Two-step Spin Transition around Room Temperature in a Fe^{III} Complex

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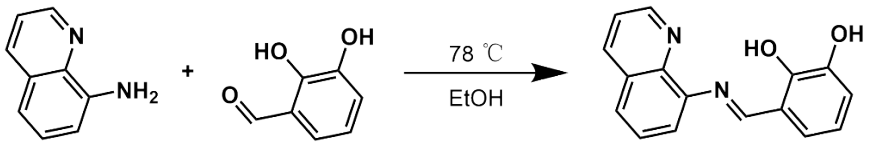
1. Synthesis and NMR spectra



Scheme S1. Schematic drawing of the synthesis of ligand **H_2L**.

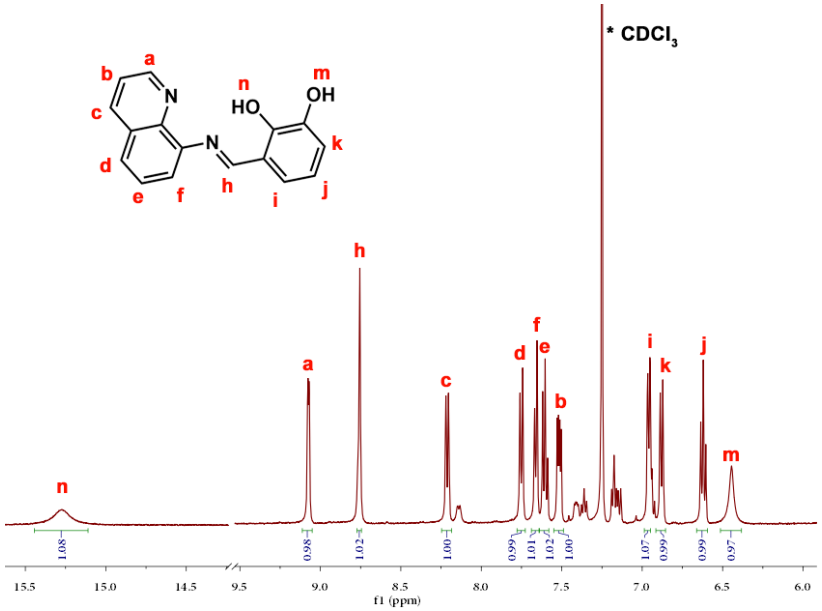


Figure S1. ^{1}H-NMR spectrum of the ligand **H_2L** in $CDCl_3$ recorded at room temperature. Solvent peak was marked with asterisk ($CDCl_3$, *).

2. IR spectroscopy

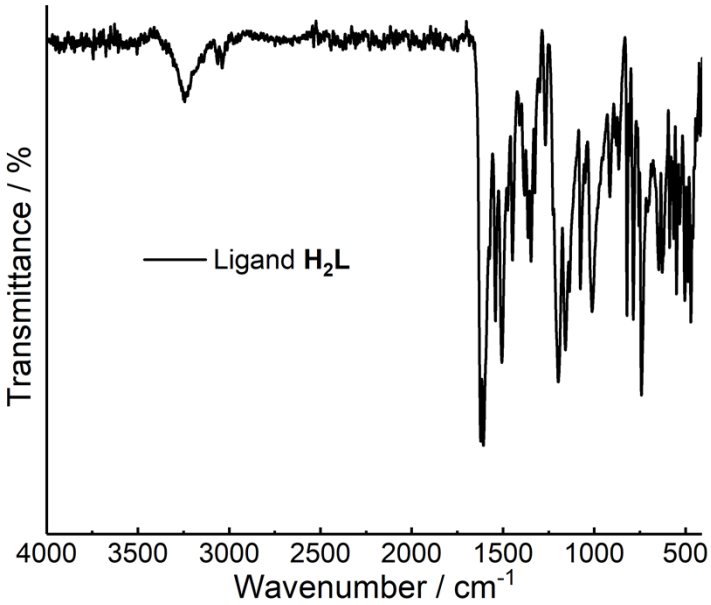


Figure S2. IR (ATR) spectrum of solid sample of ligand **H_2L**.

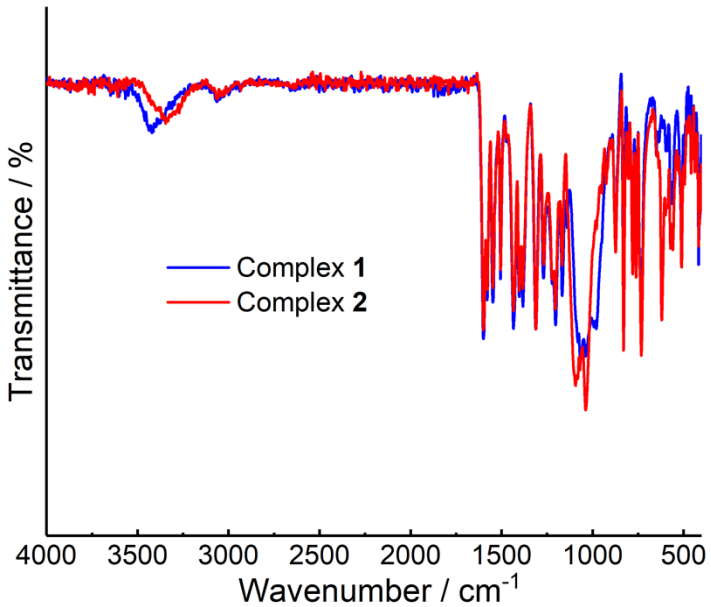


Figure S3. IR (ATR) spectra of solid samples of complexes **1** and **2**.

3. Crystallographic details

Table S1. Crystallographic data of complex **1** at different temperatures.

T / K	150	190	220	245	273	360
empirical formula	$C_{36}H_{28}BF_4FeN_6O_4$	$C_{36}H_{28}BF_4FeN_6O_4$	$C_{36}H_{28}BF_4FeN_6O_4$	$C_{36}H_{28}BF_4FeN_6O_4$	$C_{36}H_{28}BF_4FeN_6O_4$	$C_{35.43}H_{27.15}BF_4FeN_{5.71}O_4$
weight, g·mol^{-1}	751.30	751.30	751.30	751.30	751.30	739.61
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
a, Å	9.761(2)	9.7833(15)	9.8367(15)	9.715(6)	9.731(6)	9.786(6)
b, Å	11.913(3)	11.9474(18)	12.3022(18)	12.574(7)	12.572(7)	12.619(7)
c, Å	15.666(4)	15.724(2)	15.802(2)	15.494(11)	15.537(11)	15.625(11)
α, °	109.640(6)	109.494(4)	110.103(4)	70.82(2)	70.83(2)	71.31(2)
β, °	105.304(6)	105.229(4)	106.164(4)	71.741(14)	71.806(14)	72.147(14)
γ, °	92.463(6)	92.470(4)	90.677(4)	88.304(14)	88.482(14)	88.655(14)
V, Å^3	1637.4(6)	1654.3(4)	1712.5(4)	1692.1(18)	1699.6(19)	1733.7(19)
Z	2	2	2	2	2	2
ρ (cal), g·cm^{-3}	1.524	1.508	1.457	1.457	1.468	1.417
F(000)	770.0	770.0	770.0	770.0	770.0	757.0
2θ range [°]	3.764 to 50.364	3.754 to 50.056	3.55 to 51.394	3.698 to 50.372	3.692 to 50.37	3.684 to 50.242
*T*min / *T*max	0.899 / 0.908	0.899 / 0.909	0.903 / 0.912	0.902 / 0.911	0.902 / 0.911	0.904 / 0.913
measured refl.	21657	25536	20030	27040	23556	28995
unique refl. [*R*int]	5809 / 0.1017	5800 / 0.0707	5986 / 0.2750	6043 / 0.1356	6000 / 0.0826	6108 / 0.1408
goodness-of-fit (F^2)	1.061	1.066	1.767	1.093	1.024	1.029
data / restr. / param.	5809 / 52 / 510	5800 / 58 / 510	5986 / 94 / 460	6043 / 76 / 510	6000 / 76 / 510	6108 / 175 / 510
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0727, 0.1772	0.0599, 0.1443	0.2749, 0.5210	0.0757, 0.1810	0.0591, 0.1472	0.0721, 0.1850
*R*1, *wR*2 (all data)	0.1048, 0.1987	0.0838, 0.1578	0.3388, 0.5648	0.1252, 0.2106	0.0890, 0.1658	0.1264, 0.2245
res. el. dens. [e·Å^{-3}]	0.75 / -0.99	0.55 / -0.42	1.19 / -1.61	0.47 / -0.56	0.45 / -0.36	0.39 / -0.41

Table S2. Crystallographic data of complex **2** at different temperatures.

T / K	150	300
empirical formula	$C_{36}H_{28}ClFeN_6O_8$	$C_{36}H_{28}ClFeN_6O_8$
weight, g·mol^{-1}	763.94	763.94
crystal system	triclinic	triclinic
space group	*P-1*	*P-1*
λ, Å	0.71073	0.71073
a, Å	9.759(3)	9.7125(17)
b, Å	11.931(4)	12.608(2)
c, Å	15.722(5)	15.640(2)
α, °	109.164(8)	71.472(4)
β, °	104.656(7)	73.006(4)

γ, °	92.625(9)	89.279(4)
V, Å^3	1656.2(9)	1729.9(5)
Z	2	2
ρ (cal), g·cm^{-3}	1.532	1.467
F(000)	786.0	786.0
2θ range [°]	4.482 to 50.356	4.47 to 50.306
Tmin / Tmax	0.881 / 0.892	0.886 / 0.897
measured refl.	22922	24600
unique refl. [Rint]	5868 / 0.1233	5990 / 0.0620
goodness-of-fit (F^2)	1.047	1.036
data / restr. / param.	5868 / 0 / 473	5990 / 94 / 510
R1, wR2 ($I > 2\sigma(I)$)	0.0730, 0.1734	0.0645, 0.1707
R1, wR2 (all data)	0.1277, 0.2054	0.0846, 0.1882
res. el. dens. [e·Å^{-3}]	0.59 / -0.58	0.55 / -0.78

Table S3. Selected bond distances (Å) and angles (°) in complex **1**.

T / K	150	190	220[#]	245	273	360
Fe1-O1	1.876(3)	1.876(2)	1.896(9)	1.901(4)	1.901(3)	1.897(3)
Fe1-O3	1.885(3)	1.889(3)	1.884(12)	1.915(4)	1.914(3)	1.915(3)
Fe1-N1	1.982(4)	1.985(3)	2.040(7)	2.154(4)	2.154(3)	2.158(4)
Fe1-N2	1.941(4)	1.944(3)	1.919(15)	2.110(4)	2.115(3)	2.117(4)
Fe1-N3	1.970(4)	1.978(3)	1.983(8)	2.160(5)	2.148(3)	2.148(4)
Fe1-N4	1.928(4)	1.934(3)	2.012(16)	2.115(4)	2.114(3)	2.116(4)
O2-H···F	2.805(6)	2.828(2)	2.804(3)	2.808(9)	2.808(5)	2.787(5)
O4-H···N5	2.831(3)	2.845(1)	2.885(8)	2.833(9)	2.846(1)	2.844(8)
O1-Fe1-O3	95.57(13)	95.46(11)	93.9(4)	97.16(16)	97.11(12)	97.11(16)
O1-Fe1-N1	173.76(14)	174.07(12)	172.3(4)	164.32(15)	164.28(11)	164.66(14)
O1-Fe1-N2	93.92(14)	93.92(12)	91.1(5)	87.83(16)	87.82(12)	88.17(15)
O1-Fe1-N3	88.64(14)	88.70(12)	89.9(4)	89.43(16)	89.44(12)	89.29(16)
O1-Fe1-N4	89.21(14)	89.23(11)	92.6(5)	101.18(16)	101.10(12)	100.79(15)
O3-Fe1-N1	89.68(14)	89.51(12)	89.1(4)	89.76(15)	89.75(12)	89.85(15)
O3-Fe1-N2	87.48(14)	87.41(12)	92.0(5)	102.23(16)	102.07(11)	101.71(14)
O3-Fe1-N3	175.46(14)	175.40(12)	174.3(5)	164.06(16)	164.25(12)	164.59(15)
O3-Fe1-N4	94.70(15)	94.78(12)	91.7(6)	88.16(16)	88.17(12)	87.84(15)
N2-Fe1-N1	82.91(15)	83.05(13)	81.7(4)	76.93(16)	76.89(12)	77.01(16)
N2-Fe1-N3	93.94(16)	94.26(13)	92.2(4)	92.48(17)	92.44(12)	92.46(16)
N3-Fe1-N1	86.22(15)	86.45(12)	87.6(3)	87.58(16)	87.60(12)	87.46(15)
N4-Fe1-N1	93.74(15)	93.58(12)	94.4(4)	93.06(16)	93.21(12)	93.09(15)
N4-Fe1-N2	176.00(15)	175.98(13)	174.6(5)	165.39(16)	165.58(11)	166.09(15)
N4-Fe1-N3	83.64(16)	83.31(13)	83.9(5)	76.30(17)	76.49(13)	77.17(16)

[#] Please note the data at 220 K falls on the spin transition region.

Table S4. Selected bond distances (Å) and angles (°) in complex **2**.

T / K	150	300
Fe1-O1	1.871(4)	1.895(3)
Fe1-O3	1.873(4)	1.911(3)
Fe1-N1	1.969(4)	2.153(3)
Fe1-N2	1.935(5)	2.113(3)
Fe1-N3	1.968(5)	2.158(3)
Fe1-N4	1.928(5)	2.111(3)
O2-H···O	2.914(5)	2.900(8)
O4-H···N5	2.814(2)	2.848(5)
O1-Fe1-O3	95.64(16)	97.38(13)
O1-Fe1-N1	174.01(18)	164.25(12)
O1-Fe1-N2	94.18(17)	88.24(11)
O1-Fe1-N3	88.44(17)	89.27(13)
O1-Fe1-N4	88.74(16)	100.40(11)
O3-Fe1-N1	89.62(17)	90.21(12)
O3-Fe1-N2	87.06(17)	101.91(12)
O3-Fe1-N3	175.50(17)	164.39(12)
O3-Fe1-N4	94.72(18)	88.12(12)
N2-Fe1-N1	83.22(18)	76.66(12)
N2-Fe1-N3	94.55(19)	92.37(13)
N3-Fe1-N1	86.41(18)	86.93(12)
N4-Fe1-N1	93.68(18)	93.60(12)
N4-Fe1-N2	176.42(18)	165.90(12)
N4-Fe1-N3	83.44(19)	76.76(13)

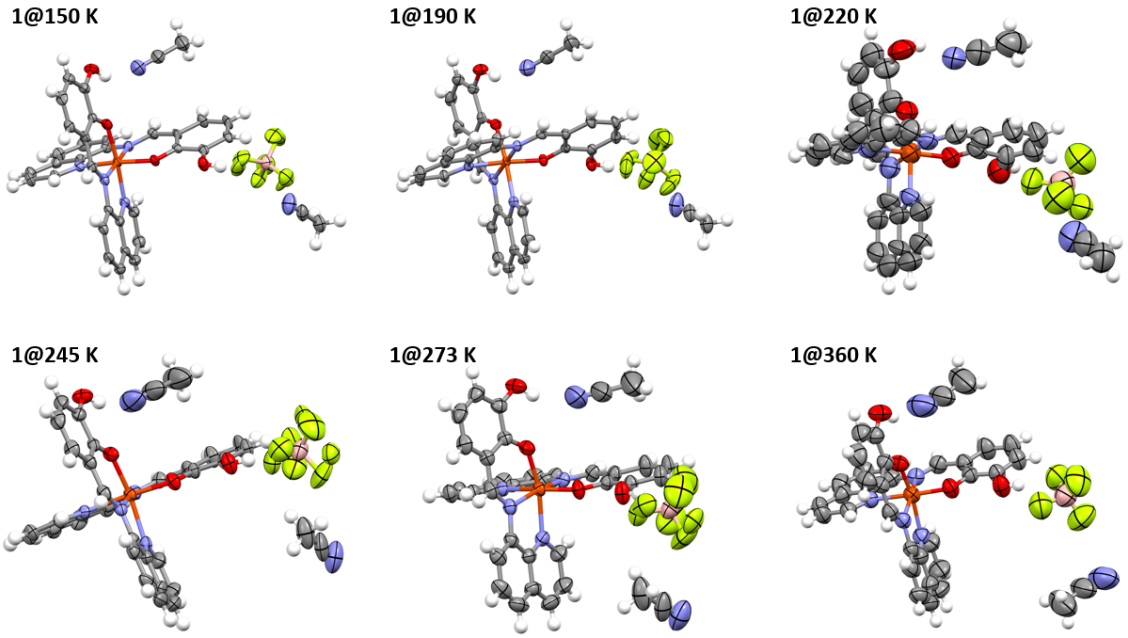


Figure S4. Plots (50% probability thermal ellipsoids) of the molecular structure of **1** at indicated temperatures.

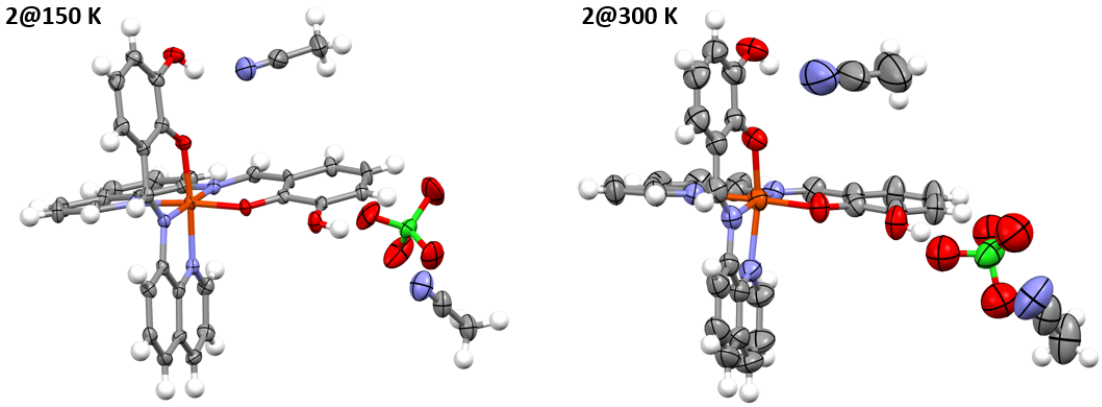


Figure S5. Plots (50% probability thermal ellipsoids) of the molecular structure of **2** at indicated temperatures.

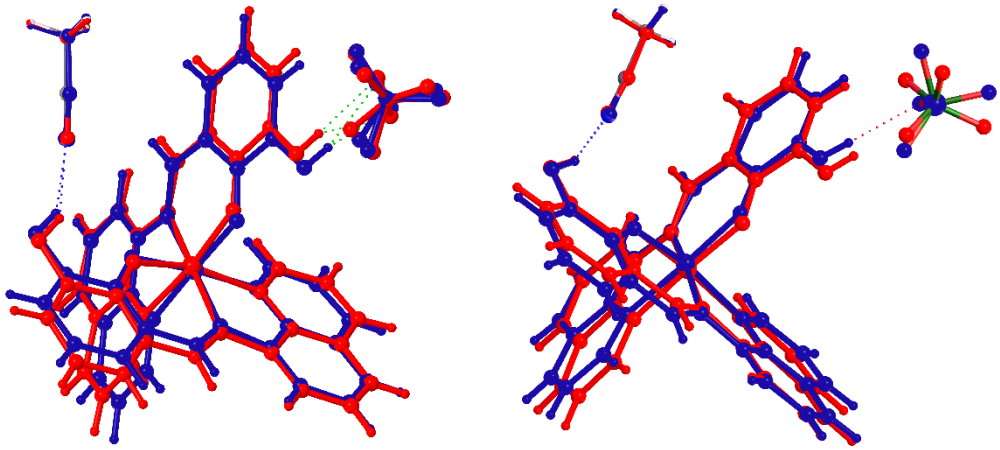


Figure S6. Molecule overlay of the complexes **1** and **2** at 150 K (blue Group) and 300 K (red Group).

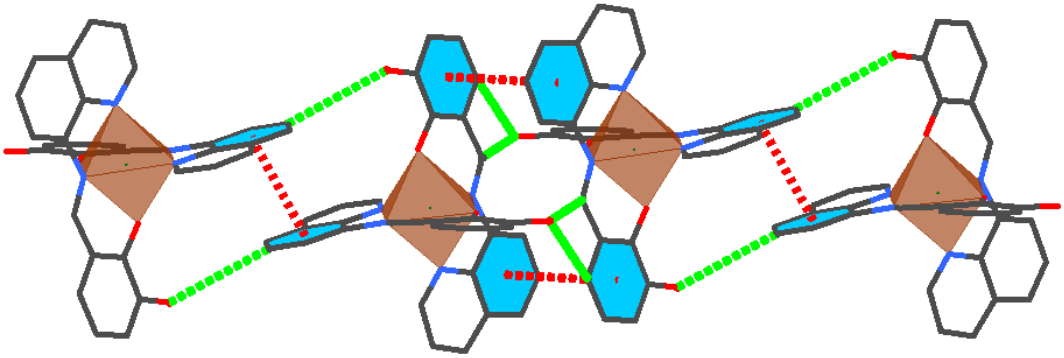


Figure S7. 1D chain structure in complex **2** at 150 K. The green dashed lines represent the C–H···O interactions and the red dashed lines represent the π–π interactions.

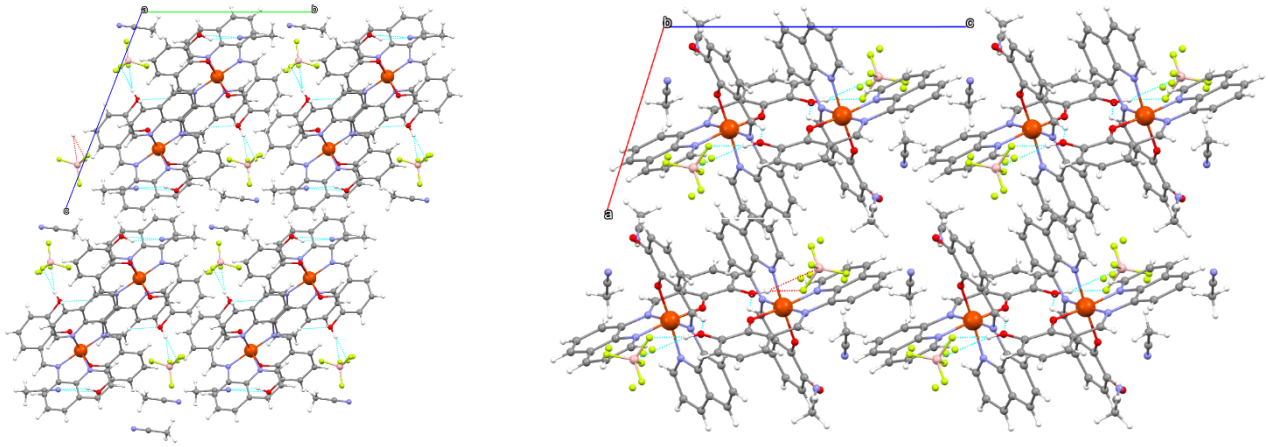


Figure S8. Packing models along the *a* and *b* axes of complex **1**. The blue dashed lines represent the hydrogen bondings.

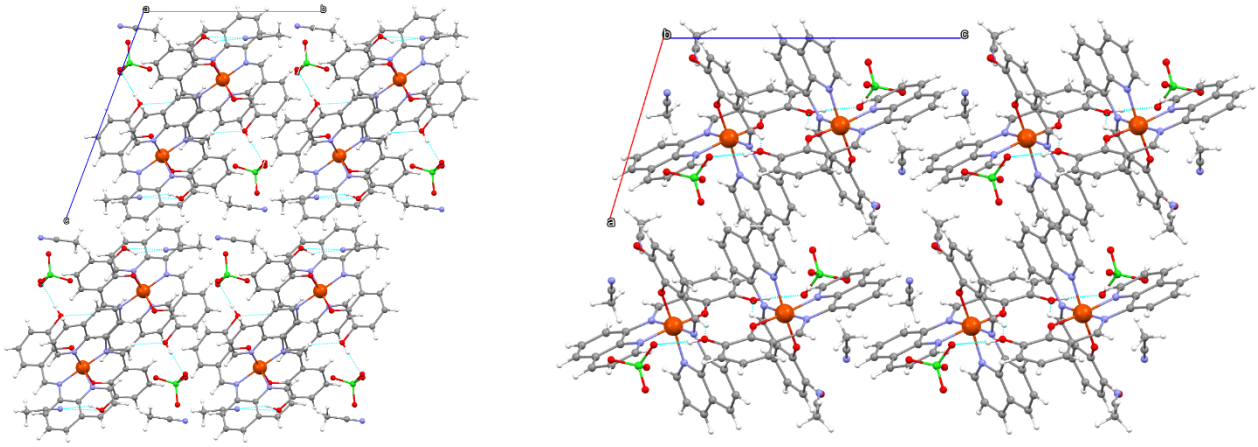


Figure S9. Packing models along the *a* and *b* axes of complex **2**. The blue dashed lines represent the hydrogen bondings.

4. Powder XRD analyses

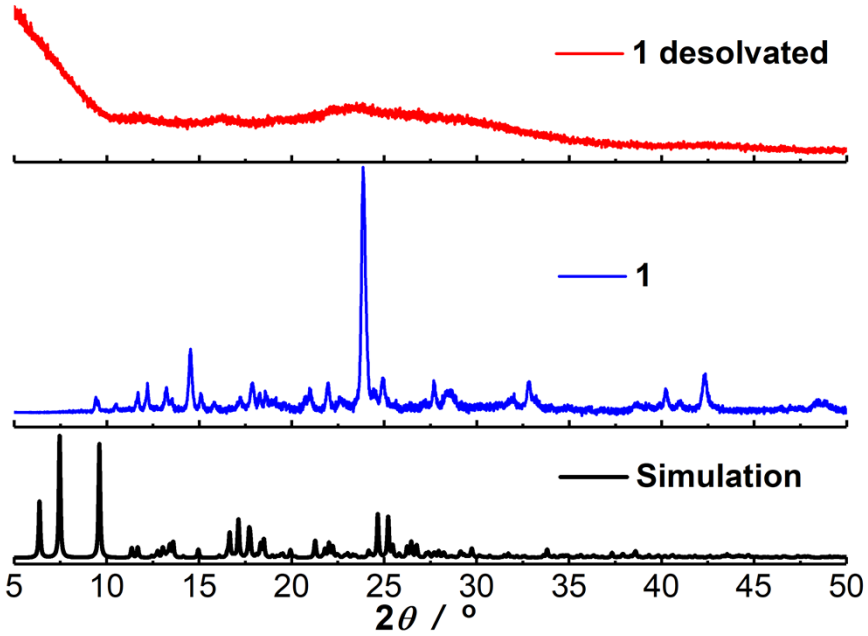


Figure S10. Powder XRD analyses of complex **1** and the desolvated sample. The black line is the simulated pattern based on the single crystal diffraction data.

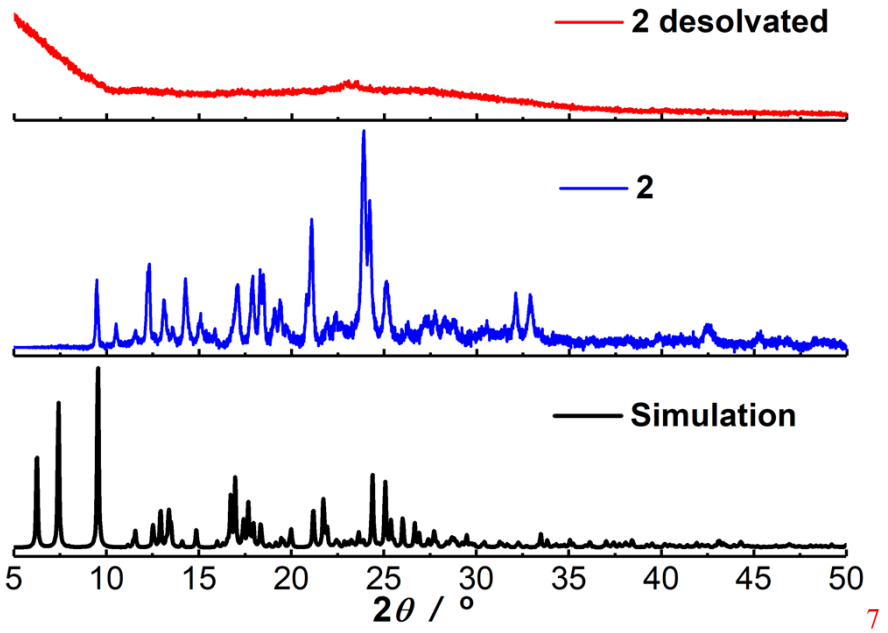


Figure S11. Powder XRD analyses of complex **2** and the desolvated sample. The black line is the simulated pattern based on the single crystal diffraction data.

5. Thermogravimetric analyses

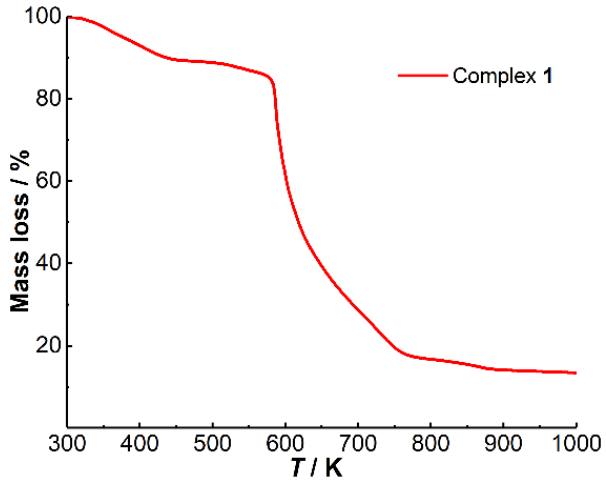


Figure S12. Thermogravimetric profile of complex·**2** collected at a heating rate of 10 ℃/min in N_2 atmosphere.

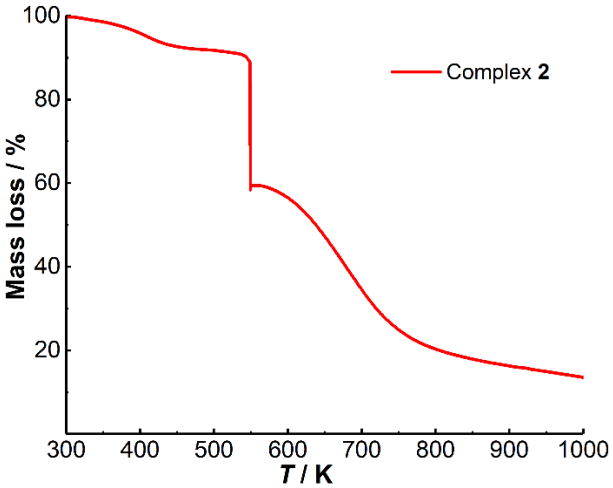


Figure S13. Thermogravimetric profile of complex·**2** collected at a heating rate of 10 ℃/min in N_2 atmosphere.

6. DSC measurements

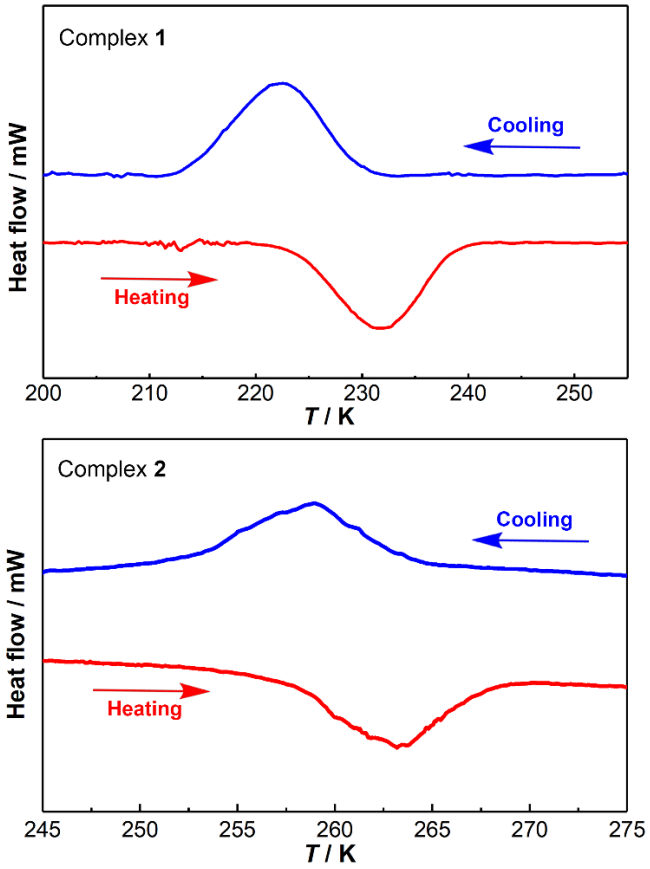


Figure S14. DSC data for complexes **1** (top) and **2** (bottom) measured by heating and cooling at 10 ˚C/min.

7. Coordination polyhedron analyses

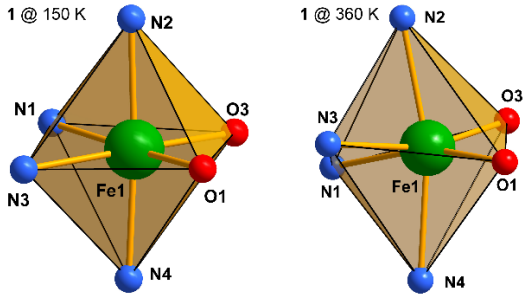


Figure S15. Coordination polyhedron of Fe^{III} ion in complex **1** at the indicated temperatures.

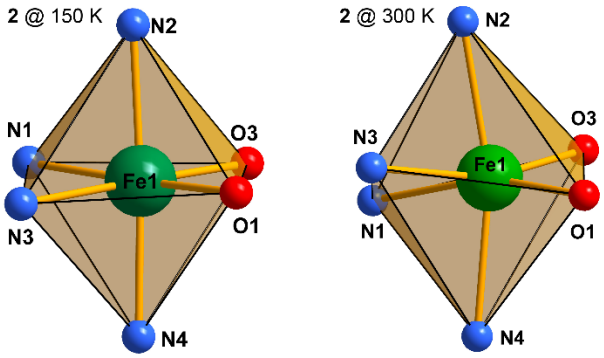


Figure S16. Coordination polyhedron of Fe^{III} ion in complex **2** at the indicated temperatures.

Table S5. The *CShM* values calculated by *SHAPE* 2.1[1, 2] of the Fe^{III} ions in **1** at different temperatures.

Temperature	150 K	190 K	220 K	245 K	273 K	360 K
Hexagon (D_{6h})	30.501	30.462	31.787	33.755	33.693	33.558
Pentagonal pyramid (C_{5v})	27.636	27.636	27.721	24.420	24.450	24.668
Octahedron (O_h)	0.255	0.263	0.306	1.382	1.370	1.299
Trigonal prism (D_{3h})	14.594	14.603	14.834	12.053	12.094	12.254
pentagonal pyramid (C_{5v})	31.136	31.118	31.184	27.964	27.993	28.176

Table S6. The *CShM* values calculated by *SHAPE* 2.1[1, 2] of the Fe^{III} ions in **2** at different temperatures.

Temperature	150 K	300 K
Hexagon (D_{6h})	30.412	33.561
Pentagonal pyramid (C_{5v})	27.594	24.610
Octahedron (O_h)	0.268	1.328
Trigonal prism (D_{3h})	14.520	12.402
pentagonal pyramid (C_{5v})	31.079	28.116

8. Hirshfeld surfaces

Table S7. Relative contributions from various intermolecular contacts to the Hirshfeld surface of complexes **1** and **2**.

Complex	**1**		**2**	
Temperature	150 K	360 K	150 K	300 K
H···N	8%	8.7%	7.8%	8.7%
H···F	10.4%	11.9%		
H···O	11.9%	12.9%	22.7%	25.6%

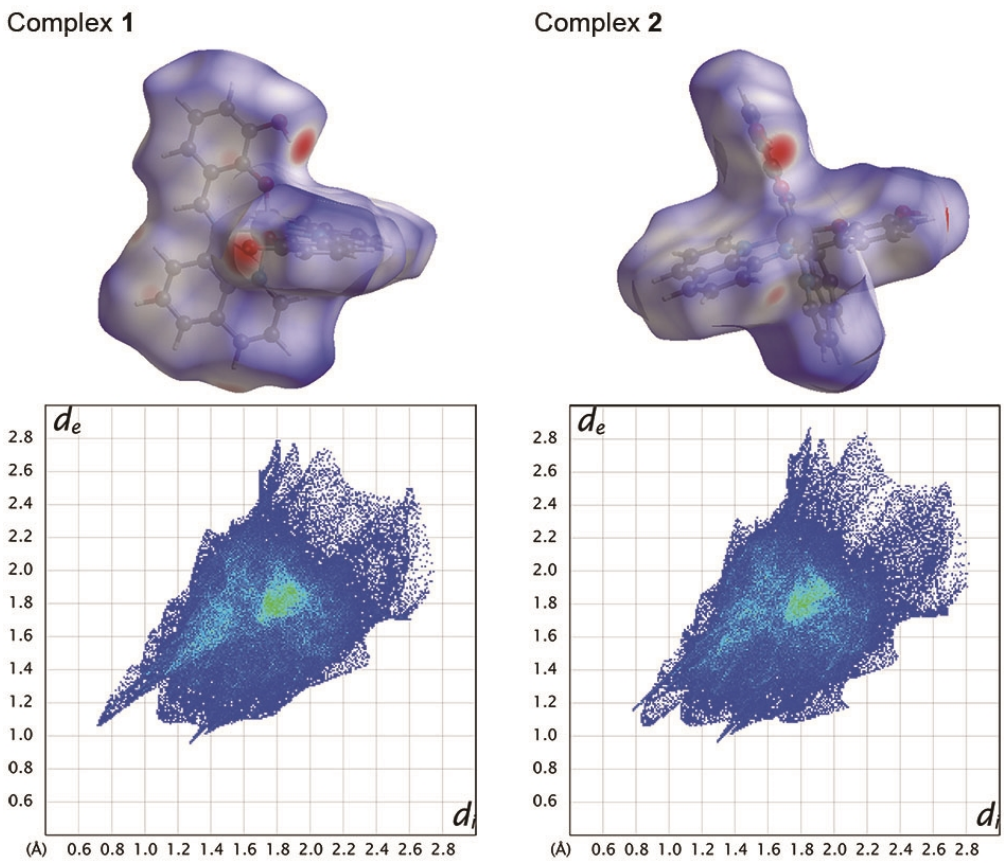


Figure S17. The Hirshfeld models (top) and two-dimensional fingerprint profiles (bottom) of complexes **1** (left) at 360 K and **2** (right) at 300 K.

9. References

1. D. Casanova, P. Alemany, J. M. Bofill and S. Alvarez, *Chem. Eur. J.*, 2003, **9**, 1281-1295.
2. S. Alvarez and M. Llunell, *J. Chem. Soc., Dalton Trans.*, 2000, DOI: 10.1039/B004878J, 3288-3303.