

# High temperature spin crossover behaviour of mononuclear bis-(thiocyanato)iron(II) complexes with judiciously designed bidentate N-donor Schiff bases with varying substituent

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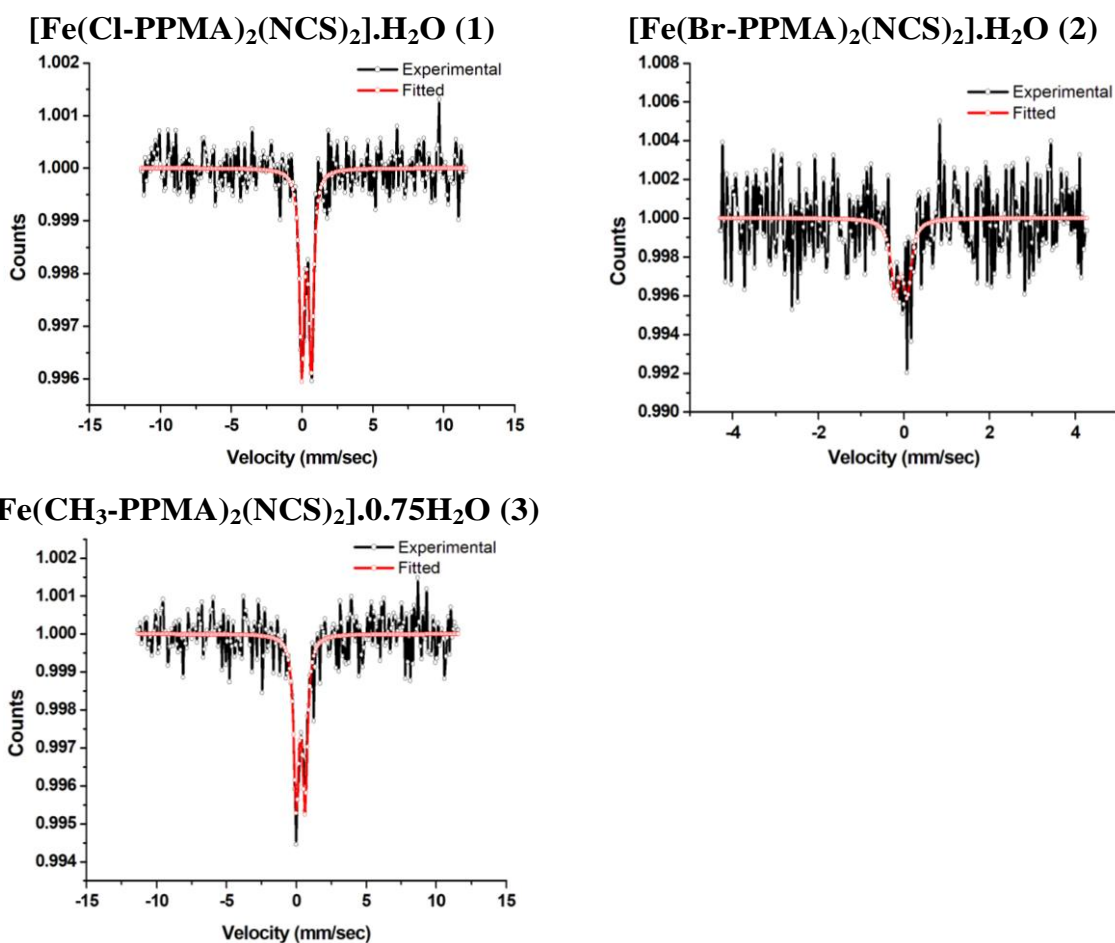
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## Supporting Information

Table S1 Mössbauer spectral data of 1-3 at 296 K

Compound	Isomer Shift ( $\delta$ ) (mm/sec)	Quadrupole splitting ( $\Delta EQ$ ) (mm/sec)
1	0.3163 $\pm$ 0.01196	0.6668 $\pm$ 0.02131
2	0.0626 $\pm$ 0.024	0.282 $\pm$ 0.071
3	0.2992 $\pm$ 0.01517	0.6308 $\pm$ .0259

Figure S1 Mössbauer spectra of complexes 1-3 at 296 K



**Table S2** Crystal data and structure refinement parameters for **1-3** at RT

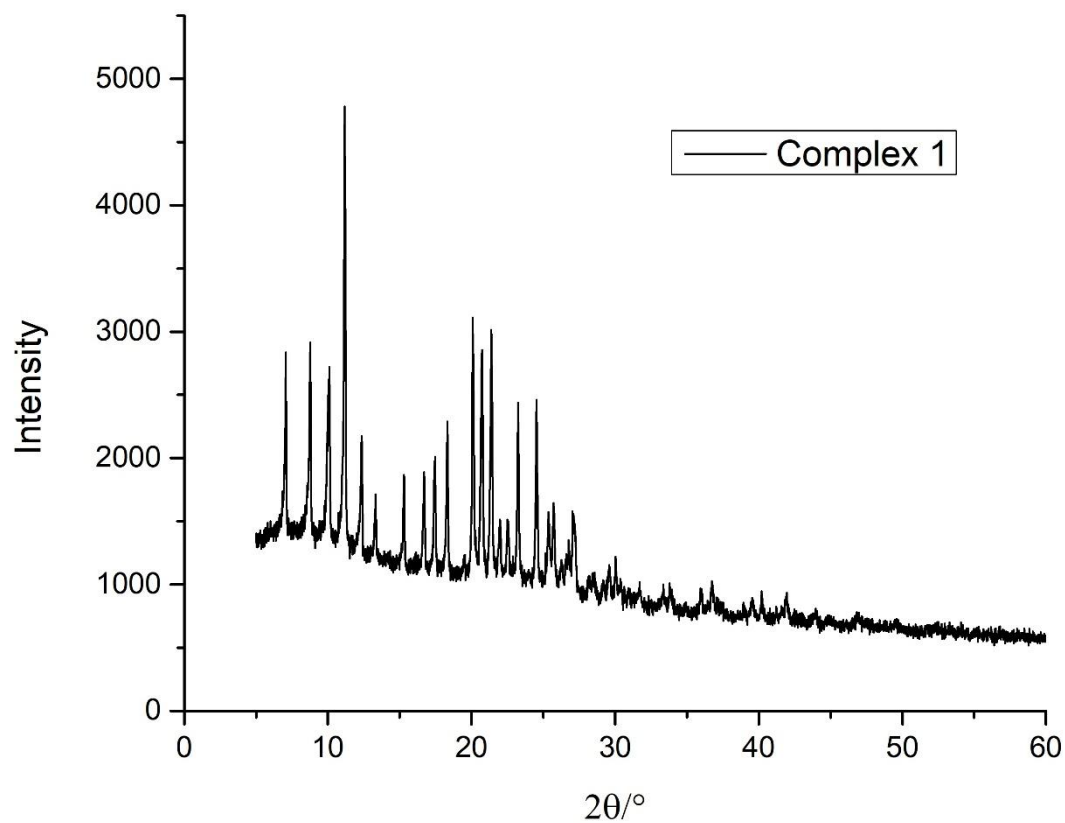
	<b>1<sup>RT</sup></b>	<b>2<sup>RT</sup></b>	<b>3<sup>RT</sup></b>
<b>Formula</b>	$C_{36}H_{26}N_6S_2Cl_2Fe$	$C_{38}H_{26}N_6S_2Br_2Fe$	$C_{40}H_{32}N_6S_2Fe$
<b>Formula Weight (g/mol)</b>	757.52	846.44	716.68
<b>Size (mm<sup>3</sup>)</b>	0.60×0.20×0.18	0.60×0.40×0.12	0.45×0.15×0.12
<b>Crystal system</b>	Tetragonal		
<b>Space group</b>	$P4_32_12$ (No. 96)	$P4_12_12$ (No. 92)	$P4_12_12$ (No. 92)
<b>a (Å)</b>	17.6439(7)	17.7700(8)	17.7428(6)
<b>c (Å)</b>	12.2291(5)	12.1810(5)	12.2100(4)
<b>Volume (Å<sup>3</sup>)</b>	3807.0(3)	3846.4(4)	3843.8(3)
<b><math>\rho_{calc}</math> (g.cm<sup>-3</sup>)</b>	1.322	1.462	1.238
<b><math>\mu</math> (mm<sup>-1</sup>)</b>	0.681	2.613	0.536
<b>GOF on <math>F^2</math></b>	1.028	1.009	1.015
<b><math>R_1, wR_2</math></b>	0.0372	0.0430	0.0386
<b><math>[I &gt; 2\sigma(I)]</math></b>	0.0726	0.0736	0.0768
<b><math>R_1, wR_2</math></b>	0.0609	0.0823	0.0597
<b>[all data]</b>	0.0828	0.0850	0.0848
<b>Largest diff. peak/hole (e.Å<sup>-3</sup>)</b>	0.238/-0.207	0.339/-0.365	0.282/-0.153
<b>Flack value</b>	-0.005(9)	-0.024(6)	-0.014(8)
<b>CCDC</b>	1978235	1978236	1978237

**Table S3** The coordination sphere parameters for **1-3** at RT

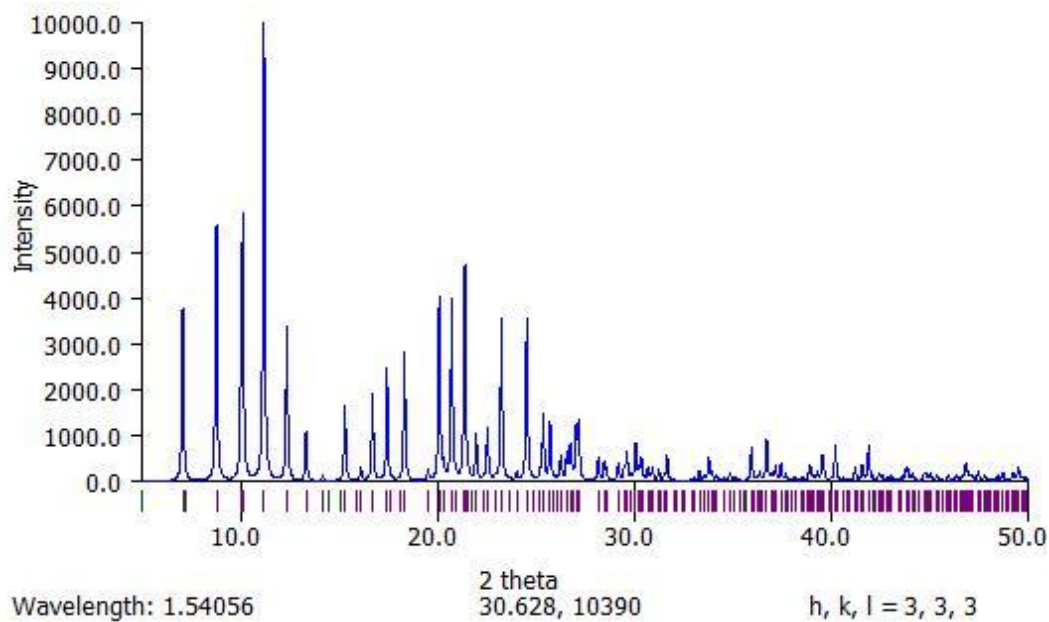
	<b>1<sup>RT</sup></b>	<b>2<sup>RT</sup></b>	<b>3<sup>RT</sup></b>
<b>Fe1-N1(pyridine)/Å</b>	1.977(2)	1.977(3)	1.971(2)
<b>Fe1-N2(imine)/Å</b>	1.970(2)	1.965(4)	1.958(2)
<b>Fe1-N3(NCS)/Å</b>	1.956(3)	1.967(4)	1.962(3)
<b>&lt;Fe-N&gt;/Å</b>	1.966	1.969	1.963
<b><math>\zeta</math>/Å</b>	0.041	0.027	0.033
<b><math>\Sigma</math>/°</b>	43.8	44.5	42.8
<b><math>\Theta</math>/°</b>	136	136	138
<b>Spin state</b>	LS	LS	LS

Symmetry code: (i) y, x, -z + 1. LS = Low spin.

**Figure S2** (a) Experimental and (b) simulated powder-XRD plots of complex **1** at 300 K.

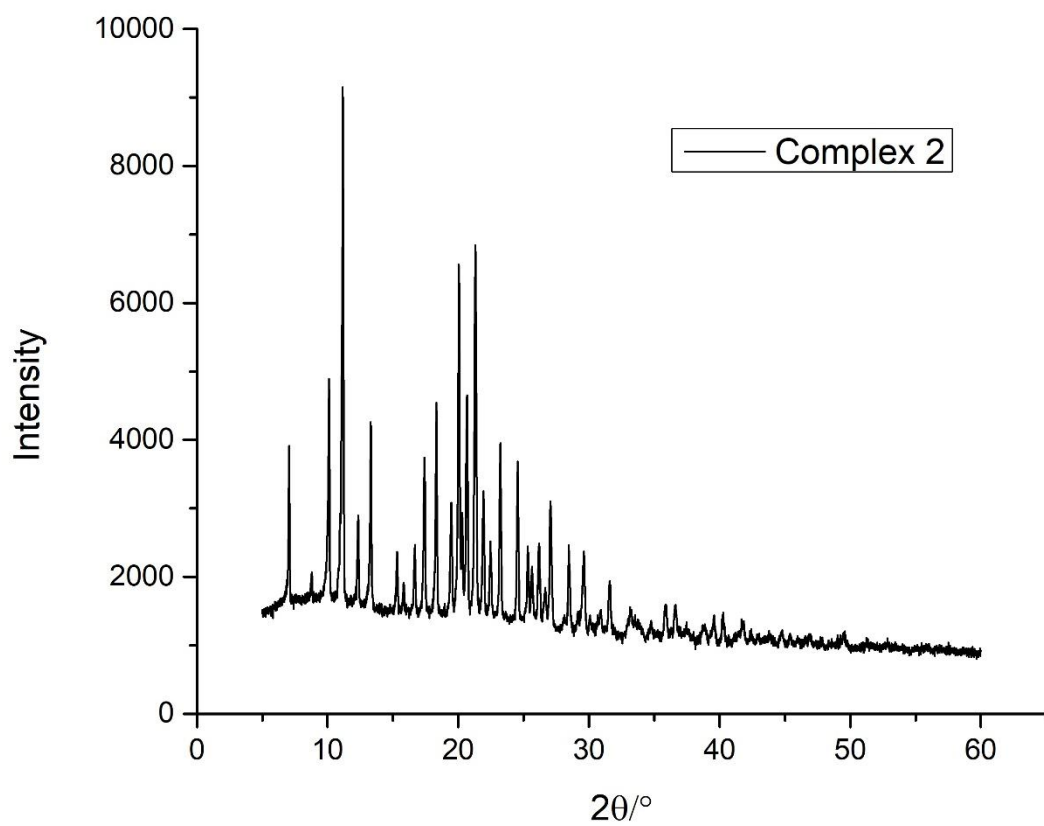


(a)

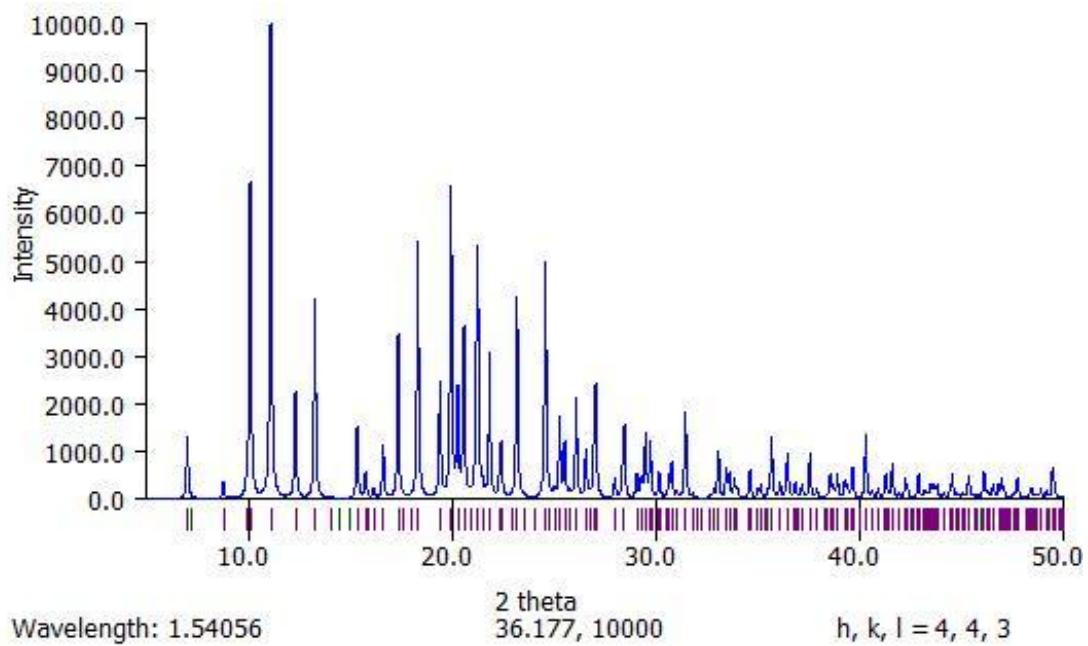


(b)

**Figure S3** (a) Experimental and (b) simulated powder-XRD plots of complex **2** at 300 K.

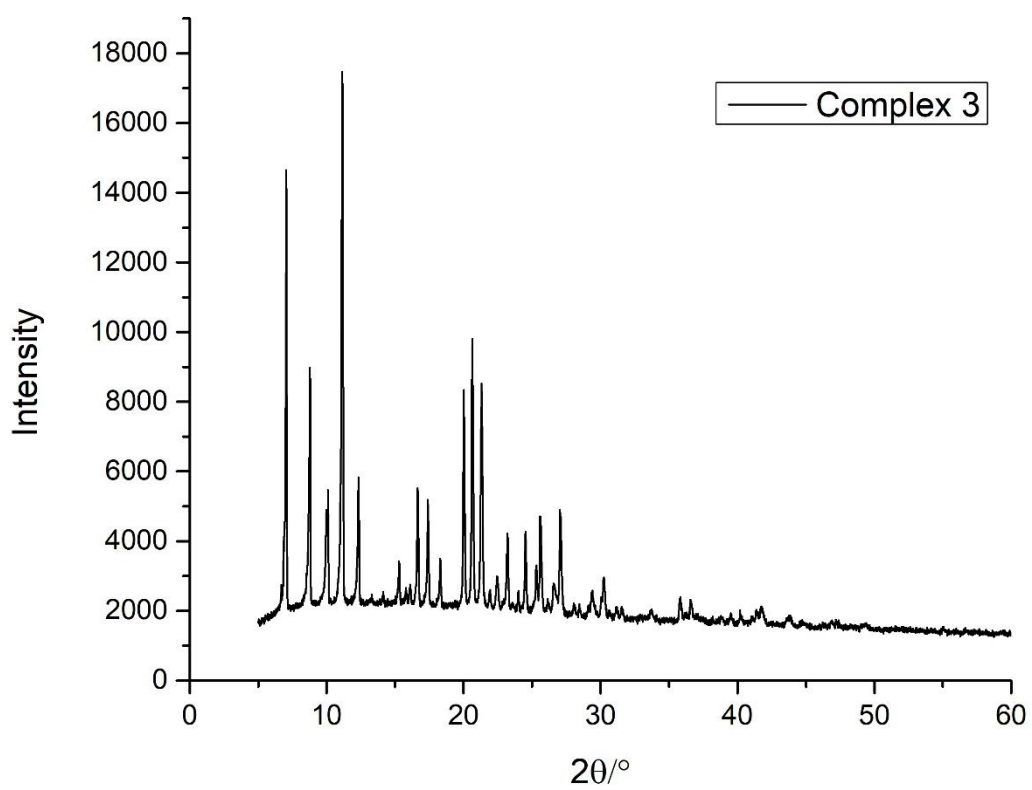


(a)

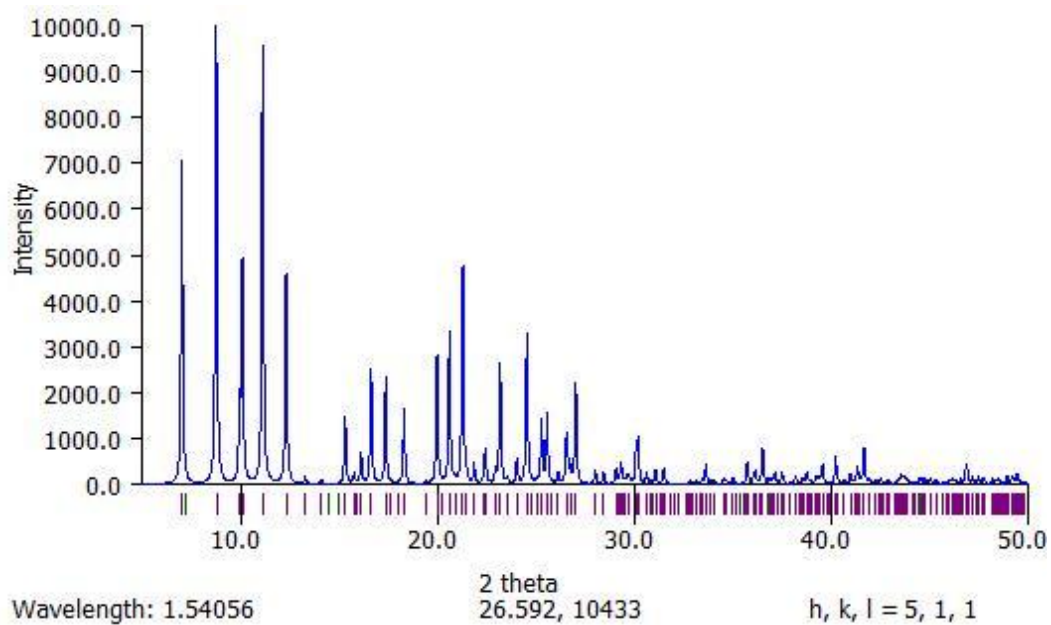


(b)

**Figure S4** (a) Experimental and (b) simulated powder-XRD plots of complex **3** at 300 K.



(a)



(b)

Figure S5 TGA plot of complexes 1-3 in the temperature range 30-800 °C.

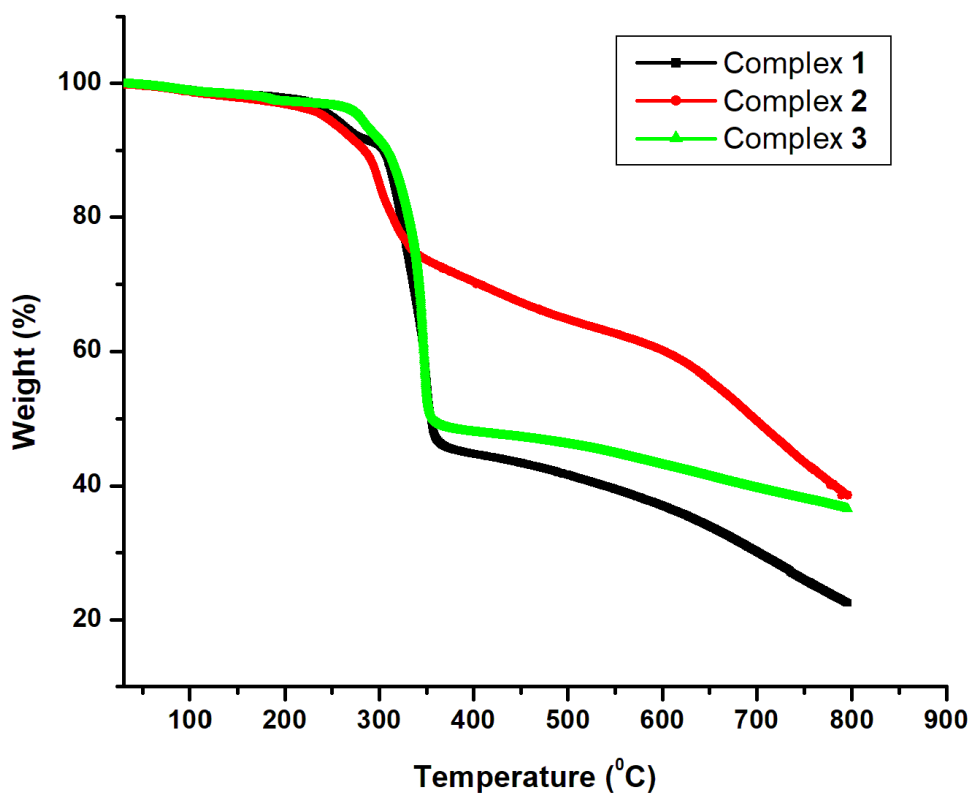
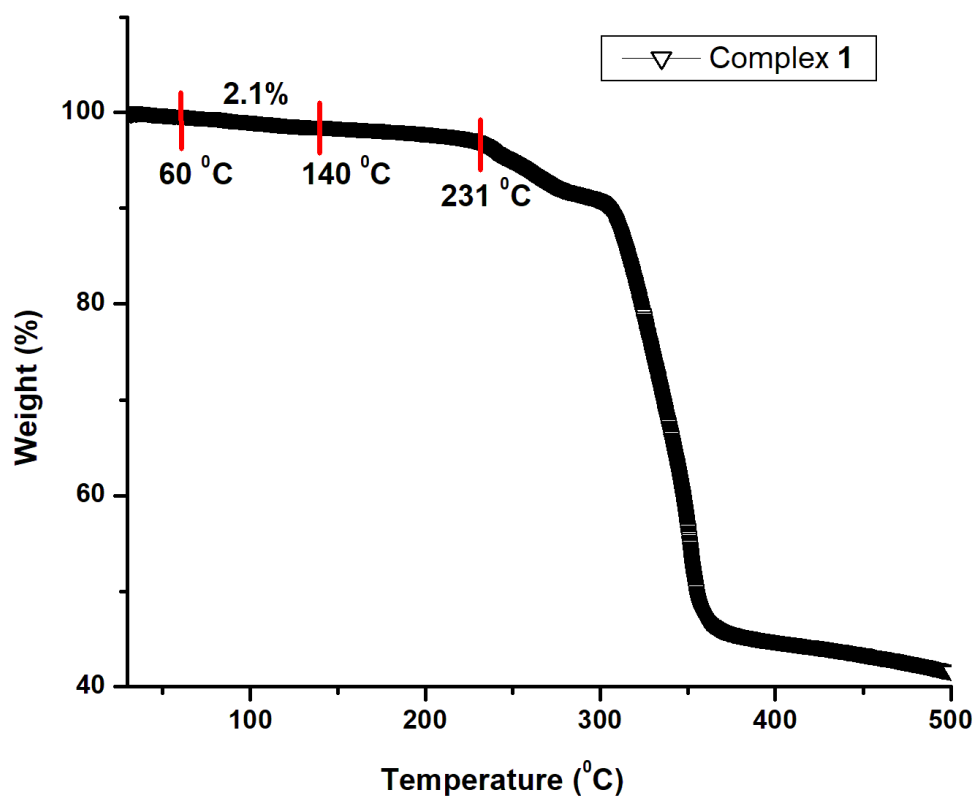
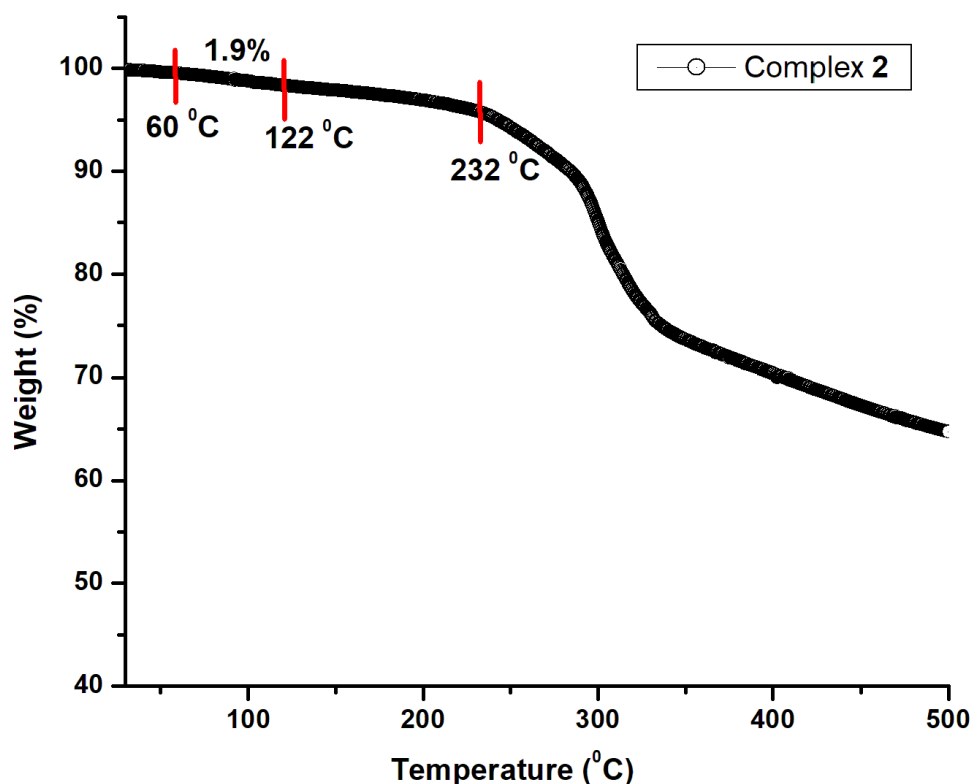


Figure S6 TGA plot and loss of water in complex 1.



**Figure S7** TGA plot and loss of water in complex **2**.



**Table S4** Selected crystallographic parameters at various temperatures for **1**

	<b>1</b> <sup>150K</sup>	<b>1</b> <sup>250K</sup>	<b>1</b> <sup>300K</sup>	<b>1</b> <sup>350K</sup>	<b>1</b> <sup>400K</sup>	<b>1</b> <sup>450K</sup>
<b>Formula</b>	$C_{76}H_{52}N_{12}S_4Cl_4Fe_2$				$C_{76}H_{52}N_{12}S_4Cl_4Fe_2$	
<b>F. W. (g/mol)</b>	1515.03				1515.03	
<b>Size (mm<sup>3</sup>)</b>	0.20×0.06×0.06					
<b>Space group</b>	$P4_32_12$					
<b>a (Å)</b>	17.4989(11)	17.586(3)	17.6150(6)	17.6560(7)	17.6740(7)	17.7562(15)
<b>c (Å)</b>	12.1221(11)	12.194(2)	12.2291(5)	12.3860(6)	12.5284(6)	12.5703(13)
<b>Volume (Å<sup>3</sup>)</b>	3711.9(6)	3771.2(14)	3794.5(3)	3861.1(4)	3913.5(4)	3963.2(8)
<b><math>\rho_{calc}</math> (g.cm<sup>-3</sup>)</b>	1.356	1.334	1.326	1.303	1.286	1.270
<b><math>\mu</math> (mm<sup>-1</sup>)</b>	0.698	0.687	0.683	0.671	0.662	0.654
<b>GOF on F<sup>2</sup></b>	0.969	1.049	1.023	1.040	1.049	1.124
<b><math>R_1, wR_2</math> [<math>I &gt; 2\sigma(I)</math>]</b>	0.0354 0.0706	0.0324 0.0691	0.0384 0.0873	0.0424 0.0936	0.0523 0.1217	0.0810 0.1783
<b><math>R_1, wR_2</math> [all data]</b>	0.0498 0.0741	0.0403 0.0726	0.0498 0.0929	0.0632 0.1065	0.0921 0.1466	0.1290 0.2117
<b>Largest diff. peak/hole (e.Å<sup>-3</sup>)</b>	0.270/-0.295	0.318/- 0.329	0.285/- 0.314	0.213/- 0.218	0.32/-0.21	0.40/-0.23
<b>Flack value</b>	0.002(10)	0.03(2)	0.007(4)	0.000(4)	0.004(5)	0.019(6)
<b>CCDC</b>	1979597	1979599	2009216	1979600	1979604	1979602

**Table S5** Selected crystallographic parameters at various temperatures for **2**

	<b>2</b> <sup>150K</sup>	<b>2</b> <sup>250K</sup>	<b>2</b> <sup>300K</sup>	<b>2</b> <sup>350K</sup>	<b>2</b> <sup>400K</sup>	<b>2</b> <sup>450K</sup>
<b>Formula</b>	C <sub>38</sub> H <sub>26</sub> N <sub>6</sub> S <sub>2</sub> Br <sub>2</sub> Fe	C <sub>76</sub> H <sub>52</sub> N <sub>12</sub> S <sub>4</sub> Br <sub>4</sub> Fe <sub>2</sub>		C <sub>76</sub> H <sub>52</sub> N <sub>12</sub> S <sub>4</sub> Br <sub>4</sub> Fe <sub>2</sub>		
<b>F. W.(g/mol)</b>	846.44	1692.87		1692.87		
<b>Size (mm<sup>3</sup>)</b>	0.24×0.10×0.06					
<b>Space group</b>	<i>P4<sub>1</sub>2<sub>1</sub>2</i>					
<b>a (Å)</b>	17.6160(17)	17.6816(11)	17.7390(4)	17.6859(12)	17.7629(19)	17.834(4)
<b>c (Å)</b>	12.106(2)	12.1451(11)	12.1851(4)	12.3676(13)	12.4907(14)	12.571(3)
<b>Volume (Å<sup>3</sup>)</b>	3756.8(10)	3797.0(6)	3834.3(2)	3868.5(7)	3941.1(10)	3998(2)
<b><math>\rho_{calc}</math> (g.cm<sup>-3</sup>)</b>	1.497	1.481	1.466	1.453	1.427	1.406
<b><math>\mu</math> (mm<sup>-1</sup>)</b>	2.675	2.647	2.621	2.598	2.550	2.514
<b>GOF on F<sup>2</sup></b>	1.055	1.047	1.030	1.103	1.111	1.103
<b><math>R_1, wR_2</math> [<math>I &gt; 2\sigma(I)</math>]</b>	0.0309 0.0892	0.0453 0.0715	0.0450 0.0777	0.0688 0.1001	0.0759 0.1060	0.0892 0.1176
<b><math>R_1, wR_2</math> [all data]</b>	0.0339 0.0911	0.0600 0.0755	0.0596 0.0821	0.1539 0.1190	0.1728 0.1269	0.1943 0.1414
<b>Largest diff. peak/hole (e.Å<sup>-3</sup>)</b>	0.314/-0.596	0.418/-0.391	0.362/- 0.371	0.95/-0.86	0.85/-0.66	0.61/-0.30
<b>Flack value</b>	0.003(2)	0.033(14)	0.046(16)	0.016(3)	0.029(5)	0.032(5)
<b>CCDC</b>	1979605	1979607	2009217	1979608	1979609	1979611

**Table S6** Evolution of the coordination sphere parameters as a function of temperature for **1**

	<b>1</b> <sup>150K</sup>	<b>1</b> <sup>250K</sup>	<b>1</b> <sup>300K</sup>	<b>1</b> <sup>350K</sup>	<b>1</b> <sup>400K</sup>	<b>1</b> <sup>450K</sup>
<b>Fe-N<sub>pyridine</sub> (Å)</b>	1.963(3)	1.968(2)	1.977(3)	2.037(3)	2.109(4)	2.151(7)
<b>Fe-N<sub>imine</sub> (Å)</b>	1.954(2)	1.942(19)	1.962(3)	2.044(3)	2.144(4)	2.201(6)
<b>Fe-N<sub>NCS</sub> (Å)</b>	1.950(3)	1.957(2)	1.950(3)	1.983(4)	2.039(6)	2.071(10)
<b>&lt;Fe-N&gt; (Å)</b>	1.955(2)	1.956(2)	1.963(3)	2.021(3)	2.097(5)	2.141(8)
<b><math>\zeta</math> (Å)</b>	0.031	0.032	0.058	0.158	0.235	0.281
<b><math>\Sigma</math> (°)</b>	41.6	42.4	43.6	52.3	65.1	71.4
<b><math>\Phi</math> (°)</b>	131	133	138	158	190	208
<b>V(FeN<sub>6</sub>) Å<sup>3</sup></b>	9.861	9.935	9.977	10.858	12.005	12.703
<b>Spin state</b>	LS	LS (95%)	LS (94%)	HS (34%)	HS (71%)	HS (94%)



**Table S7** Evolution of the coordination sphere parameters as a function of temperature for **2**

	<b>2</b> <sup>150K</sup>	<b>2</b> <sup>250K</sup>	<b>2</b> <sup>300K</sup>	<b>2</b> <sup>350K</sup>	<b>2</b> <sup>400K</sup>	<b>2</b> <sup>450K</sup>
<b>Fe-N (Å)</b>	1.967(3) 1.957(3) 1.960(3)	1.970(3) 1.961(3) 1.957(3)	1.977(4) 1.968(3) 1.966(4)	2.040(8) 2.067(8) 1.996(10)	2.161(9) 2.108(10) 2.026(11)	2.206(10) 2.135(11) 2.044(12)
<b>&lt;Fe-N&gt; (Å)</b>	1.961(3)	1.963(4)	1.970(4)	2.0349(9)	2.098(10)	2.128(11)
<b>ζ (Å)</b>	0.025	0.030	0.031	0.157	0.289	0.34
<b>Σ (°)</b>	42	43	45	55	66	71
<b>Φ (°)</b>	133	134	138	160	188	198
<b>V(FeN<sub>6</sub>) Å<sup>3</sup></b>	9.950	9.986	10.099	11.044	12.010	12.502
<b>Spin state</b>	LS (95%)	LS (94%)	LS (90%)	HS (40%)	HS (71%)	HS (87%)

**Table S8** Selected crystallographic parameters at various temperatures for **3**

<b>Temperature/K</b>	<b>3</b> <sup>150K</sup>	<b>3</b> <sup>250K</sup>	<b>3</b> <sup>400K</sup>	<b>3</b> <sup>420K</sup>	<b>3</b> <sup>250Kcooling</sup>	<b>3</b> <sup>90Kcooling</sup>
<b>Formula</b>	C <sub>80</sub> H <sub>64</sub> N <sub>12</sub> S <sub>4</sub> Fe <sub>2</sub>		C <sub>80</sub> H <sub>64</sub> N <sub>12</sub> S <sub>4</sub> Fe <sub>2</sub>			
<b>F. W. (g/mol)</b>	1433.37		1433.37			
<b>Size (mm<sup>3</sup>)</b>	0.16×0.08×0.04					
<b>Space group</b>	P4 <sub>1</sub> 2 <sub>1</sub> 2					
<b>a (Å)</b>	17.5623(8)	17.6315(3)	17.6961(5)	17.725(3)	17.5254(7)	17.3815(7)
<b>c (Å)</b>	12.1023(8)	12.1717(3)	12.5406(5)	12.578(2)	12.2143(6)	12.1164(5)
<b>Volume (Å<sup>3</sup>)</b>	3732.8(4)	3783.8(16)	3927.1(3)	3951.7(15)	3751.5(4)	3660.6(3)
<b>ρ<sub>calc</sub> (g·cm<sup>-3</sup>)</b>	1.275	1.258	1.212	1.205	1.269	1.300
<b>μ (mm<sup>-1</sup>)</b>	0.552	0.545	0.525	0.521	0.549	0.563
<b>GOF on F<sup>2</sup></b>	1.067	1.020	1.011	0.935	0.982	1.049
<b>R<sub>1</sub>, wR<sub>2</sub> [I&gt;2σ(I)]</b>	0.0264 0.0651	0.0461 0.0922	0.0491 0.0983	0.0463 0.0905	0.0502 0.0766	0.0434 0.0684
<b>R<sub>1</sub>, wR<sub>2</sub> [all data]</b>	0.0288 0.0667	0.0883 0.0922	0.1171 0.1159	0.1867 0.1159	0.1240 0.0903	0.0697 0.0730
<b>Largest diff. peak/hole (e·Å<sup>-3</sup>)</b>	0.418/- 0.178	0.591/- 0.392	0.21/-0.16	0.18/-0.17	0.34/-0.48	0.48/-0.61
<b>Flack value</b>	0.009(15)	0.003(7)	0.022(8)	0.036(12)	0.007(9)	0.018(8)
<b>CCDC</b>	1979617	1979618	1979620	1979621	1979622	1979623