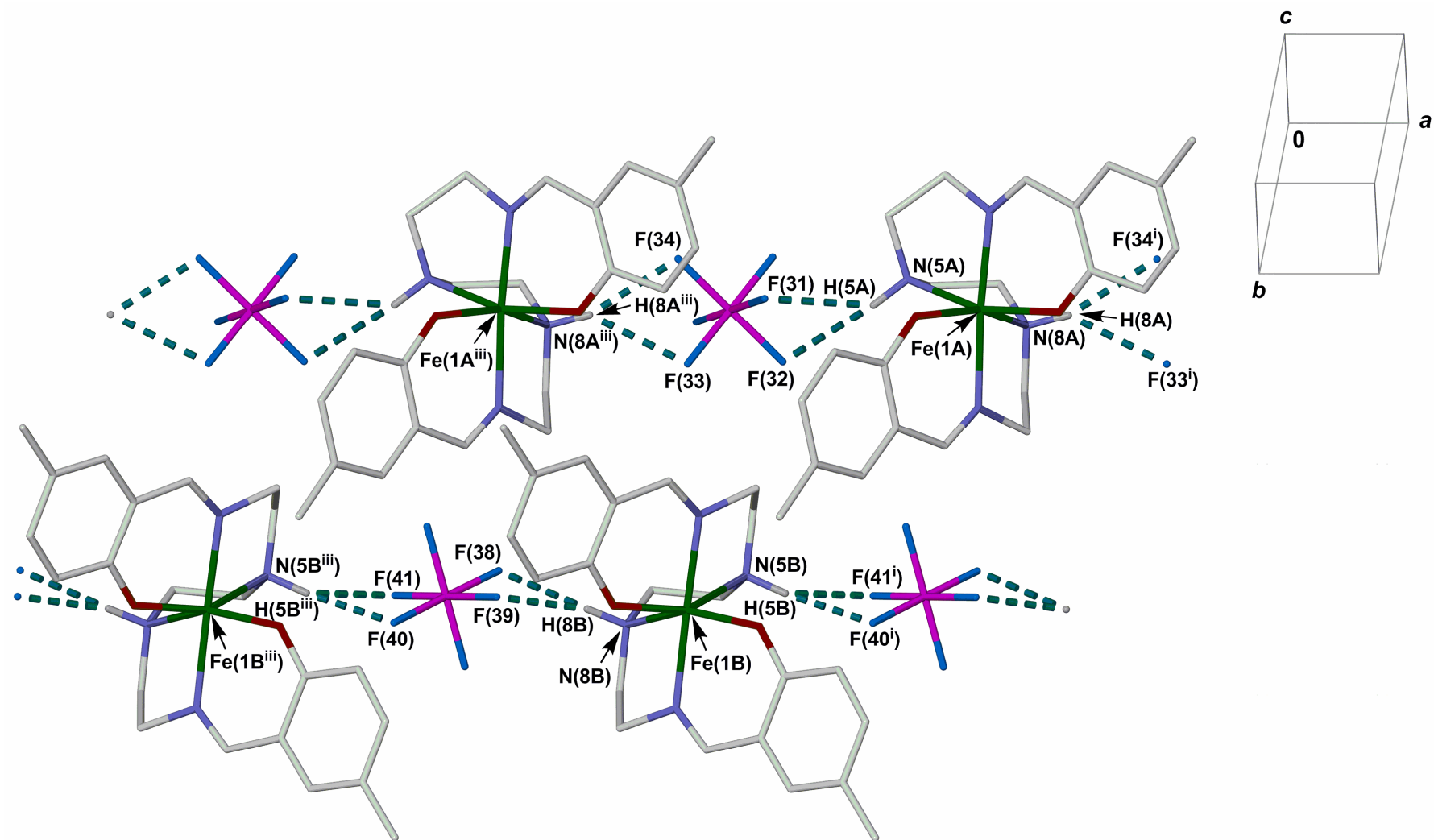


Figure S2 Partial packing diagram of $[\text{Fe}(\text{L}^5)]\text{PF}_6$, showing the arrangement of the two unique molecules into separate chains through N–H...F hydrogen bonding (Table S3). The orientation of the unit cell in this arbitrary view is shown in inset (not to scale). For clarity all atoms are shown with arbitrary radii, and all C-bound H atoms have been omitted. Colour code: C, white; H, grey; F, cyan; Fe, green; N, blue; O, red; P, pink. Symmetry codes : (i) $1+x, y, z$; (iii) $-1+x, y, z$.

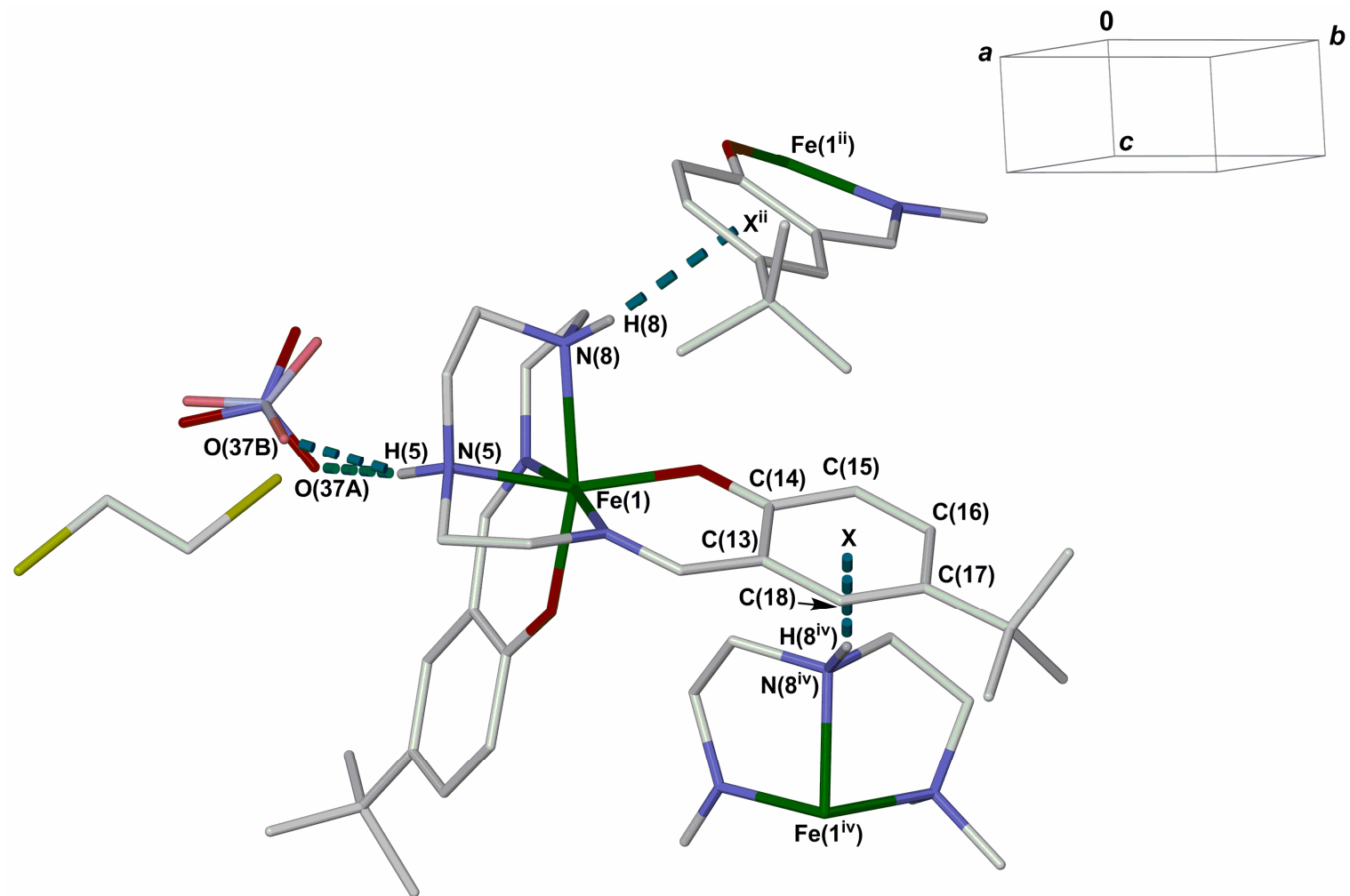


Figure S3 Partial packing diagram of [Fe(L⁷)]NO₃·C₂H₄Cl₂, showing the association of the molecules into chains linked by N–H...π interactions (Table S3). The orientation of the unit cell in this arbitrary view is shown in inset (not to scale). Both orientations of the disordered nitrate ion are shown, with the minor orientation having paler colouration. For clarity all atoms are shown with arbitrary radii, and all C-bound H atoms have been omitted. Colour code: C, white; H, grey; Cl, yellow; Fe, green; N, blue; O, red. Symmetry codes : (ii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (iv) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

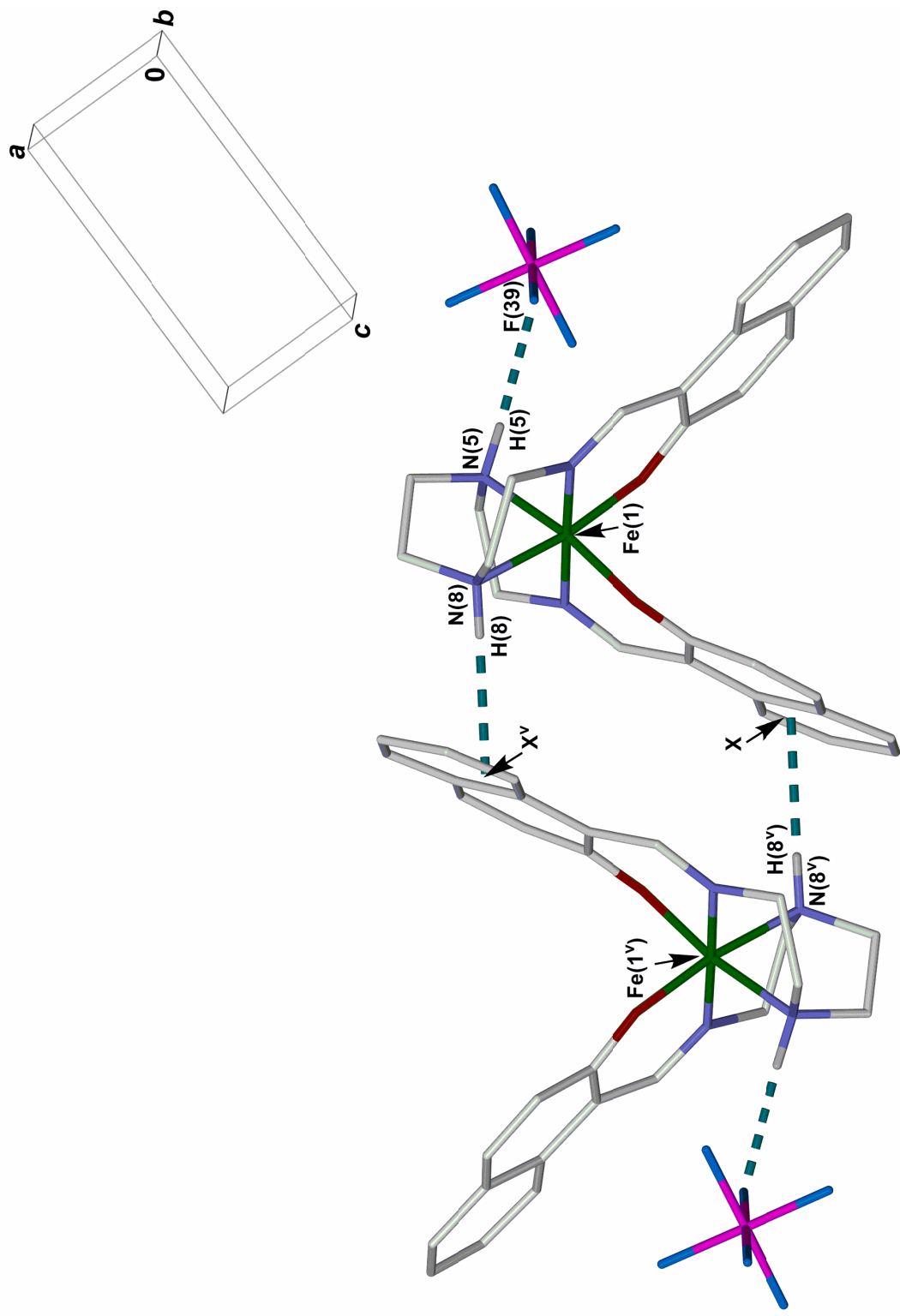


Figure S4 Partial packing diagram of [Fe(L⁸)]PF₆·(C₂H₅)₂O, showing the association of the molecules into dimers through N–H...F and N–H... π interactions (Table S3). The orientation of the unit cell in this arbitrary view is shown in inset (not to scale). For clarity all atoms are shown with arbitrary radii, and all C-bound H atoms have been omitted. The lattice solvent does not take part in any intermolecular interactions, and is not shown. Colour code: C, white; H, grey; Fe, green; N, blue; O, red; P, pink. Symmetry code: (v) 2–x, –y, 1–z.

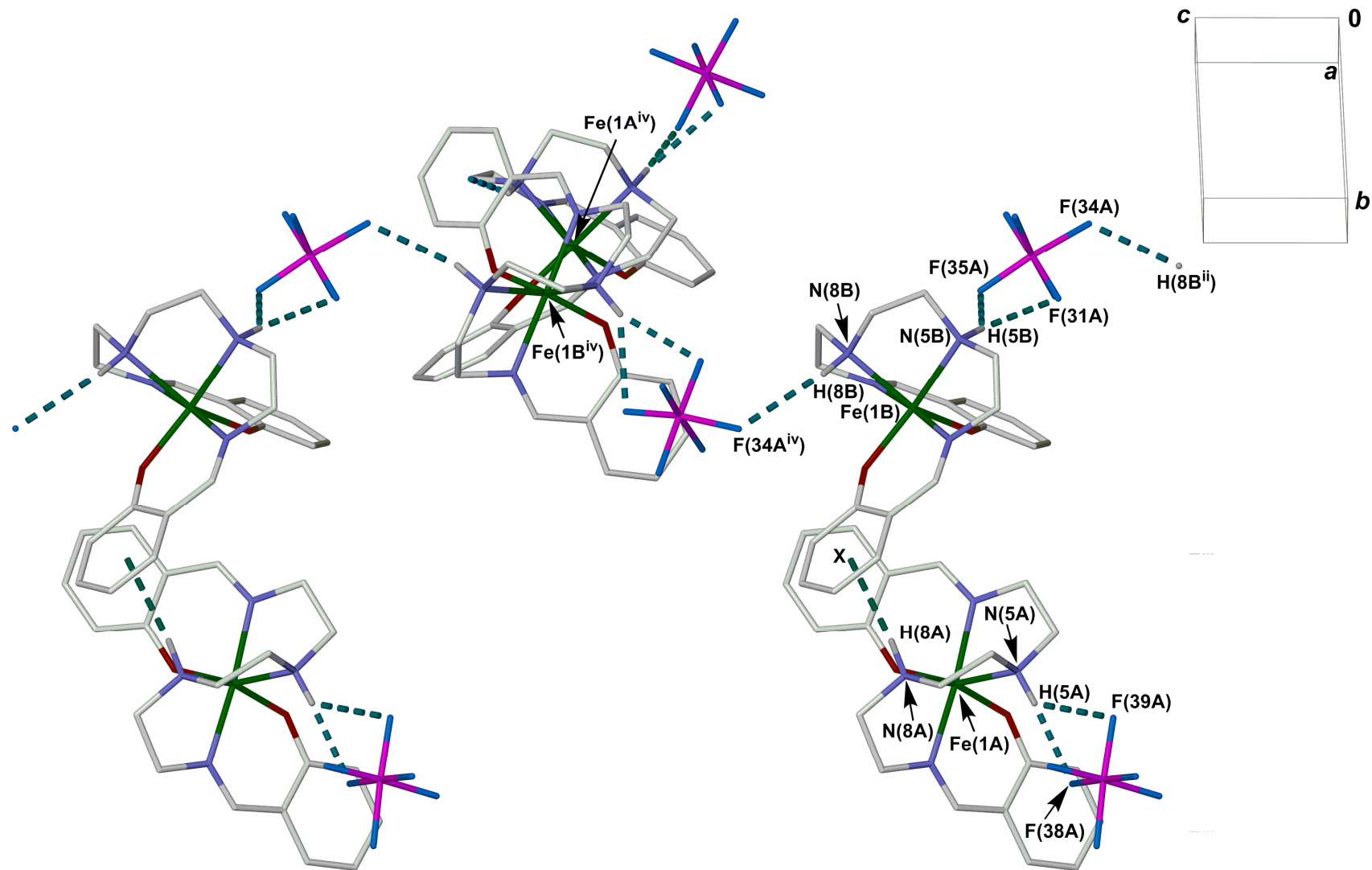


Figure S5 Partial packing diagram of [Fe(L¹)]PF₆. The 'A' molecules associate with the 'B' molecules through a N-H... π interaction, while these dyads in turn form chains parallel to *c* via N-H...F hydrogen bonding to the 'B' molecules (Table S3). The orientation of the unit cell in this arbitrary view is shown in inset (not to scale). Only one orientation of the disordered PF₆⁻ anions is shown. For clarity all atoms are shown with arbitrary radii, and all C-bound H atoms have been omitted. Colour code: C, white; H, grey; F, cyan; Fe, green; N, blue; O, red; P, pink. Symmetry codes : (ii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (iv) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

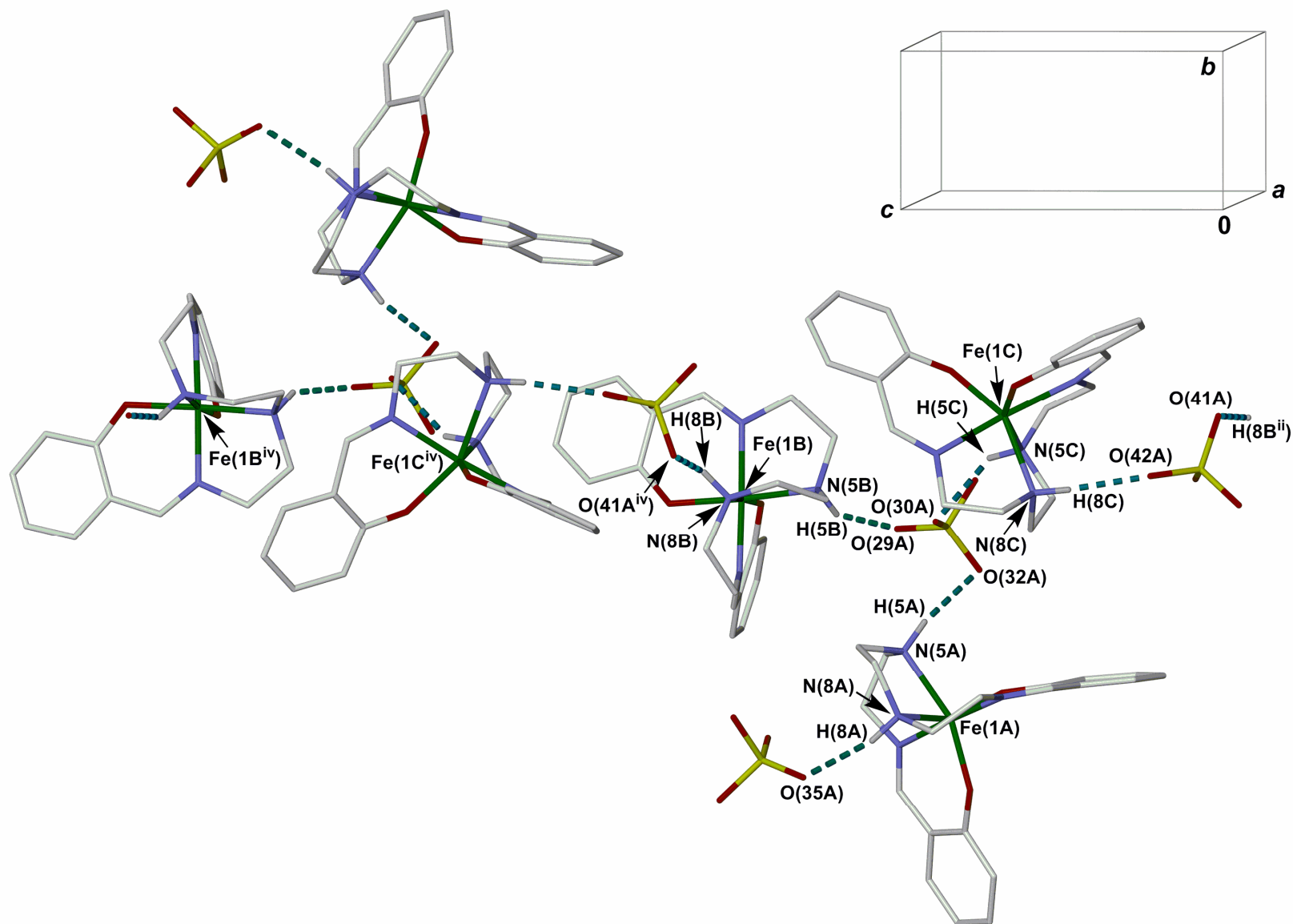


Figure S6 Partial packing diagram of [Fe(L¹)]ClO₄. The ‘D’ half-molecules occupy the same lattice site as the ‘C’ half-molecules. The ‘B’ and ‘C/D’ sites alternate in zig-zag chains parallel to *c*, linked by N–H...O hydrogen bonding to bridging ClO₄[−] ions. The ‘A’ molecules associate with the chains by an additional N–H...O interaction (Table S3). The orientation of the unit cell in this arbitrary view is in inset (not to scale), and only one orientation of each disordered residue is shown. All atoms have arbitrary radii, and all C-bound H atoms have been omitted. Colour code: C, white; H, grey; Cl, yellow; Fe, green; N, blue; O, red. Symmetry codes : (ii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (iv) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

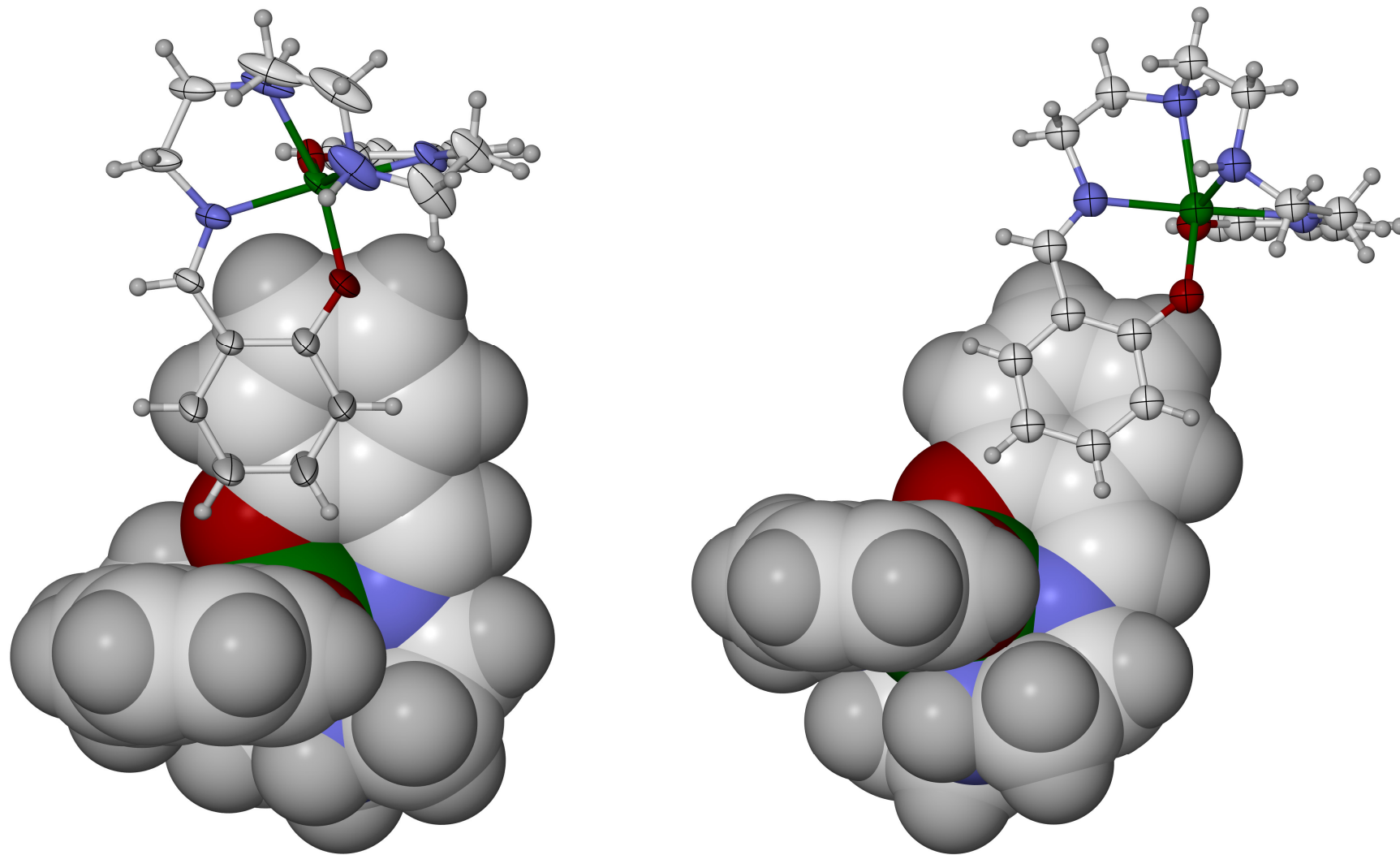


Figure S7 Left: diagram showing the dimerisation of molecule A in $[\text{Fe}(\text{L}^1)]\text{ClO}_4$ with its symmetry equivalent, related by $1-x, -y, 1-z$, through π - π and edge-to-face C-H... π interactions. We propose the latter prevent this molecule from undergoing spin-crossover on steric grounds. Right: the comparable dimerisation of complex cations in $[\text{Fe}(\text{L}^1)][\text{Ni}(\text{dmit})_2]$, via the same symmetry relation.¹⁴ The reduced π - π offset means there is no comparable edge-to-face C-H... π contact between these molecules, which do undergo thermal spin-transitions.

Table S4 Structural parameters for iron(III) complexes of hexadentate saltrien-type ligands (Å, °). The ligand numbers and references are those from the main paper. See the main text for the definitions of Σ and Θ .

	Spin state	av. Fe–N{amine}	av. Fe–N{imine}	av. Fe–O	Σ	Θ	Spin-crossover on cooling?	Ref
[Fe(L ¹)]PF ₆ , 140 K, molecule A	High-spin	2.210(3)	2.131(3)	1.920(2)	95.0(5)	236	No	This work
[Fe(L ¹)]PF ₆ , 140 K, molecule B	High-spin	2.214(3)	2.132(3)	1.927(2)	105.0(5)	323	No	This work
[Fe(L ¹)]BPh ₄ ·½(CH ₃) ₂ CO	High-spin	2.215(1)	2.137(1)	1.924(1)	94.1(2)	239	No	This work
[Fe(L ¹)]BPh ₄ ·½C ₂ H ₄ Cl ₂	High-spin	2.212(1)	2.144(1)	1.929(1)	95.5(3)	240	No	This work
[Fe(L ¹)]ClO ₄ , molecule A	High-spin	2.205(7)	2.109(6)	1.913(5)	96.0(6)	254	No	This work
[Fe(L ¹)]Ni(dmit) ₂ , 293 K	High-spin	2.189(4)	2.121(4)	1.909(3)	96.9(4)	250	Yes	14
[Fe(L ²)]PF ₆	High-spin	2.183(7)	2.090(7)	1.894(5)	89(2)	263	Yes	12
[Fe(L ³)]PF ₆ ·½H ₂ O	High-spin	2.209(8)	2.105(8)	1.902(6)	85.5(14)	204	No	12
[Fe(L ⁵)]PF ₆ , molecule A	High-spin	2.218(1)	2.124(1)	1.9315(9)	93.9(2)	244	No	This work
[Fe(L ⁵)]PF ₆ , molecule B	High-spin	2.246(1)	2.133(1)	1.9321(9)	118.8(2)	358	No	This work
[Fe(L ⁷)]NO ₃ ·C ₂ H ₄ Cl ₂	High-spin	2.170(1)	2.117(1)	1.9199(9)	109.4(2)	284	Not above 100 K	This work
[Fe(L ¹)]Ni(dcbdt) ₂	85% High-spin	2.116(2)	2.040(2)	1.888(2)	56.9(4)	187	No	15
[Fe(L ²)]ClO ₄ , 293 K	60% High-spin	2.105(2)	2.029(2)	1.877(2)	68.7(6)	199	Yes	12
[Fe(L ¹)]BPh ₄ ·(CH ₃) ₂ CO, 293 K	40% High-spin	2.069(3)	1.988(3)	1.875(3)	50.1(7)	117	Yes	29
[Fe(L ³)]ClO ₄ , 293 K	10% High-spin	2.022(4)	1.952(4)	1.882(2)	49.0(11)	94	n/a	12
[Fe(L ¹)]ClO ₄ , molecule B	Low-spin	2.023(7)	1.949(6)	1.885(5)	46.3(7)	83		This work
[Fe(L ¹)]Cl·2H ₂ O	Low-spin	2.006(2)	1.930(2)	1.884(1)	43.4(2)	69		17
[Fe(L ¹)]Br·H ₂ O	Low-spin	2.000(3)	1.931(4)	1.879(2)	45.1(7)	71		18
[Fe(L ¹)]NO ₃ ·H ₂ O	Low-spin	1.999(2)	1.932(2)	1.882(2)	46.9(3)	74		17
[Fe(L ¹)]Ni(dmit) ₂ , 180 K	Low-spin	2.003(3)	1.929(2)	1.874(2)	40.3(5)	56		14
[Fe(L ⁴)]ClO ₄ ^a	Low-spin	2.004(3)	1.938(3)	1.871(3)	45.6(7)	79		30
[Fe(L ⁸)]PF ₆ ·(C ₂ H ₅) ₂ O	Low-spin	2.022(2)	1.939(2)	1.900(1)	43.5(4)	98		This work

^a μ_{eff} not reported, but compound is almost certainly low-spin.

Table S5 Structural changes during spin-crossover for the one compound in Table S3, for which both high-spin and low-spin structural data are available (Å, °). See the main text for the definitions of Σ , Θ , τ and α .

	$\Delta r_{\text{Fe-N}\{\text{amine}\}}$	$\Delta r_{\text{Fe-N}\{\text{imine}\}}$	$\Delta r_{\text{Fe-O}}$	$\Delta \Sigma$	$\Delta \Phi$	$\Delta \tau$	$\Delta \alpha$	Ref
[Fe(L ¹)]Ni(dmit) ₂	0.186(7)	0.192(6)	0.035(5)	56.6(6)	194	+17.0, +18.3 ^a	0.2	14

^aPositive $\Delta \tau$ values mean that both phenoxy groups rotate about the metal ion in the same direction.