Electronic Supplementary Material for CrystEngComm

Supporting information

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Experimental details

X-ray Crystallography. The data were collected on a Bruker Apex 2000 diffractometer using Mo Kα radiation (graphite monochromated) (λ=0.71073Å) with $\omega/2\theta$ scan mode at 173 K. Lorentz-polarization and absorption corrections were applied. The structure was solved by direct methods using the program SHELXS-97, and refined using weighted full-matrix least-squares on F^2. The refinement and further calculations were performed with the SHELXL-97 program package. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically, while the hydrogen atoms of water molecules were found in the Fourier difference map. The remaining solvent molecules were strongly disordered, and the program SQUEEZE in PLATON99 was used to calculate the potential solvent accessible area in the unit cell. All the hydrogen atoms were assigned the same isotropic temperature factors and included in the structure-factor calculations. Crystal data for **1** is summarized in Table 1. Selected interatomic distances and interatomic angles for complex **1** are summarized in Table 2 and Table 3, respectively.

Magnetic Measurements. Variable-temperature magnetic susceptibility was performed with Quantum Design MPMS-XL7 SQUID magnetometer equipped in the temperature range of 1.8-300K with a 2 KOe magnet. Data were collected on polycrystalline samples. Pascal's constants were used to estimate the diamagnetic correction for complex **1**, which was subtracted from the experimental susceptibility to give the molar magnetic susceptibility (χ_M).

Other Measurements. Elemental analyses for C, H were performed on a Perkin-Elmer 240C analyzer. The IR spectra were taken on a Vector 22 Brucker Spectrophotometer (400-4000cm^{-1}) with KBr pellets. Thermal gravimetric analyses for complex **1** were measured on a Pyris 1 TGA instrument.

Crystallographic details

Table 1 X-ray Crystallographic Data and Structure Refinements for complex **1**

formula	$Fe_{10}C_{100}H_{142}O_{56}$
fw	2798.64
cryst syst	hexagonal
space group	R-3
a, Å	51.227(3)
c, Å	12.8243(8)
α, deg	90
γ, deg	120
V, Å^3	29145(3)
Z	3
*T,*K	173(2)
d_{calcd}, g/cm^3	1.435
λ	0.71073
abs coeff, cm-1	1.172cm-1
R1	0.0599
wR2	0.1227

Table 2 Selected Interatomic Distances (Å) for complex **1**

Fe(1)-O(25)	1.934(3)	Fe(3)-O(21)	1.992(2)
Fe(1)-O(16)	1.965(2)	Fe(3)-O(8)	2.056(3)
Fe(1)-O(18)	1.972(2)	Fe(3)-O(12)	2.068(3)
Fe(1)-O(17)	1.977(2)	Fe(3)-Fe(4)	3.0215(9)
Fe(1)-O(3)	2.058(2)	Fe(4)-O(23)	1.923(2)
Fe(1)-O(6)	2.066(2)	Fe(4)-O(24)	1.957(2)
Fe(1)-Fe(2)	3.0289(9)	Fe(4)-O(21)	1.970(2)
Fe(2)-O(17)	1.983(2)	Fe(4)-O(22)	1.982(3)
Fe(2)-O(19)	1.983(3)	Fe(4)-O(15)	2.025(2)
Fe(2)-O(20)	1.987(3)	Fe(4)-O(11)	2.064(2)
Fe(2)-O(18)	2.006(2)	Fe(4)-Fe(5)	3.0315(9)
Fe(2)-O(5)	2.034(2)	Fe(5)-O(25)	1.960(2)
Fe(2)-Fe(3)	3.0191(9)	Fe(5)-O(16)	1.985(2)
Fe(3)-O(20)	1.945(3)	Fe(5)-O(23)	1.999(2)
Fe(3)-O(22)	1.970(3)	Fe(5)-O(14)	2.034(3)
Fe(3)-O(19)	1.971(3)	Fe(5)-O(2)	2.074(2)

Table 3 Selected Interatomic Angles (deg) for complex **1**

O(25)-Fe(1)-O(16)	76.52(10)	O(17)-Fe(2)-Fe(1)	40.03(7)	O(24)-Fe(4)-O(15)	92.86(10)
O(25)-Fe(1)-O(18)	99.81(10)	O(19)-Fe(2)-Fe(1)	108.82(7)	O(21)-Fe(4)-O(15)	92.74(10)
O(16)-Fe(1)-O(18)	97.86(9)	O(20)-Fe(2)-Fe(1)	138.43(8)	O(22)-Fe(4)-O(15)	170.11(10)
O(25)-Fe(1)-O(17)	175.82(10)	O(18)-Fe(2)-Fe(1)	40.00(6)	O(23)-Fe(4)-O(11)	168.74(10)
O(16)-Fe(1)-O(17)	99.81(10)	O(5)-Fe(2)-Fe(1)	79.89(7)	O(24)-Fe(4)-O(11)	93.45(10)
O(18)-Fe(1)-O(17)	78.56(9)	O(9)-Fe(2)-Fe(1)	129.83(7)	O(21)-Fe(4)-O(11)	90.00(10)
O(25)-Fe(1)-O(3)	90.73(10)	Fe(3)-Fe(2)-Fe(1)	142.41(3)	O(22)-Fe(4)-O(11)	90.04(10)
O(16)-Fe(1)-O(3)	88.02(9)	O(20)-Fe(3)-O(22)	96.81(11)	O(15)-Fe(4)-O(11)	86.68(10)
O(18)-Fe(1)-O(3)	168.86(9)	O(20)-Fe(3)-O(19)	78.30(11)	O(23)-Fe(4)-Fe(3)	112.25(7)
O(17)-Fe(1)-O(3)	91.15(10)	O(22)-Fe(3)-O(19)	96.36(10)	O(24)-Fe(4)-Fe(3)	135.07(7)
O(25)-Fe(1)-O(6)	94.02(10)	O(20)-Fe(3)-O(21)	172.57(11)	O(21)-Fe(4)-Fe(3)	40.57(7)
O(16)-Fe(1)-O(6)	169.04(10)	O(22)-Fe(3)-O(21)	77.67(10)	O(22)-Fe(4)-Fe(3)	40.00(7)
O(18)-Fe(1)-O(6)	89.12(9)	O(19)-Fe(3)-O(21)	97.21(10)	O(15)-Fe(4)-Fe(3)	130.11(7)
O(17)-Fe(1)-O(6)	89.82(10)	O(20)-Fe(3)-O(8)	92.15(11)	O(11)-Fe(4)-Fe(3)	78.85(7)
O(3)-Fe(1)-O(6)	86.56(9)	O(22)-Fe(3)-O(8)	170.32(10)	O(23)-Fe(4)-Fe(5)	40.30(7)
O(25)-Fe(1)-Fe(2)	139.24(7)	O(19)-Fe(3)-O(8)	89.02(10)	O(24)-Fe(4)-Fe(5)	39.69(7)
O(16)-Fe(1)-Fe(2)	112.23(7)	O(21)-Fe(3)-O(8)	93.71(10)	O(21)-Fe(4)-Fe(5)	138.95(7)
O(18)-Fe(1)-Fe(2)	40.82(7)	O(20)-Fe(3)-O(12)	94.10(11)	O(22)-Fe(4)-Fe(5)	110.05(7)
O(17)-Fe(1)-Fe(2)	40.18(7)	O(22)-Fe(3)-O(12)	89.67(10)	O(15)-Fe(4)-Fe(5)	79.13(7)
O(3)-Fe(1)-Fe(2)	128.09(7)	O(19)-Fe(3)-O(12)	170.78(10)	O(11)-Fe(4)-Fe(5)	128.95(7)
O(6)-Fe(1)-Fe(2)	78.53(7)	O(21)-Fe(3)-O(12)	90.87(10)	Fe(3)-Fe(4)-Fe(5)	144.31(3)
O(17)-Fe(2)-O(19)	96.60(10)	O(8)-Fe(3)-O(12)	86.03(10)	O(25)-Fe(5)-O(24)	173.26(10)
O(17)-Fe(2)-O(20)	172.68(10)	O(20)-Fe(3)-Fe(2)	40.35(8)	O(25)-Fe(5)-O(16)	75.47(10)
O(19)-Fe(2)-O(20)	77.05(11)	O(22)-Fe(3)-Fe(2)	109.22(7)	O(24)-Fe(5)-O(16)	101.93(10)
O(17)-Fe(2)-O(18)	77.63(9)	O(19)-Fe(3)-Fe(2)	40.38(8)	O(25)-Fe(5)-O(23)	98.74(10)
O(19)-Fe(2)-O(18)	96.19(10)	O(21)-Fe(3)-Fe(2)	136.66(7)	O(24)-Fe(5)-O(23)	75.33(10)
O(20)-Fe(2)-O(18)	99.26(10)	O(8)-Fe(3)-Fe(2)	80.05(7)	O(16)-Fe(5)-O23	98.20(10)
O(17)-Fe(2)-O(5)	92.08(9)	O(12)-Fe(3)-Fe(2)	130.80(7)	O(25)-Fe(5)-O(14)	92.66(10)
O(19)-Fe(2)-O(5)	170.78(10)	O(20)-Fe(3)-Fe(4)	135.87(8)	O(24)-Fe(5)-O(14)	90.31(10)
O(20)-Fe(2)-O(5)	94.47(10)	O(22)-Fe(3)-Fe(4)	40.28(7)	O(16)-Fe(5)-O(14)	167.45(9)
O(18)-Fe(2)-O(5)	88.67(10)	O(19)-Fe(3)-Fe(4)	109.85(7)	O(23)-Fe(5)-O(14)	87.51(10)
O(17)-Fe(2)-O(9)	92.95(10)	O(21)-Fe(3)-Fe(4)	40.03(7)	O(25)-Fe(5)-O(2)	93.70(10)
O(19)-Fe(2)-O(9)	88.76(10)	O(8)-Fe(3)-Fe(4)	130.16(7)	O(24)-Fe(5)-O(2)	92.42(10)
O(20)-Fe(2)-O(9)	90.56(11)	O(12)-Fe(3)-Fe(4)	79.22(7)	O(16)-Fe(5)-O(2)	88.02(9)
O(18)-Fe(2)-O(9)	169.78(9)	Fe(2)-Fe(3)-Fe(4)	142.56(3)	O(23)-Fe(5)-O(2)	167.14(9)
O(5)-Fe(2)-O(9)	87.70(11)	O(23)-Fe(4)-O(24)	77.40(10)	O(14)-Fe(5)-O(2)	88.68(10)
O(17)-Fe(2)-Fe(3)	135.40(7)	O(23)-Fe(4)-O(21)	99.74(10)	O(25)-Fe(5)-Fe(4)	135.74(7)
O(19)-Fe(2)-Fe(3)	40.09(7)	O(24)-Fe(4)-O(21)	173.58(10)	O(24)-Fe(5)-Fe(4)	39.33(7)
O(20)-Fe(2)-Fe(3)	39.33(8)	O(23)-Fe(4)-O(22)	97.47(10)	O(16)-Fe(5)-Fe(4)	113.29(6)
O(18)-Fe(2)-Fe(3)	110.37(6)	O(24)-Fe(4)-O(22)	96.65(10)	O(23)-Fe(5)-Fe(4)	38.49(7)
O(5)-Fe(2)-Fe(3)	130.75(7)	O(21)-Fe(4)-O(22)	77.92(10)	O(14)-Fe(5)-Fe(4)	78.03(7)
O(9)-Fe(2)-Fe(3)	79.10(7)	O(23)-Fe(4)-O(15)	87.23(10)	O(2)-Fe(5)-Fe(4)	128.65(6)

Table 4 π-π stacking and hydrogen – bond geometry (Å,º) for complex **1**
Cg1 is the center of gravity of phenyl group

D-H…A	D -H	H…A	D…A	D-H…A
C14-H…Cg1	0.93	2.643	3.468	148.20
C39-H39A…O6	0.93	2.708	3.310	120.67

symmetry code: C14: x, y, -1+z; Cg1; x, y, z; C39: x, y, z; O6 and O 3: 1/3+y, 2/3-x+y, 1.6667-z.

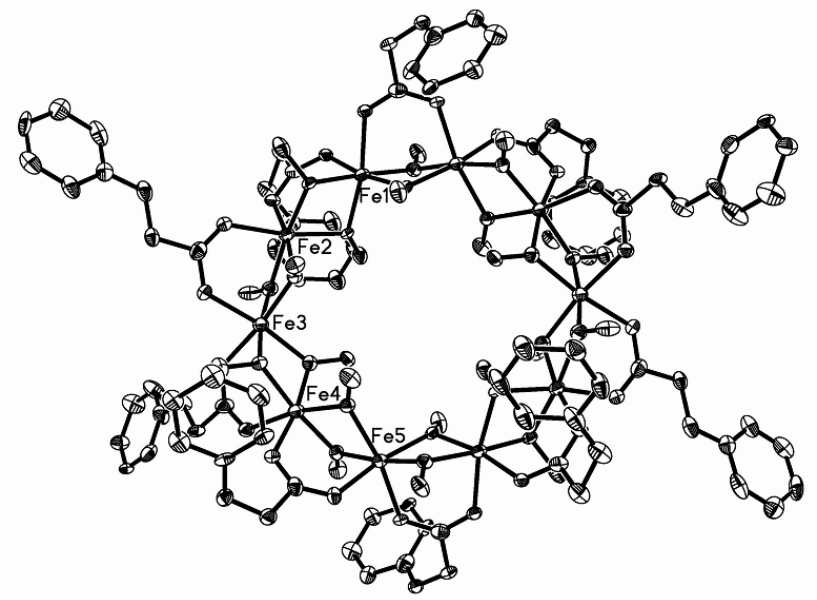

Figure 1 Molecular structure of the complex **1** (ORTEP drawing with 30% probabilities).

TGA

Thermal gravimetric (TG) analyses for crystal samples of **1** were performed from 20 to 700ºC (Figure 1). The weight loss of 3.91% from 20 to 200 °C (calcd 3.86%), corresponds to the release of almost all water molecules.

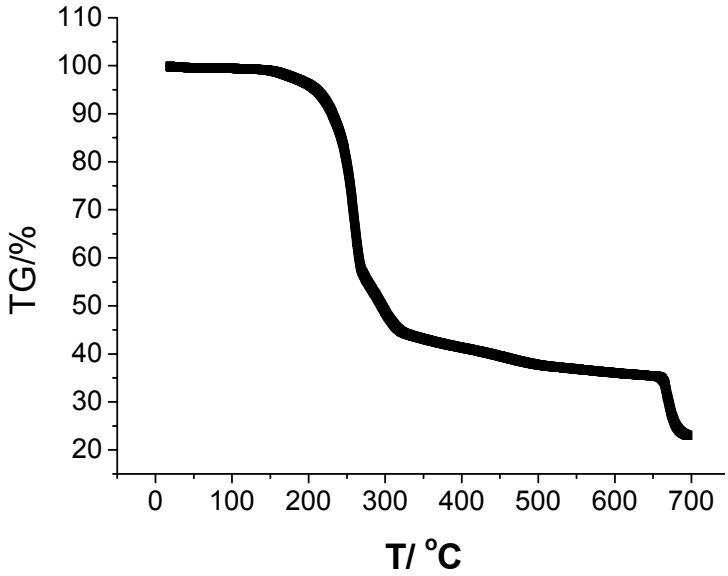

Figure 1 TGA curve of complex **1**

Magnetic details

Variable-temperature magnetic susceptibility measurements data were collected on microcrystalline samples of complex **1** in the 1.8-300 K range at 2 KOe field (Figure 1). The susceptibility, increases below 300K, reaches maximum at 65K, and decreases rapidly at lower temperatures. This behavior is characteristic of antiferromagnetic interactions between the high–spin iron (III) ions (S=5/2). Quantitative least-squares fitting of the susceptibility data for 1 using the classical spin[1] treatment gave an exchange interaction parameter J of approximately –5.36 cm^{-1} with the Hamiltonian $H = -2J\sum_{i=1}^{N-1} S_i \cdot S_{i+1} - 2JS_1 \cdot S_N$ and g=2.03. The calculated χ and χmT values are shown as a solid lines in Figure 7.

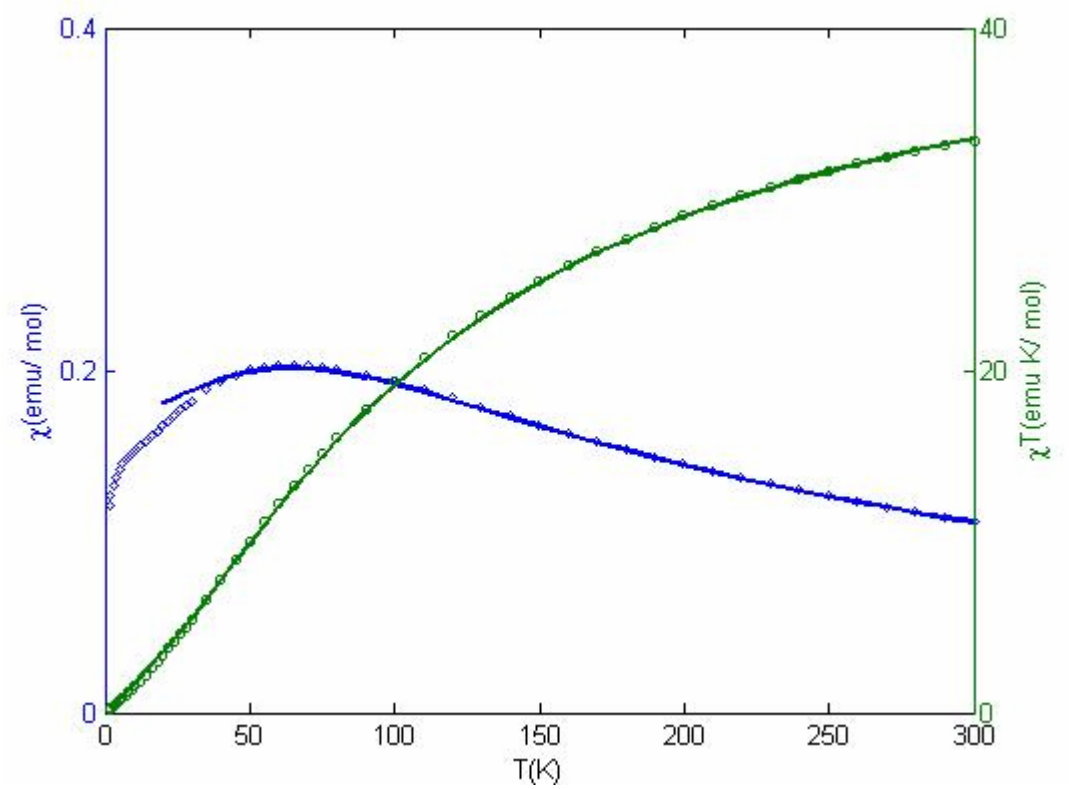

Figure 1. Magnetic susceptibility measurements of the complex 1 in the range 1.8-300K at 2 KOe applied magnetic field: "·" , "∘" refer to $\mathbf{X}_m T$ and $\mathbf{X}_m$, respectively, —represent the best fit to the data.

(1) Smith, T.; Fredberg, S. A.*Phys. Rev*. **1968**, 176(2), 660.