Electronic Supplementary Information (ESI)

Manipulating the spin crossover behaviour in a series of cyanide-bridged $\{Fe^{III}_2Fe^{II}_2\}$ molecular squares through NCE^- co-ligands

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Table S1. Selected bond angles (degree) around metal centers for **1**, **2** and **3**.

Bond Angles (degree)						
	1$^{100\ K}$	**1**$^{300\ K}$	**2**$^{100\ K}$	**2**$^{300\ K}$	**3**$^{100\ K}$	**3**$^{300\ K}$
C1-Fe1-C2	88.50(11)	88.32(18)	87.9(6)	87.1(4)	88.11(11)	88.0(3)
C1-Fe1-C3	86.74(12)	88.1(2)	84.2(7)	85.4(6)	87.86(13)	85.4(5)
C1-Fe1-N8	176.90(11)	179.7(2)	174.7(6)	175.2(5)	179.19(11)	175.1(4)
C1-Fe1-N9	90.49(10)	90.30(17)	90.9(5)	92.5(4)	90.72(11)	91.4(3)
C1-Fe1-N10	92.62(11)	90.62(18)	95.0(7)	94.0(5)	91.55(12)	94.1(5)
C2-Fe1-C3	87.69(12)	85.0(2)	87.4(7)	88.1(5)	85.27(13)	87.0(5)
C2-Fe1-N8	90.96(10)	91.55(17)	91.2(6)	90.7(4)	91.16(11)	90.6(3)
C2-Fe1-N9	178.10(11)	175.5(2)	178.8(6)	179.2(5)	175.86(12)	178.9(5)
C2-Fe1-N10	92.40(11)	93.51(19)	91.3(6)	91.2(5)	94.03(12)	92.1(4)
C3-Fe1-N8	90.19(11)	92.2(2)	90.5(6)	90.3(5)	91.72(12)	89.8(5)
C3-Fe1-N9	90.65(11)	90.7(2)	92.1(6)	91.2(5)	90.72(12)	92.0(4)
C3-Fe1-N10	179.35(12)	178.0(2)	178.5(8)	179.0(6)	179.10(15)	178.9(5)
N8-Fe1-N9	89.96(9)	89.85(16)	90.0(5)	89.6(3)	89.98(10)	89.9(3)
N8-Fe1-N10	90.45(10)	89.12(18)	90.3(6)	90.3(5)	88.87(11)	90.6(4)
N9-Fe1-N10	89.26(10)	90.8(2)	89.2(6)	89.6(4)	89.97(11)	89.0(4)
N1-Fe2-N2	89.06(9)	92.67(15)	89.3(5)	92.9(3)	89.19(10)	91.9(3)
N1-Fe2-N4	178.31(10)	173.67(18)	178.8(5)	172.6(4)	178.56(11)	174.2(3)
N1-Fe2-N5	88.78(9)	91.34(15)	89.4(5)	90.7(4)	89.91(10)	89.8(3)
N1-Fe2-N6	87.76(10)	87.74(17)	89.2(6)	88.7(4)	88.19(11)	88.1(3)
N1-Fe2-N7	90.60(10)	93.78(19)	88.8(6)	92.5(4)	89.68(11)	91.1(4)
N2-Fe2-N4	89.75(9)	90.05(15)	89.6(5)	91.6(3)	89.50(10)	91.0(3)
N2-Fe2-N5	177.84(9)	171.70(16)	178.7(6)	173.9(4)	178.95(11)	176.7(4)
N2-Fe2-N6	88.27(10)	88.58(16)	87.4(6)	87.9(4)	89.36(11)	88.5(3)
N2-Fe2-N7	90.36(10)	92.86(19)	90.2(6)	93.4(4)	88.75(11)	92.3(3)
N4-Fe2-N5	92.41(9)	85.25(16)	91.8(5)	84.2(4)	91.40(10)	87.1(3)
N4-Fe2-N6	90.99(10)	86.63(16)	90.4(6)	85.6(4)	92.39(11)	87.0(3)
N4-Fe2-N7	90.62(10)	91.78(18)	91.5(6)	93.1(4)	89.70(12)	93.7(3)
N5-Fe2-N6	91.66(10)	84.33(16)	92.4(6)	87.3(4)	91.16(11)	88.7(4)
N5-Fe2-N7	89.65(10)	94.11(19)	89.9(6)	91.3(4)	90.71(12)	90.5(4)
N6-Fe2-N7	177.88(10)	177.9(2)	176.9(6)	178.1(4)	177.17(11)	178.9(3)

Table S2. Selected bond lengths around metal centers for **1**, **2** and **3**.

Bond Lengths (Å)						
	1$^{100\ K}$	**1**$^{300\ K}$	**2**$^{100\ K}$	**2**$^{300\ K}$	**3**$^{100\ K}$	**3**$^{300\ K}$
Fe1-C1	1.923(3)	1.917(4)	1.927(18)	1.912(11)	1.923(3)	1.914(10)
Fe1-C2	1.922(3)	1.930(4)	1.905(16)	1.889(11)	1.931(3)	1.923(9)
Fe1-C3	1.947(3)	1.937(6)	1.97(2)	1.936(16)	1.932(4)	1.923(15)
Fe1-N8	2.007(2)	2.016(4)	1.990(14)	2.000(10)	2.010(2)	1.996(8)
Fe1-N9	2.009(2)	2.008(4)	2.012(13)	1.999(8)	1.996(3)	2.008(7)
Fe1-N10	1.985(2)	2.001(5)	1.968(15)	1.977(12)	1.998(3)	1.977(11)
Fe2-N1	1.947(2)	2.104(4)	1.926(14)	2.088(10)	1.938(2)	2.030(8)
Fe2-N2	1.942(2)	2.117(4)	1.904(13)	2.079(9)	1.948(2)	2.034(7)
Fe2-N4	2.005(2)	2.211(4)	2.004(14)	2.221(10)	1.997(2)	2.130(6)
Fe2-N5	2.001(2)	2.249(4)	1.977(12)	2.183(10)	2.009(2)	2.123(8)
Fe2-N6	2.018(2)	2.259(5)	2.033(14)	2.219(11)	2.008(3)	2.110(10)
Fe2-N7	1.945(3)	2.071(5)	1.887(17)	2.099(14)	1.958(3)	2.034(13)

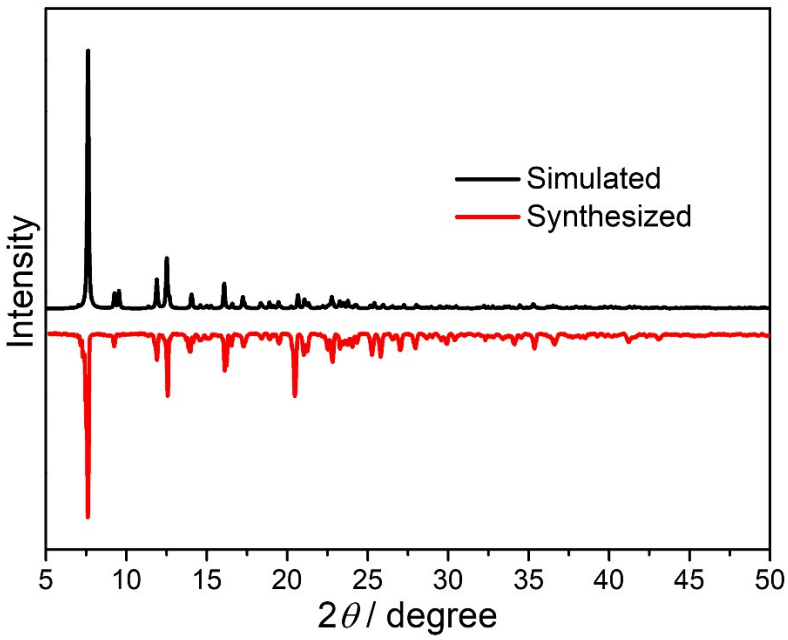

Fig.S1 X-ray powder diffraction diagrams of **1** (red) and the simulated spectra from single crystal data at 300 K (black).

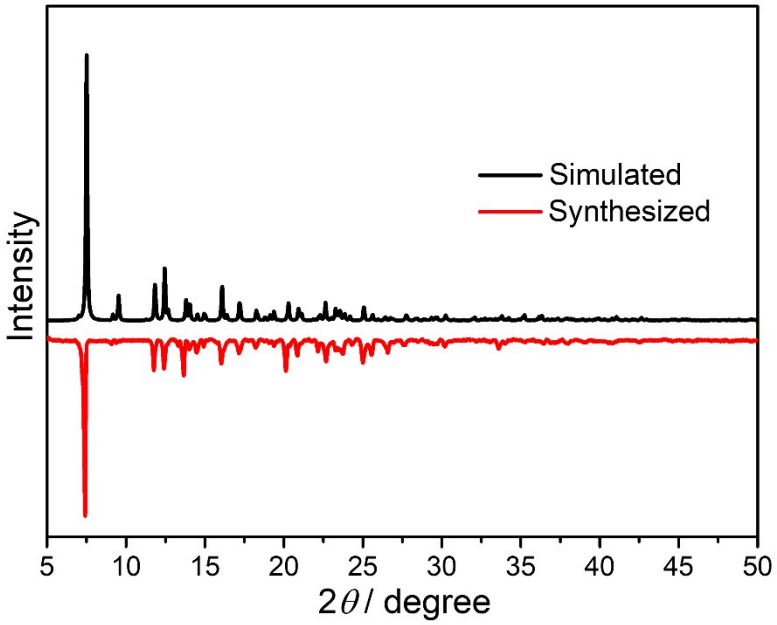

Fig.S2 X-ray powder diffraction diagrams of **2** (red) and the simulated spectra from single crystal data at 300 K (black).

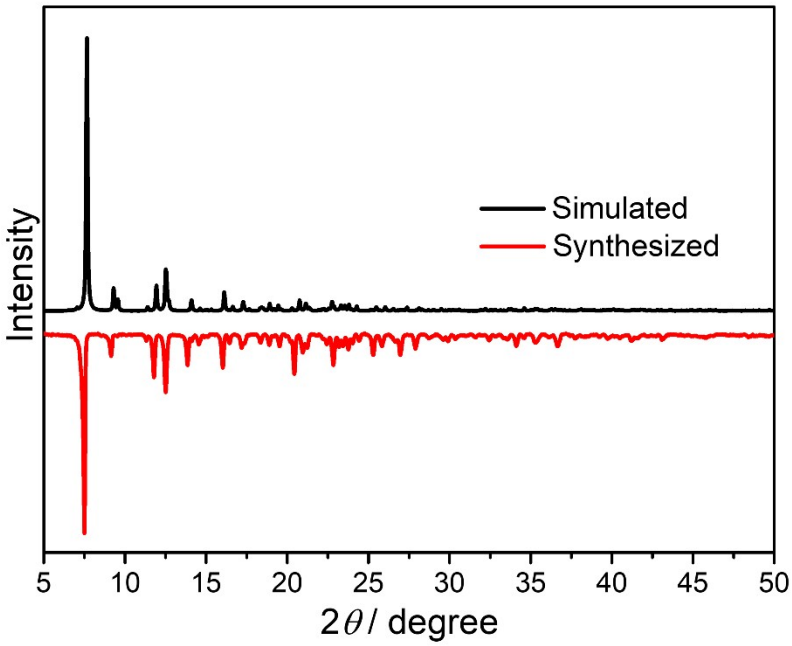

Fig.S3 X-ray powder diffraction diagrams of **3** (red) and the simulated spectra from single crystal data at 300 K (black)

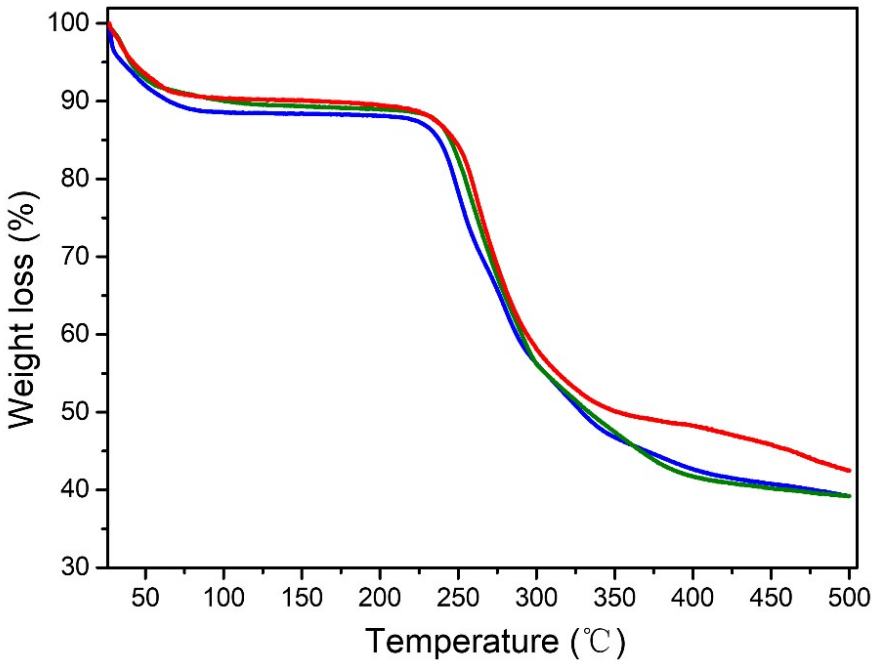

Fig.S4 Thermogravimetric (TGA) plot of **1** (blue), **2** (olive) and **3** (red) at a rate of 3 K/min under an argon atmosphere.

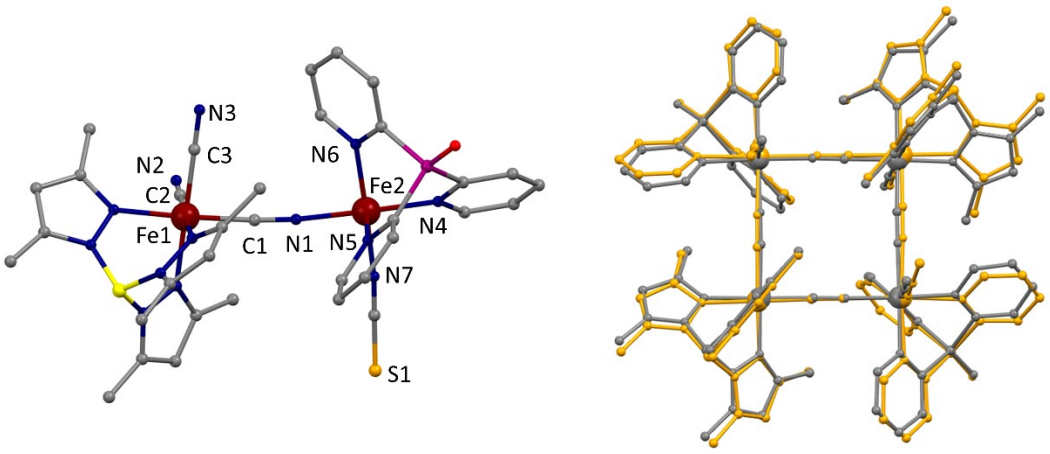

Fig.S5 (Left) The asymmetric unit of **1** at 100 K and (Right) overlapped X-ray crystal structures for **1** at 100 K (gray) and 300 K (orange), Hydrogen atoms and solvents are omitted for clarity.

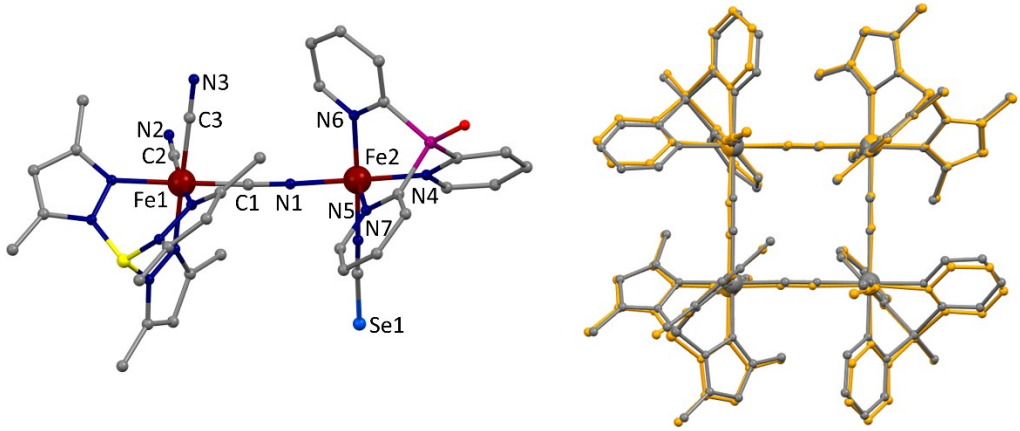

Fig.S6 (Left) The asymmetric unit of **2** at 100 K and (Right) overlapped X-ray crystal structures for **2** at 100 K (gray) and 300 K (orange), Hydrogen atoms and solvents are omitted for clarity.

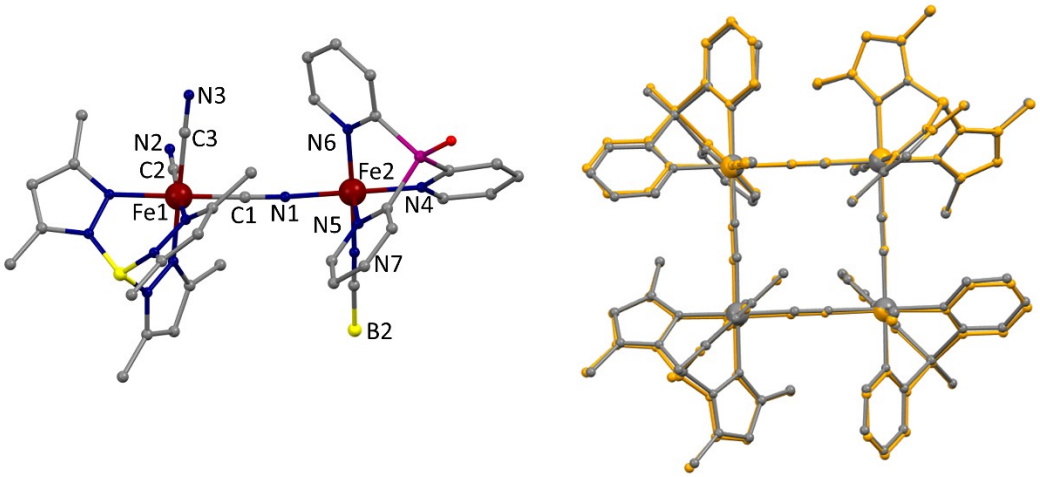

Fig.S7 (Left) The asymmetric unit of **3** at 100 K and (Right) overlapped X-ray crystal structures for **3** at 100 K (gray) and 300 K (orange), Hydrogen atoms and solvents are omitted for clarity.

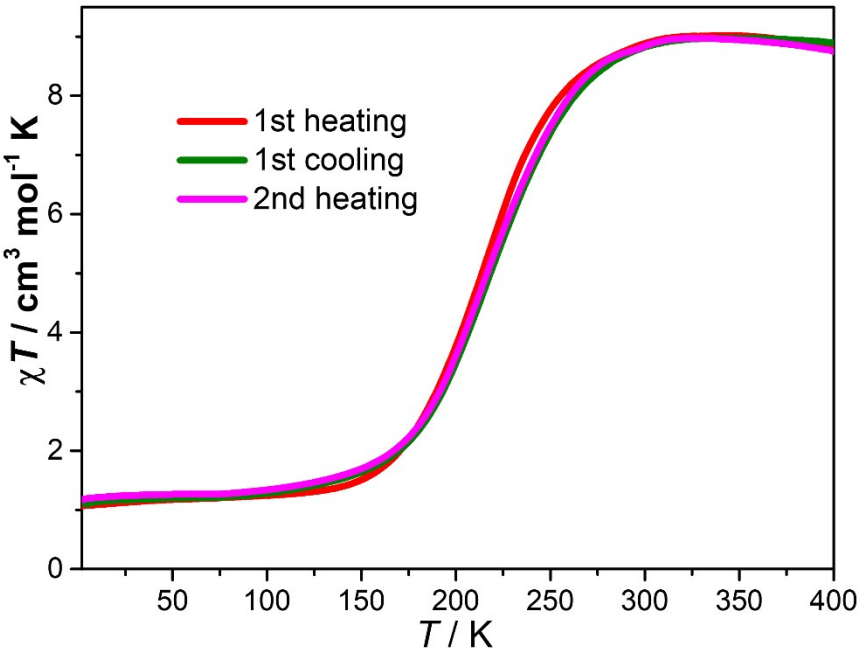

Fig.S8 Variable-temperature susceptibilities of **1** and its desovated phase in the cooling and heating cycle (scan rate: 2 K min^{-1}).

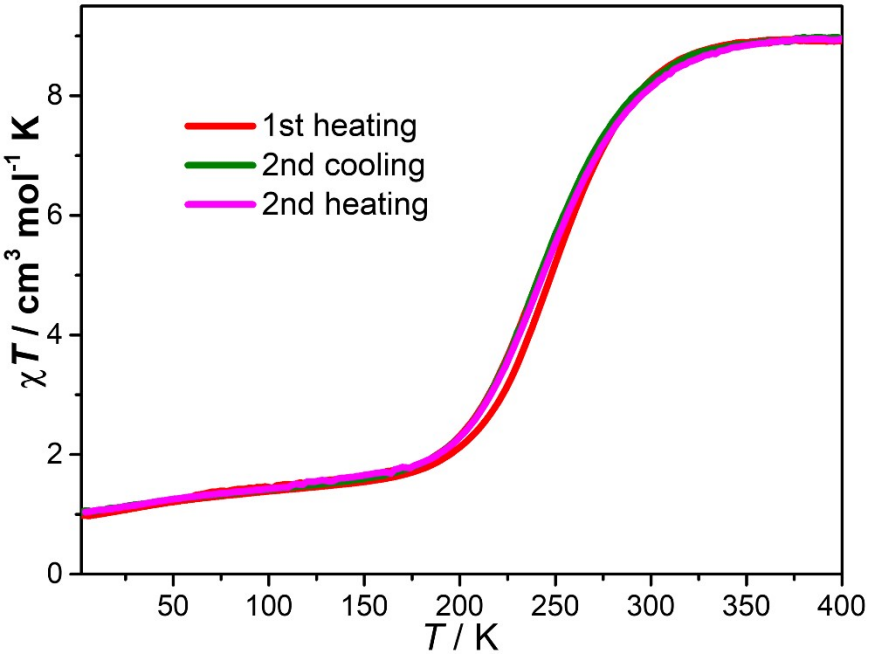

Fig.S9 Variable-temperature susceptibilities of **2** and its desovated phase in the cooling and heating cycle (scan rate: 2 K min^{-1}).

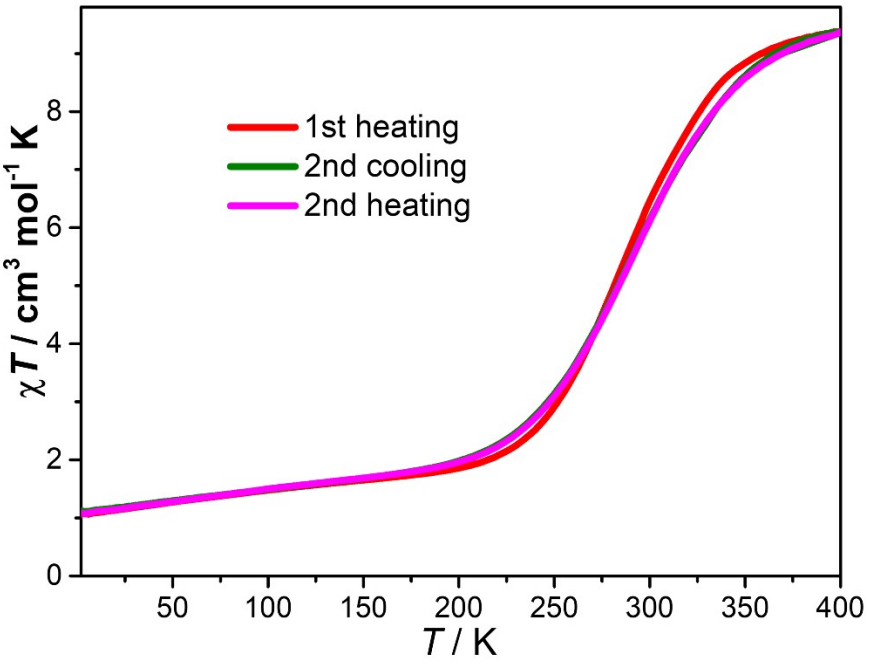

Fig.S10 Variable-temperature susceptibilities of **3** and its desovated phase in the cooling and heating cycle (scan rate: 2 K min^{-1}).

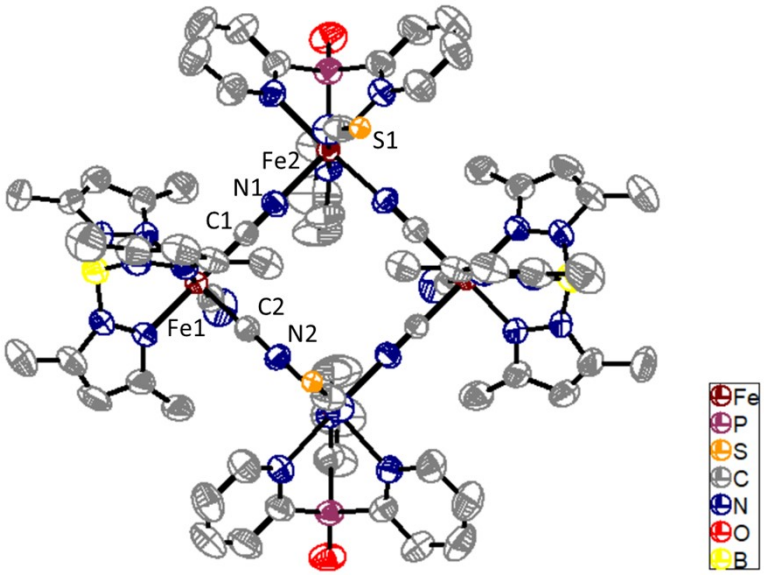

Fig.S11 Crystal structure of **1** at 300 K drawn with ellipsoids at the 50% probability level. The hydrogen atoms have been omitted for the sake of clarity.

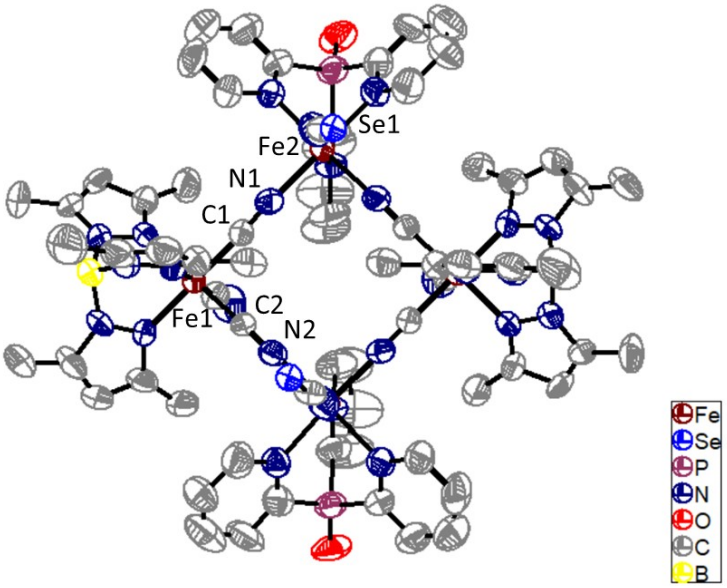

Fig.S12 Crystal structure of **2** at 300 K drawn with ellipsoids at the 50% probability level. The hydrogen atoms have been omitted for the sake of clarity.

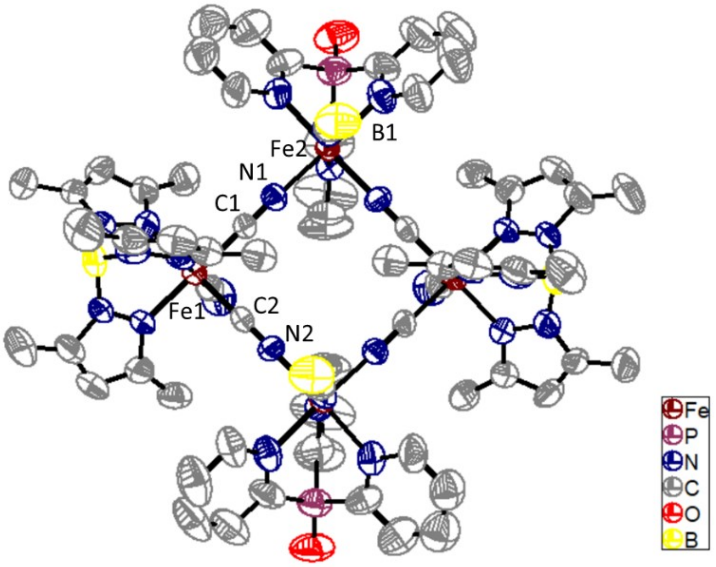

Fig.S13 Crystal structure of **3** at 300 K drawn with ellipsoids at the 50% probability level. The hydrogen atoms have been omitted for the sake of clarity.

Density Functional Theory Calculations

Investigation of the spin multiplicity of individual Fe sites in the $\{Fe^{III}_2Fe^{II}_2\}$ compounds using the full molecular structure.

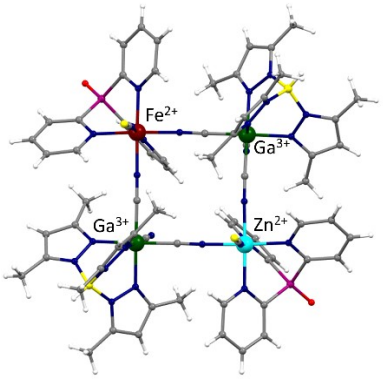

Fig. S14 Example of the structure of the compounds investigated with one Fe^{2+} ion replaced by Zn^{2+} ion and two Fe^{3+} ions replaced by two Ga^{3+} ions

Table S3. Energy calculated from a single-point-calculation for each Fe site in each structure.

Iron position	**Spin Multiplicity**	**Energy (cm^{-1})**					
		1^{100K}	**1**^{300K}	**2**^{100K}	**2**^{300K}	**3**^{100K}	**3**^{300K}
Fe1	2	0.0	0.0	0.0	0.0	0.0	0.0
	4	21864.3	13397.8	18673.3	19837.2	14023.3	14039.4
	6	22190.7	22160.0	22565.1	22604.1	22355.3	24216.6
Fe1A	2	0.0	0.0	0.0	0.0	0.0	0.0
	4	21864.9	13397.3	18673.7	19837.4	14023.1	14039.8
	6	22191.2	22160.2	22565.1	22603.7	22355.4	24217.3
Fe2	1	0.0	5645.9	0.0	4313.1	0.0	0.0
	3	9697.9	6710.6	10201.4	6042.1	9998.2	5177.6
	5	11852.2	0.0	13574.5	0.0	12661.8	1997.1
Fe2A	1	0.0	5646.7	0.0	4330.6	0.0	0.0
	3	9698.2	6710.6	10827.4	6059.2	10540.9	4880.2
	5	11852.6	0.0	13574.3	0.0	12658.8	1992.4

Table S4. Interaction of $\{Fe^{III}_2Fe^{II}_2\}$ compound at low temperature (100 K).

Compound	$E_{High\text{-}Spin} - E_{BrokenSym}$ (cm^{-1})	$J(1)^{1\text{-}3}$ (cm^{-1})	$J(2)^4$ (cm−1)	$J(3)^{5,6}$ (cm−1)
1	-0.736	0.74	0.37	0.74
2	2.010	-2.01	-1.00	-2.01
3	0.920	-0.92	-0.46	-0.92

The exchange parameters J(1) to J(3) are calculated in three different ways as following:

$$J(1) = \frac{-\left(E_{HS} - E_{BS}\right)}{S_{max}^{\ 2}};\ J(2) = \frac{-\left(E_{HS} - E_{BS}\right)}{S_{max} \times \left(S_{max} + 1\right)};\ J(3) = \frac{-\left(E_{HS} - E_{BS}\right)}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}}.$$

Reference:

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