Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information for

The first X-ray crystal structure determination of a dinuclear complex trapped in the [low spin–high spin] state: $[Fe^{II}_2(PMAT)_2](BF_4)_4$·DMF

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Experimental:

Preparation of $[Fe^{II}_2(PMAT)_2](BF_4)_4$ (**1**): A colourless solution of $Fe(BF_4)_2·6H_2O$ (84 mg, 0.25 mmol) in MeCN (5 mL) was added dropwise to a colourless solution of PMAT[17] (81 mg, 0.25 mmol) in MeCN (10 mL). The resulting red solution was stirred at room temperature for 1 hour during which time the product precipitated from the reaction mixture. The solid was filtered off and washed with MeCN and Et_2O. Drying *in vacuo* gave 105 mg (76 %) of $[Fe^{II}_2(PMAT)_2](BF_4)_4$ as a pale yellow powder. Elemental analysis (%) calcd. for $C_{32}H_{40}B_4F_{16}Fe_2N_{16}$ (1107.69 g mol^{-1}): C 34.70, H 3.64, N 20.23; found C 34.68, H 3.50, N 19.89. IR (KBr): ν / cm^{-1} = 3125, 2916, 1607, 1570, 1558, 1489, 1438, 1375, 1306, 1239, 1083, 1036, 891, 816, 766, 730, 668, 645, 538, 521, 467. ESI-MS (pos., MeCN): *m/z* = 163.4 $[(PMAT)H_2]^{2+}$, 325.3 $[(PMAT)H]^+$, 352.2 $[Fe(PMAT)_2]^{2+}$, 413.2 $[(PMAT)(BF_4)H_2]^+$, 790.6 $[Fe(PMAT)_2(BF_4)]^+$, 879.5 $[Fe(PMAT)_2(BF_4)_2H]^+$. Molar conductivity (DMF): Λ_m / Ω^{-1} cm^2 mol^{-1} = 224.

Magnetic susceptibility studies were carried out on **1·DMF** using a Quantum Design MPMS SQUID magnetometer with an applied field of 1 T. The polycrystalline sample was contained in a calibrated gelatine capsule which was held in the centre of a soda straw fixed to the end of the sample rod. The magnetic data were also measured with the sample dispersed in a Vaseline mull to eliminate any crystallite orientation effects often evident as anomalous μ_{eff} *vs. T* plots in orbitally degenerate systems such as octahedral Fe^{II}. None was evident here. The magnetisation values of the instrument were calibrated against a standard palladium sample, supplied by Quantum Design, and also against chemical calibrants such as $CuSO_4·5H_2O$ and $[Ni(en)_3](S_2O_3)$.

The Mössbauer spectrum was obtained using a conventional constant acceleration drive with a symmetrical sawtooth waveform. The source of ^{57}Co in rhodium was maintained at room temperature. The iron complex was loaded into a piston type Perspex holder. The holder was placed in a cold-finger type cryostat in good thermal contact with the reservoir which contained liquid nitrogen. Drive calibration was carried out using an α-Fe foil and isomer shifts are quoted relative to α-Fe at room temperature. The spectrum was fitted to Lorentzian lines, with the matching lines of a doublet constrained to have the same intensity and linewidth.

X-Ray data were collected at 123 and 298 K on a 0.25 × 0.30 × 0.40 mm^3 prism of **1·DMF** ($C_{35}H_{47}B_4F_{16}Fe_2N_{17}O$), obtained by evaporation of a 4:1 MeCN/DMF solution, using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation. Extensive hydrogen bonding, between the hydrogen atoms on the nitrogen atoms of PMAT and the BF_4^- anions and DMF solvate, is present in both structures. CCDC 247510 and 247511 contain the supplementary crystallographic data for this paper. These data can be obtained online free of charge from http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

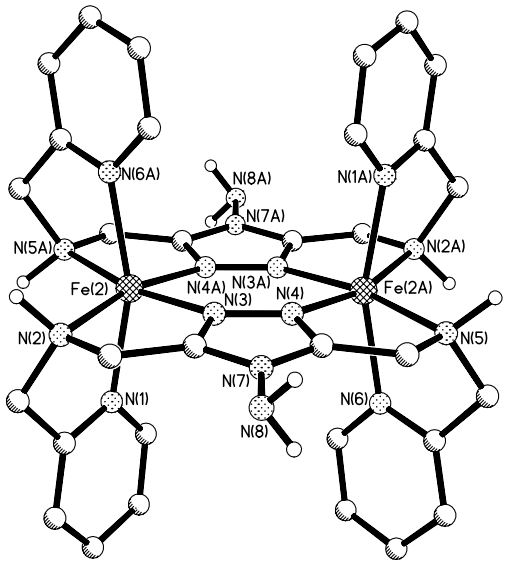

Fig. S1 Perspective view of **1·DMF** at 298 K. The BF_4^- anions, the DMF solvate and all hydrogen atoms, except those bonded to nitrogen atoms, have been omitted for clarity. Symmetry operation used to generate equivalent atoms: (A) –x, –y+1, –z+1.

*Selected distances [Å] of **1·DMF** at 298 K:*

Fe(2)–N(1) 2.148(4), Fe(2)–N(2) 2.289(5), Fe(2)–N(3) 2.123(4), Fe(2)–N(4A) 2.116(4), Fe(2)–N(5A) 2.303(5), Fe(2)–N(6A) 2.147(5), Fe(2)···Fe(2A) 4.297(2).

*N–Fe–N and N–N–Fe angles [°] for **1·DMF** at 298 K:*

N(4A)–Fe(2)–N(3) 92.80(15), N(4A)–Fe(2)–N(6A) 94.54(17), N(3)–Fe(2)–N(6A) 100.17(17), N(4A)–Fe(2)–N(1) 97.15(17), N(3)–Fe(2)–N(1) 93.84(16), N(6A)–Fe(2)–N(1) 161.26(18), N(4A)–Fe(2)–N(2) 166.40(16), N(3)–Fe(2)–N(2) 75.92(16), N(6A)–Fe(2)–N(2) 94.91(18), N(1)–Fe(2)–N(2) 76.40(17), N(4A)–Fe(2)–N(5A) 75.93(16), N(3)–Fe(2)–N(5A) 167.66(17), N(6A)–Fe(2)–N(5A) 76.13(18), N(1)–Fe(2)–N(5A) 92.57(17), N(2)–Fe(2)–N(5A) 115.90(17), N(4)–N(3)–Fe(2) 133.6(3).

*Summary of hydrogen bonding for **1·DMF** at 298 K [H···A < r(A) + 2.000 Å and <DHA > 110°]:*

D–H	d(D–H)	d(H···A)	<DHA	d(D···A)	A
N2–H2X	0.949	1.940	153.27	2.820	F26_b [–x, –y, –z+1]
N2–H2X	0.949	2.220	151.80	3.090	F22_a [–x, –y, –z+1]
N2–H2X	0.949	2.330	149.53	3.185	F23_a [–x, –y, –z+1]
N5–H5X	0.952	2.243	146.04	3.079	F16_b [–x–1, –y+1, –z+1]
N5–H5X	0.952	2.300	152.89	3.177	F17_b [–x–1, –y+1, –z+1]
N5–H5X	0.952	2.537	167.63	3.472	F14_a [–x–1, –y+1, –z+1]
N5–H5X	0.952	2.603	140.57	3.392	F13_a [–x–1, –y+1, –z+1]
N8–H8X	0.930	2.104	134.15	2.831	F25_b
N8–H8X	0.930	2.313	124.95	2.946	O100
N8–H8X	0.930	2.364	139.00	3.126	F21_a
N8–H8Y	0.951	2.026	133.45	2.768	F15_b
N8–H8Y	0.951	2.193	135.14	2.945	F11_a

*Summary of hydrogen bonding for **1·DMF** at 123 K [H···A < r(A) + 2.000 Å and <DHA > 110°]:*

D–H	d(D–H)	d(H···A)	<DHA	d(D···A)	A
N2–H2X	0.938	2.191	155.77	3.070	F12 [x–1, y, z]
N2–H2X	0.938	2.229	144.32	3.040	F13 [x–1, y, z]
N5–H5X	0.830	2.381	150.76	3.132	F43 [–x+1, –y+1, –z+2]
N5–H5X	0.830	2.605	136.34	3.257	F44 [–x+1, –y+1, –z+2]
N8–H8X	0.800	2.104	154.26	2.846	F41
N8–H8Y	0.779	2.339	153.39	3.056	F33 [x–1, y, z]
N8–H8Y	0.779	2.391	120.67	2.868	O200_b
N10–H10X	0.913	2.112	151.08	2.945	F22 [–x+1, –y, –z+1]
N10–H10X	0.913	2.423	149.93	3.246	F23 [–x+1, –y, –z+1]
N13–H13X	0.899	2.198	147.65	2.996	F31
N13–H13X	0.899	2.338	149.57	3.146	F32
N16–H16X	0.918	2.232	123.56	2.844	F21
N16–H16Y	0.650	2.316	163.01	2.944	F11

*Selected distances [Å] of **1·DMF** at 123 K:*

Fe(1)–N(1) 1.987(4), Fe(1)–N(2) 2.066(4), Fe(1)–N(3) 1.946(3), Fe(2)–N(4) 2.136(3), Fe(2)–N(5) 2.319(4), Fe(2)–N(6) 2.159(4), Fe(1)–N(9) 1.986(4), Fe(1)–N(10) 2.071(4), Fe(1)–N(11) 1.934(3), Fe(2)–N(12) 2.131(3), Fe(2)–N(13) 2.312(4), Fe(2)–N(14) 2.155(4), Fe(1)···Fe(2) 4.2124(14).

*N–Fe–N and N–N–Fe angles [°] for **1·DMF** at 123 K:*

N(11)–Fe(1)–N(3) 95.43(14), N(11)–Fe(1)-N(9) 91.69(15), N(3)-Fe(1)-N(9) 94.84(14), N(11)–Fe(1)–N(1) 94.37(14), N(3)–Fe(1)–N(1) 91.25(14), N(9)–Fe(1)–N(1) 170.96(14), N(11)–Fe(1)–N(2) 175.38(14), N(3)–Fe(1)–N(2) 81.86(14), N(9)–Fe(1)–N(2) 92.26(15), N(1)–Fe(1)–N(2) 81.99(15), N(11)–Fe(1)–N(10) 81.79(14), N(3)–Fe(1)–N(10) 175.92(15), N(9)–Fe(1)–N(10) 82.29(15), N(1)–Fe(1)–N(10) 91.93(14), N(2)–Fe(1)–N(10) 101.11(15), N(12)–Fe(2)–N(4) 87.92(13), N(12)–Fe(2)–N(14) 93.58(13), N(4)–Fe(2)–N(14) 101.83(14), N(12)–Fe(2)–N(6) 107.13(14), N(4)–Fe(2)–N(6) 94.23(14), N(14)–Fe(2)–N(6) 154.24(14), N(12)–Fe(2)–N(13) 75.13(13), N(4)–Fe(2)–N(13) 162.72(13), N(14)–Fe(2)–N(13) 76.37(14), N(6)–Fe(2)–N(13) 93.98(14), N(12)–Fe(2)–N(5) 163.15(13), N(4)–Fe(2)–N(5) 75.24(13), N(14)–Fe(2)–N(5) 89.53(14), N(6)–Fe(2)–N(5) 75.14(15), N(13)–Fe(2)–N(5) 121.65(14), N(4)–N(3)–Fe(1) 134.3(3), N(3)–N(4)–Fe(2) 133.9(2), N(12)–N(11)–Fe(1) 134.0(2), N(11)–N(12)–Fe(2) 134.4(2).