Reversible Crystal-to-Crystal Transformation and Spin Crossover (SCO) Behaviour of two Linear Trinuclear Fe(II) Complexes

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Experimental Section

Materials and Physical Measurements

All the commercial reagents and solvents were used without further purification unless otherwise stated. IR spectra were recorded as pressed KBr pellets on a Bruker Tensor 27 spectrophotometer. The C, H and N elemental analyses were carried out with an Elementar Vario-EL CHN elemental analyzer. Thermogravimetric (TG) analyses of **1** and **1a** were carried out on a NETZSCH TG209F3 thermogravimetric analyzer in flowing N_2 with a heating rate of 10 ℃/min between 30 and 700℃. Powder X-ray diffraction (PXRD) intensities were measured at room temperature using a Bruker D8 X-ray diffractometer (Cu-Kα, λ = 1.54056 Å) and the calculated patterns were created with Mercury. Magnetic susceptibility measurements between 2 and 300 K were carried out using a SQUID magnetometer with a 1000 G field. The **1a** sample for magnetic measurements was obtained by dehydrating the powder of **1** inside the SQUID cavity under 120 °C for 4 hours.

X-ray crystallography and data collection

The crystals were filtered from the solution and immediately coated with hydrocarbon oil on the microscope slide. Suitable crystals were mounted on glass fibers with silicone grease and

placed in a Bruker Smart APEX(II) area detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods and refined with a full-matrix least-squares technique using the SHELXTL program package.[1] Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystallographic Data Centre under reference numbers CCDC 1552122 for **1** at 100 K, 1054576 for **1** at 150 K, 1054573 for **1** at 296 K, 1503110 for **1a**·at 100 K, 1503111 for **1a**·at 150 K**,** 1503112 for **1a**·at 200 K**,** 1503114 for **1a**·at 296 K. The summary of crystallographic data and structural refinements for **1**·and **1a**·is in Table S1 and Table S2, respectively.

Syntheses of 1 and 1a

$[Fe_3(NH_2\text{-trz})_6(SCN)_5(H_2O)](SCN)\cdot 4H_2O$ (**1**).

A mixture of $FeSO_4$ (0.121g, 0.8 mmol), 4-amino-triazole (0.135 g, 1.6 mmol) and NH_4SCN (0.122g, 1.6 mmol) in methanol (5 mL) and distilled water (10 mL) was heated in a stainless steel reactor with 25 mL sealed Teflon liner at 100℃ for 72 h and then cooled to room temperature at a rate of 5 ℃/h. The resultant mixture was filtered and colorless block crystals were obtained by slow evaporation of the filtrate after several days, washed with distilled water and dried in air. Yield: 60.3% for 2 based on Fe^{2+}. Elemental Anal. Calcd for $2\cdot 4H_2O$ of $C_{18}H_{34}Fe_3N_{30}O_5S_6$ (%): C, 19.47; H, 3.086; N,37.84; S, 17.323. Found(%): C, 19.71; H, 2.908; N, 38.27; S, 17.077. FT-IR (KBr, cm^{-1}): 3306s, 3109s, 2077s, 1618m, 1534m, 1392w, 1215m, 1082m, 1029m, 995m, 879w, 620m, 475w.

$[Fe_3(NH_2\text{-trz})_6(SCN)_5(H_2O)]_n(SCN)_n$ (**1a**).

Crystals of **1** were heated to 400 K for 30 min and then cooled to room temperature under N_2 atmosphere. Anal. Calcd (%) for **1a** of $C_{18}H_{24}Fe_3N_{30}S_6$ (%): C, 21.18; H, 2.37; N, 41.18, Found (%): C, 20.87; H, 2.59; N, 41.03. FT-IR (KBr, cm^{-1}): 3290s, 3110s, 2080s, 1610m, 1540m, 1390w, 1210m, 1080m, 1030m, 995m, 866w, 619m, 473w.

1. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr*., 2008, **64**, 112.

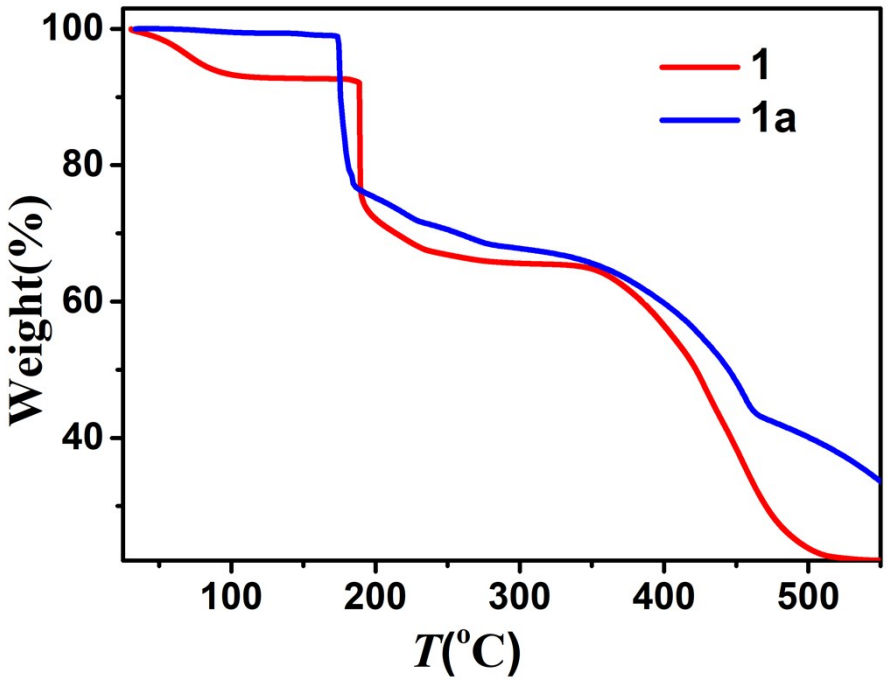

Fig. S1. Thermo-gravimetric analysis curves for **1** (red) and **1a** (blue).

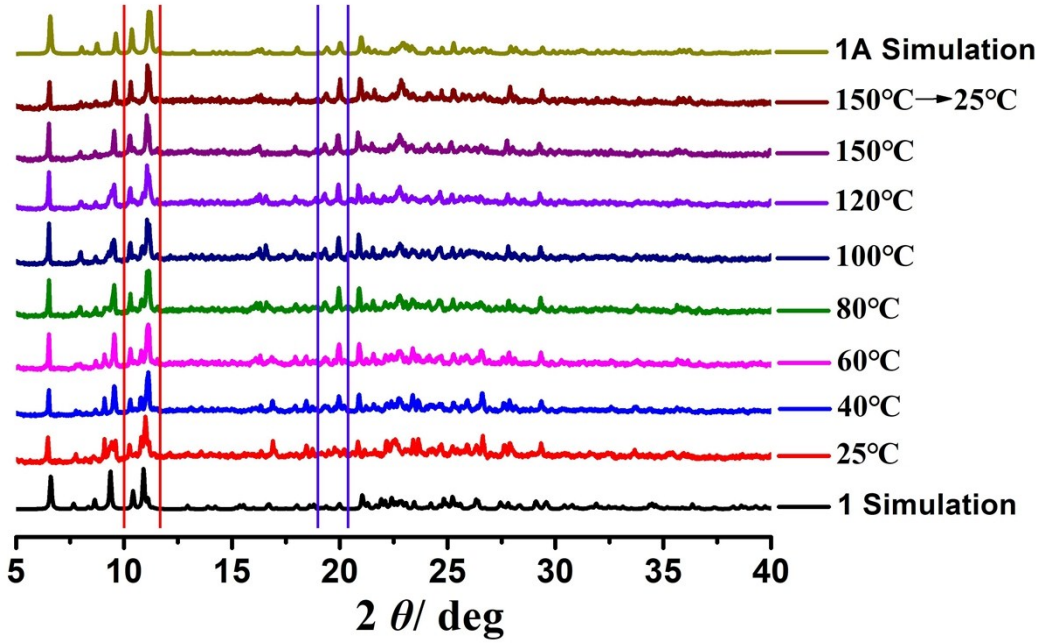

Fig. S2. Variable temperature X-ray powder diffraction data for **1** from 25 to 150 °C and then cool down to 25 °C.

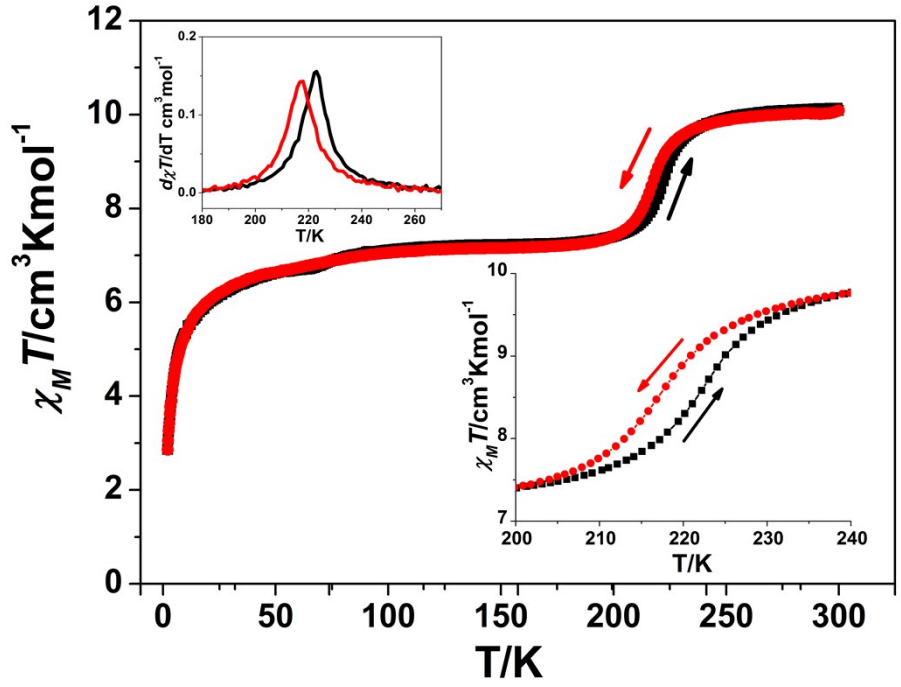

Fig. S3. Plots of $\chi_M T$ vs. T for **1**. The insert are the hysteresis and dχT/dT curves. The red line shows the cooling progress and the black indicates the heating progress.

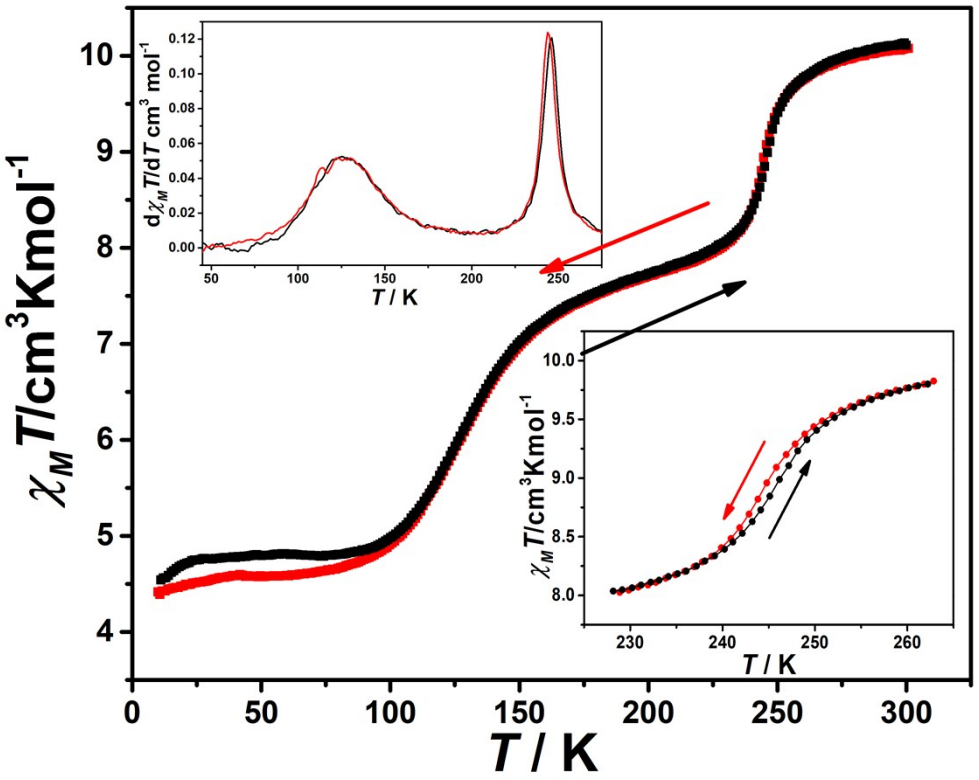

Fig. S4. Plots of $\chi_M T$ vs. T for **1a**. The insert are the hysteresis and the dχT/dT curves. The red line shows the cooling progress and the black indicates the heating progress.

Table S1. Crystal data and structure refinement for **1.**

Table S2. Crystal data and structure refinement for **1a**.

	1a
Empirical formula	$C_{18}H_{24}Fe_3N_{30}S_6$

	1		
Empirical formula		$C_{18}H_{34}Fe_3N_{30}O_5S_6$	
Formula weight		1110.66	
Temperature	100(2) K	150(2) K	296(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/ Å	11.5773(4)	11.5947(4)	11.7202(3)
b/Å	23.0123(9)	23.0335(7)	23.0483(6)
c/Å	16.4758(7)	16.4924(5)	16.8628(4)
b/°	103.2580(10)	103.262(2)°	103.4440(10)
V/Å^3	4272.5(3)	4287.1(2)	4430.34(19)
Z	4	4	4
$\rho_{calc,}$ (mg/mm^3)	1.727	1.721	1.665
μ(MoKα), (mm−1)	1.371	1.366	1.310
F(000)	2264	2264	2104
Reflections collected	61397	51186	72398
Independent reflections	9796	9846	10292
R(int)	0.0730	0.0662	0.0644
Goodness-of-fit on F^2	1.030	1.057	1.066
Final R indices [I>2sigma(I)]	R_1 = 0.0582, wR_2 = 0.1419	R_1 = 0.0500, wR_2 = 0.1354	R_1 = 0.0502, wR_2 = 0.1373
R indices (all data)	R_1 = 0.0888, wR_2 = 0.1598	R_1 = 0.0754, wR_2 = 0.1507	R_1 = 0.0787, wR_2 = 0.1542
Largest diff. peak and hole	2.327 and -1.869 e.Å^{-3}	1.553 and -0.993 e.Å^{-3}	2.140 and -0.980 e.Å^{-3}

[a]R_1 = $\sum||F_o|-|F_c||/\sum|F_o|$. [b]$wR_2$ = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Formula weight	1020.58			
Temperature	100(2) K	150(2) K	200(2) K	293(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/ Å	11.3202(5)	11.3813(6)	11.4352(6)	11.5569(5)
b/Å	21.2403(12)	21.4624(12)	21.6118(12)	21.7106(11)
c/Å	16.7606(9)	16.7387(10)	16.7548(9)	17.1108(9)
β/°	102.984(2)	103.0041(15)	103.0361(15)	103.4778(14)
V/Å^3	3927.0(4) Å^3	3983.9(4) Å^3	4034.0(4) Å^3	4175.0(4) Å^3
Z	4	4	4	4
Density (calculated)	1.726 Mg/m^3	1.702 Mg/m^3	1.680 Mg/m^3	1.624 Mg/m^3
Absorption coefficient	1.474 mm^{-1}	1.453 mm^{-1}	1.435 mm^{-1}	1.387 mm^{-1}
F(000)	2064	2064	2064	2064
Reflections collected	25564	25754	25803	25820
Independent reflections	7188	7275	7346	7603
R(int)	0.1762	0.1719	0.1737	0.0688
Goodness-of-fit on F^2	1.043	1.033	1.035	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0628, wR2 = 0.1559	R1 = 0.0664, wR2 = 0.1644	R1 = 0.0662, wR2 = 0.1635	R1 = 0.0621, wR2 = 0.1550
R indices (all data)	R1 = 0.1103, wR2 = 0.1863	R1 = 0.1198, wR2 = 0.2034	R1 = 0.1199, wR2 = 0.2044	R1 = 0.1322, wR2 = 0.2039
Largest diff. peak and hole	0.997 and -1.286 e.Å^{-3}	1.049 and -1.254 e.Å-3	1.072 and -1.061 e.Å^{-3}	0.683 and -0.669 e.Å^{-3}

Table S3. Information of hydrogen bonds in complex **1** obtained by PLATON tables.

Hydrogen Bond	Bond Distances (Å)	Bond Angles (°)	Symmetry of the acceptor
O1--H1A...S2	3.221(4)	146	1/2+x,1/2-y,-1/2+z
O1--H1B....N30	2.731(8)	169	2-x,1-y,1-z
O2--H2B...N6	3.174(6)	180	
O3--H3A...N13	3.030(18)	145	-1+x,y,z
O3--H3A...N14	3.007(19)	178	-1+x,y,z
O3--H3A...N15	3.176(17)	128	-1+x,y,z
O3--H3B...S2	3.03(2)	179	-1+x,y,-1+z

N4--H4A...S1	3.414(5)	142	1-x,-y,2-z
N4--H4B...S6	3.681(5)	155	x,-1+y,z
O4--H4C...N16	2.948(7)	178	1-x,-y,1-z
N8--H8A...S3	3.331(4)	152	1+x,y,z
N12--H12A...O4	3.069(8)	174	1/2+x,1/2-y,1/2+z
N12--H12B...S4	3.599(5)	150	-1/2+x,1/2-y,1/2+z
N16--H16A...S1	3.251(4)	111	2-x,-y,2-z
N16--H16A...S5	3.490(4)	130	2-x,-y,1-z
N16--H16B...N30	2.904(8)	124	x,-1+y,z
N20--H20B...S4	3.381(5)	142	1/2+x,1/2-y,1/2+z
N24--H24A...N29	3.146(6)	168	1-x,-y,1-z
N24--H24B...S6	3.368(4)	131	1-x,1-y,1-z
C1--H1...N24	3.446(6)	169	1-x,-y,1-z
C3--H3...O3	3.05(2)	152	1+x,y,z
C4--H4...N12	3.265(6)	151	1/2+x,1/2-y,1/2+z
C5--H5...N8	3.527(6)	171	-1/2+x,1/2-y,-1/2+z
C7--H7...O2	3.272(7)	171	
C9--H9...S6	3.523(5)	169	3/2-x,-1/2+y,3/2-z
C10--H10...N26	3.279(6)	147	1/2+x,1/2-y,-1/2+z
C11--H11...S5	3.644(5)	158	1-x,-y,1-z
C12--H12...N4	3.414(7)	164	1-x,-y,1-z

Table S4. Information of hydrogen bonds in complex **1a** obtained by PLATON tables.

Hydrogen Bond	Bond Distances (Å)	Bond Angles (°)	Symmetry of the acceptor
N4--H4A...N20	3.235(9)	125	1/2-x,-1/2+y,3/2-z
N8--H8A...S2	3.363(9)	141	-1+x,y,z
N12--H12A...S4	3.650(10)	154	1/2+x,1/2-y,-1/2+z
N16--H16A...S6	3.423(11)	139	
N16--H16B...S5	3.486(8)	138	-x,-y,2-z
N20--H20A...S6	3.694(11)	157	1/2-x,1/2+y,3/2-z
N20--H20B...S2	3.670(7)	149	-1/2+x,1/2-y,1/2+z
N24--H24A...N30	3.032(15)	153	1-x,-y,2-z
N24--H24B...N29	3.322(10)	171	1-x,-y,2-z
C1--H1...N24	3.469(10)	175	1-x,-y,2-z
C2--H2...S1	3.602(9)	148	1-x,-y,1-z
C5--H5...N8	3.396(10)	174	1/2+x,1/2-y,1/2+z
C10--H10...N26	3.329(10)	142	-1/2+x,1/2-y,1/2+z
C10--H10...N27	3.281(10)	137	-1/2+x,1/2-y,1/2+z
C11--H11...S5	3.601(8)	158	1-x,-y,2-z
C12--H12...N4	3.492(9)	163	1-x,-y,2-z

Table S5. Selected bond distances for complex **1** at different temperatures.

Selected bonds	Bond Distances (Å)

	296(2) K	150(2) K	100(2) K
Fe1-N1	2.173(3)	2.013(3)	1.995(3)
Fe1-N5	2.172(3)	2.021(3)	2.005(3)
Fe1-N9	2.147(3)	2.010(3)	1.993(4)
Fe1-N13	2.166(3)	2.017(3)	1.996(4)
Fe1-N17	2.198(3)	2.035(3)	2.013(3)
Fe1-N21	2.193(3)	2.021(3)	2.005(3)
Fe2-N2	2.176(3)	2.163(3)	2.150(3)
Fe2-N6	2.233(2)	2.213(4)	2.197(4)
Fe2-N10	2.176(3)	2.161(3)	2.149(3)
Fe2-N25	2.110(3)	2.107(3)	2.104(3)
Fe2-N26	2.120(3)	2.103(3)	2.100(4)
Fe2-N27	2.128(4)	2.117(4)	2.122(5)
Fe3-O1	2.123(4)	2.117(4)	2.117(4)
Fe3-N14	2.221(3)	2.192(3)	2.196(3)
Fe3-N18	2.219(3)	2.197(3)	2.197(4)
Fe3-N22	2.176(4)	2.154(4)	2.153(4)
Fe3-N28	2.108(4)	2.104(4)	2.115(5)
Fe3-N29	2.130(4)	2.114(4)	2.120(4)

Table S6. Selected bond angles for complex **1** at different temperatures.

Selected bond angles	bond angles (°)		
	296(2) K	150(2) K	100(2) K
N1-Fe1-N5	90.50(10)	91.95(12)	91.91(14)
N1-Fe1-N9	93.27(10)	93.29(13)	93.34(14)
N1-Fe1-N13	87.20(11)	86.77(13)	86.69(14)
N1-Fe1-N17	174.94(11)	176.54(13)	176.70(14)
N1-Fe1-N21	86.96(11)	86.85(12)	86.92(14)
N5-Fe1-N9	88.88(10)	89.46(13)	89.66(14)
N5-Fe1-N13	90.07(11)	88.83(13)	88.67(14)
N5-Fe1-N17	91.19(10)	89.08(12)	89.17(14)
N5-Fe1-N21	176.67(11)	177.33(14)	177.30(15)
N9-Fe1-N13	178.85(12)	178.30(13)	178.32(14)
N9-Fe1-N17	91.53(11)	90.02(13)	89.79(14)
N9-Fe1-N21	89.11(11)	88.23(13)	87.98(14)
N13-Fe1-N17	88.03(12)	89.95(13)	90.22(14)
N13-Fe1-N21	91.96(12)	93.48(13)	93.70(14)
N17-Fe1-N21	91.51(11)	92.26(12)	92.13(14)
N2-Fe2-N6	86.84(10)	84.24(12)	84.10(13)
N2-Fe2-N10	90.47(11)	87.65(11)	87.18(13)
N2-Fe2-N25	87.63(12)	87.39(12)	88.17(14)
N2-Fe2-N26	172.35(12)	171.23(14)	171.51(14)
N2-Fe2-N27	92.28(12)	92.97(14)	93.20(14)

N6-Fe2-N10	87.03(10)	83.06(12)	82.92(13)
N6-Fe2-N25	92.75(12)	94.08(13)	94.31(16)
N6-Fe2-N26	86.17(13)	87.45(13)	87.61(13)
N6-Fe2-N27	174.54(12)	173.08(12)	173.31(13)
N10-Fe2-N25	178.10(13)	174.50(13)	174.81(15)
N10-Fe2-N26	92.29(12)	94.14(12)	93.63(13)
N10-Fe2-N27	87.58(11)	90.51(13)	90.84(13)
N25-Fe2-N26	89.58(13)	90.42(13)	90.63(14)
N25-Fe2-N27	92.61(14)	92.11(13)	91.72(16)
N26-Fe2-N27	94.96(14)	95.60(14)	95.24(14)
O1-Fe3-N14	86.16(13)	87.43(13)	87.81(13)
O1-Fe3-N18	93.82(13)	94.79(13)	95.04(13)
O1-Fe3-N22	176.65(13)	176.74(12)	176.73(13)
O1-Fe3-N28	92.56(16)	92.92(15)	93.01(16)
O1-Fe3-N29	88.74(14)	88.78(13)	88.51(16)
N14-Fe3-N18	87.15(11)	84.52(12)	83.83(13)
N14-Fe3-N22	92.16(12)	89.45(13)	89.04(13)
N14-Fe3-N28	174.54(15)	173.66(14)	173.01(16)
N14-Fe3-N29	90.28(13)	91.75(12)	91.95(16)
N18-Fe3-N22	88.99(13)	85.86(13)	85.46(14)
N18-Fe3-N28	87.64(14)	89.15(14)	89.18(16)
N18-Fe3-N29	176.24(13)	174.71(13)	174.37(16)
N22-Fe3-N28	89.38(15)	90.28(15)	90.23(16)
N22-Fe3-N29	88.37(13)	90.36(13)	90.75(16)
N28-Fe3-N29	95.01(15)	94.58(14)	95.01(18)

Table S7. Selected bond distances for complex **1a** at different temperatures.

Selected bonds	Bond Distances (Å)		
	293(2) K	150(2) K	100(2) K
Fe1-N1	2.166(6)	1.991(6)	1.969(6)
Fe1-N5	2.162(5)	1.997(5)	1.990(5)
Fe1-N9	2.152(6)	1.979(6)	1.966(6)
Fe1-N13	2.149(6)	1.982(6)	1.978(6)
Fe1-N17	2.197(6)	2.008(6)	2.006(6)
Fe1-N21	2.201(5)	2.006(5)	2.007(5)
Fe2-N2	2.172(6)	2.072(6)	1.962(6)
Fe2-N6	2.217(6)	2.112(6)	1.982(6)
Fe2-N10	2.179(5)	2.081(5)	1.976(5)
Fe2-N25	2.123(7)	2.046(7)	1.956(5)
Fe2-N26	2.130(7)	2.063(8)	1.976(6)
Fe2-N27	2.133(8)	2.067(8)	1.979(6)
Fe3-N14	2.221(5)	2.196(5)	2.190(5)
Fe3-N18	2.211(6)	2.186(6)	2.192(6)

Fe3-N22	2.217(6)	2.189(6)	2.187(6)
Fe3-N28	2.108(7)	2.109(5)	2.116(5)
Fe3-N29	2.119(7)	2.107(7)	2.100(6)
Fe3-S3_a	2.604(3)	2.558(2)	2.550(2)

Symmetry code: a = -1/2+x,1/2-y,1/2+z.

Table S8. Selected bond angles for complex **1a** at different temperatures.

Selected bond angles	bond angles (°)		
	296(2) K	150(2) K	100(2) K
N1-Fe1-N5	90.2(2)	91.3(2)	90.2(2)
N1-Fe1-N9	92.5(2)	92.4(2)	91.2(2)
N1-Fe1-N13	88.5(2)	87.8(2)	88.4(2)
N1-Fe1-N17	176.8(2)	178.0(2)	178.7(2)
N1-Fe1-N21	88.6(2)	88.0(2)	88.1(2)
N5-Fe1-N9	88.1(2)	89.2(2)	88.7(2)
N5-Fe1-N13	92.1(2)	90.3(2)	90.5(2)
N5-Fe1-N17	90.3(2)	89.6(2)	90.2(2)
N5-Fe1-N21	175.9(2)	176.6(2)	176.0(2)
N9-Fe1-N13	179.0(2)	179.4(2)	179.1(2)
N9-Fe1-N17	90.7(2)	89.4(2)	90.1(2)
N9-Fe1-N21	88.0(2)	87.5(2)	87.8(2)
N13-Fe1-N17	88.4(2)	90.4(2)	90.3(2)
N13-Fe1-N21	91.8(2)	93.1(2)	93.0(2)
N17-Fe1-N21	91.1(2)	91.3(2)	91.7(2)
N2-Fe2-N6	86.7(2)	85.7(2)	88.9(2)
N2-Fe2-N10	91.5(2)	88.9(2)	91.2(2)
N2-Fe2-N25	88.2(3)	88.7(2)	87.9(2)
N2-Fe2-N26	89.9(2)	91.1(2)	89.8(2)
N2-Fe2-N27	176.0(3)	174.8(3)	178.8(2)
N6-Fe2-N10	85.4(2)	84.0(2)	87.8(2)
N6-Fe2-N25	94.8(2)	96.6(2)	93.1(2)
N6-Fe2-N26	172.7(2)	172.7(2)	177.8(2)
N6-Fe2-N27	89.6(3)	89.6(3)	90.3(2)
N10-Fe2-N25	179.6(3)	177.5(3)	178.7(3)
N10-Fe2-N26	88.2(2)	89.4(2)	90.5(2)
N10-Fe2-N27	86.8(3)	88.3(3)	87.9(2)
N25-Fe2-N26	91.6(3)	90.0(3)	88.6(2)
N25-Fe2-N27	93.6(3)	94.2(3)	92.9(2)
N26-Fe2-N27	93.7(3)	93.2(3)	91.1(2)
N14-Fe3-N18	86.7(2)	83.7(2)	83.6(2)
N14-Fe3-N22	89.6(2)	85.9(2)	85.55(19)
N14-Fe3-N28	175.4(2)	173.1(2)	172.4(2)
N14-Fe3-N29	90.1(2)	91.6(2)	91.4(2)

S3_a-Fe3-N14	87.10(17)	88.06(16)	88.52(13)
N18-Fe3-N22	87.5(2)	83.6(2)	83.5(2)
N18-Fe3-N28	88.9(2)	90.2(2)	90.3(2)
N18-Fe3-N29	173.4(2)	170.2(2)	169.6(2)
S3_a-Fe3-N18	96.48(17)	96.50(17)	95.23(16)
N22-Fe3-N28	89.1(2)	90.3(2)	89.2(2)
N22-Fe3-N29	86.7(3)	87.5(3)	87.0(2)
S3_a-Fe3-N22	174.62(18)	173.89(15)	174.03(14)
N28-Fe3-N29	94.2(3)	94.0(2)	93.9(2)
S3_a-Fe3-N28	94.5(2)	95.8(2)	96.62(16)
S3_a-Fe3-N29	89.1(2)	91.9(2)	93.81(17)

Symmetry code: a = -1/2+x,1/2-y,1/2+z.