Electronic Supplementary Information for Dalton Transactions

Synthesis, structures and spin crossover properties of infinite 3D frameworks of iron(II) containing organodinitrile bridging ligands

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Electronic Supplementary Information

Fig. S1 Schematic representation for comparison of distorted octahedral geometry around Fe(II) centres in (a) **1** and (b) **2** at 103 (red) and 233 K (yellow).

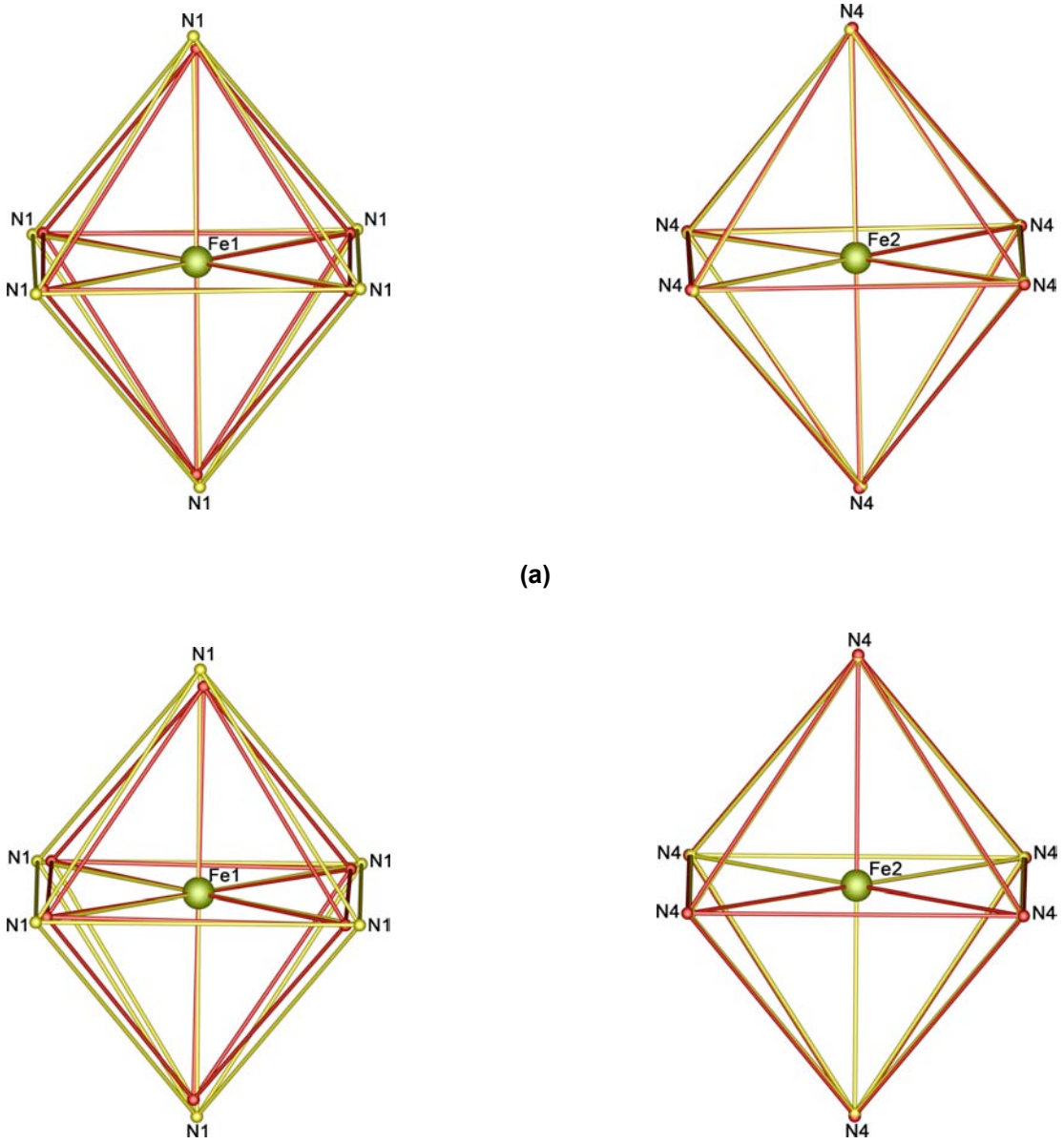
Fig. S2 Views of AIBN ligands in (a) **1** and (b) **2** at 103 (red) and 233 K (yellow).

Fig. S3 View slightly offset from the crystallographic *b* axis showing the 2-D layered structure in **2a**. Inclusion of $[FeCl_4]^-$ is represented by the space filling models. Hydrogen atoms are omitted for clarity.

Table S1 Selected bond lengths and angles for $[Fe(ACCN)_3]^{2+}$ cations in **3** and **4** at 123 K (Å, °).

Table S2 Selected bond lengths and angles for $[Fe(AIBN)_2(H_2O)_2]^{2+}$ cations in $[Fe(AIBN)_2(H_2O)_2][FeCl_4]_2$, **2a** at 123 K (Å, °).

Table S3 Hydrogen bond geometries for **2a** (Å, °).



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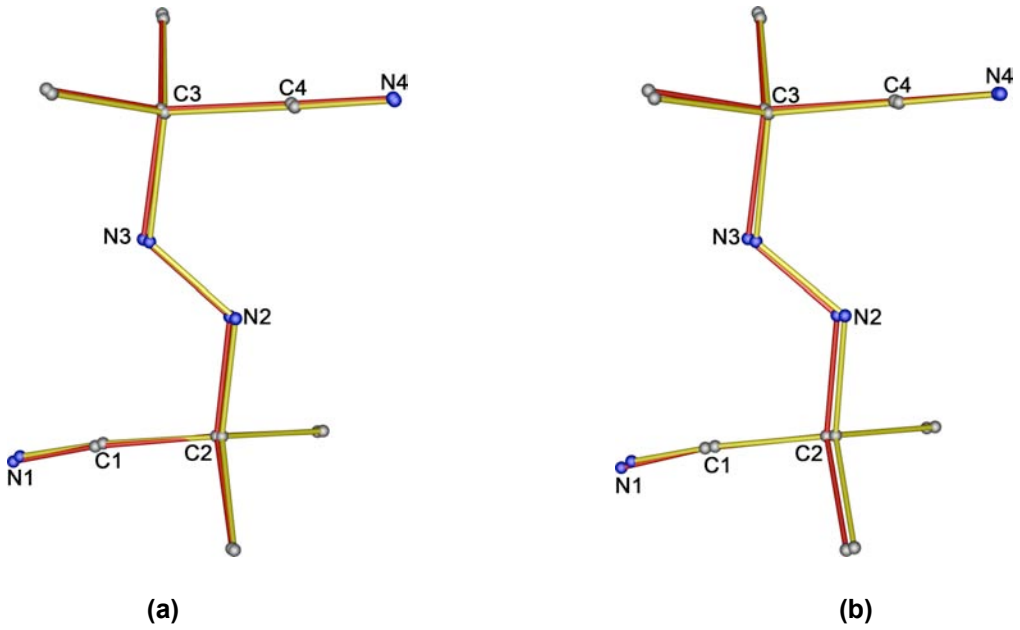

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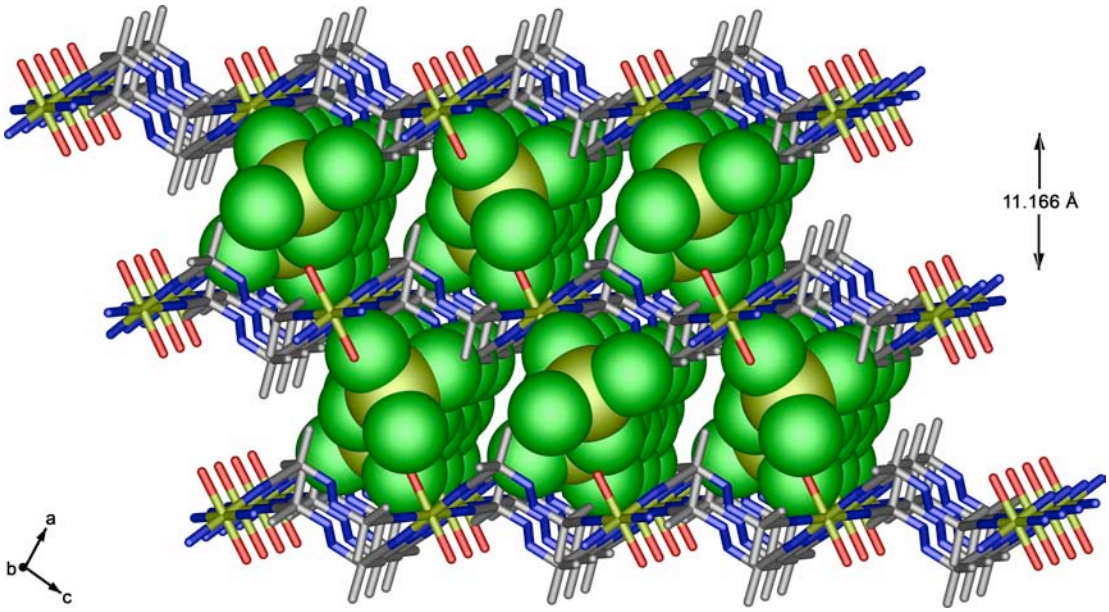

Fig. S3 View slightly offset from the crystallographic *b* axis showing the 2D layered structure in **2a**. Inclusion of $[FeCl_4]^-$ is represented by the space filling models. Hydrogen atoms are omitted for clarity.

Table S1 Selected bond lengths and angles for $[Fe(ACCN)_3]^{2+}$ cations in **3** and **4** at 123 K (Å, °). [a]

	$[Fe(ACCN)_3][InCl_4]_2$ (3)	**$[Fe(ACCN)_3][FeCl_4]_2$ (4)**
Fe1−N11	2.164(3)	2.159(5)
Fe1−N21	2.150(3)	2.160(5)
Fe1−N31	2.140(3)	2.142(5)
Fe1−N41	2.123(3)	2.125(5)
Fe1−N51	2.172(3)	2.179(5)
Fe1−N61	2.164(3)	2.159(5)
Fe1···Fe1^{i}	10.6461(9)	10.6032(17)
Fe1···Fe1^{ii}	10.8428(9)	10.8290(17)
Fe1···Fe1^{iii}	10.9464(5)	10.9068(9)
Fe1···Fe1^{iv}	10.9464(5)	10.9068(9)
Fe1···Fe1^{v}	11.9861(9)	11.9265(18)
Fe1···Fe1^{vi}	12.0096(9)	11.9705(17)
C11−N11	1.147(4)	1.131(8)
C21−N21	1.143(4)	1.131(8)
C31−N31	1.138(4)	1.143(8)
C41−N41	1.142(4)	1.130(8)
C51−N51	1.142(4)	1.145(8)
C61−N61	1.143(4)	1.160(8)
C12−N12	1.499(4)	1.506(8)
C22−N22	1.489(4)	1.479(8)
C32−N32	1.502(4)	1.501(8)
C42−N42	1.483(4)	1.471(8)
C52−N52	1.484(4)	1.489(7)
C62−N62	1.486(4)	1.484(8)
N11−Fe1−N21	179.2(1)	179.3(2)
N11−Fe1−N31	90.3(1)	89.8(2)
N11−Fe1−N41	89.6(1)	89.6(2)
N11−Fe1−N51	90.24(9)	90.4(2)
N11−Fe1−N61	89.65(9)	89.3(2)
N21−Fe1−N31	89.7(1)	90.3(2)
N21−Fe1−N41	90.4(1)	90.2(2)

Table S1 (Continued).

	$[Fe(ACCN)_3][InCl_4]_2$ (3)	**$[Fe(ACCN)_3][FeCl_4]_2$ (4)**
N21−Fe1−N51	88.93(9)	88.9(2)
N21−Fe1−N61	91.18(9)	91.5(2)
N31−Fe1−N41	178.2(1)	178.3(2)
N31−Fe1−N51	88.81(9)	88.9(2)
N31−Fe1−N61	88.8(1)	88.5(2)
N41−Fe1−N51	89.36(9)	89.5(2)
N41−Fe1−N61	93.0(1)	93.0(2)
N51−Fe1−N61	177.62(9)	177.4(2)
Σ_{Fe1}	9.1	10.5

[a] Estimated standard deviations of the least significant digits are given in parentheses. Symmetry codes: (i) 2−*x*, 1−*y*, −*z*; (ii) 2−*x*, 1−*y*, 1−*z*; (iii) 1+*x*, *y*, *z*; (iv) *x*−1, *y*, *z*; (v) 2−*x*, −*y*, −*z*; (vi) 2−*x*, −*y*, 1−*z*.

Table S2 Selected bond lengths and angles for $[Fe(AIBN)_2(H_2O)_2]^{2+}$ cations in $[Fe(AIBN)_2(H_2O)_2][FeCl_4]_2$, **2a** at 123 K (Å, °). [a]

Fe1−N1	2.144(1)	N2−N3	1.229(2)
Fe1−N4^{i}	2.171(1)	C1−C2	1.487(2)
Fe1−O1	2.084(1)	C3−C4	1.488(2)
C1−N1	1.135(2)	C2−N2	1.494(2)
C4−N4	1.135(2)	C3−N3	1.489(2)
Fe1···Fe1^{i}	10.3521(2)	Fe1···Fe1^{ii}	12.9995(3)
Fe1···Fe1^{iii}	16.1444(4)		
N1−Fe1−N1^{iv}	180	N4^{iv}−Fe1−N4^{v}	180
N1−Fe1−N4^{v}	85.54(5)	N4^{iv}−Fe1−O1	91.14(6)
N1−Fe1−N4^{vi}	94.46(5)	N4^{v}−Fe1−O1	88.86(6)
N1−Fe1−O1	90.55(5)	O1−Fe1−O1^{iv}	180
N1−Fe1−O1^{iv}	89.45(5)		

[a] Estimated standard deviations of the least significant digits are given in parentheses. Symmetry codes: (i) 1/2−*x*, 1/2+*y*, 1/2−*z*; (ii) *x*, 1+*y*, *z*; (iii) *x*−1/2, 1/2−*y*, 1/2−*z*; (iv) −*x*, −*y*, −*z*+1; (v) *x*−1/2, −*y*+1/2, *z*−1/2; (vi) −*x*+1/2, *y*−1/2, −*z*+3/2; (vi) −*x*+1/2, *y*+1/2, −*z*+3/2.

Table S3 Hydrogen bond geometries for $[Fe(AIBN)_2(H_2O)_2][FeCl_4]_2$, **2a** (Å, °). [a]

D−H···A	[D−H]	[H···A]	[D···A]	∠[D−H−A]
O1−H1···Cl4^{i}	0.81(2)	2.54(2)	3.267(1)	150(2)
O1−H2···Cl1	0.82(2)	2.38(2)	3.168(2)	163(2)

[a] Estimated standard deviations of the least significant digits are given in parentheses.

Symmetry code: (i) 1/2−*x*, 1/2+*y*, 1/2−*z*.