Supporting Information

A Neutral Fe(III) Compound Exhibiting A Two-Step Spin Transition and Dielectric Anomalies

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Tables/Figures Captions:

Table S1 Crystallographic data from $Mo(K\alpha)$ and synchrotron X-ray diffraction studies of compound **1** at variable temperatures.

Scheme S1 Schematic illustration for the deprotonation of the ligand.

 Table S2 Bond distances of compound 1 selected for X-ray diffraction.

Table S3 Bond distances for 1 from synchrotron diffraction at different temperatures.

Table S4 Hydrogen bond distances of compound 1 at variable temperatures (Å and °)

from synchrotron X-ray diffraction.

Fig. S1 Variable-temperature IR for compound 1 at 110 K, 260 K and 300 K.

Fig. S2 Packing diagram for 1 along *c* axis.

Fig. S3 Differentiation of the magnetic data, showing the transition temperatures.

Fig. S4 Experimental and calculated powder XRD pattern at room temperature.

Fig. S5 Plot of $\delta \chi T / \delta T$ versus temperature indicating *T*(LIESST) value of 40 K at the minimum.

Fig. S6 Mössbauer spectra at 110 K (top), 260 K (middle) and 300 K (bottom), respectively.

Fig. S7 DSC results for **1**, showing two anomaly peaks consistent with spin transition and dielectric anomalies.

Fig. S8 (a) The dielectric losses of **1** at different frequencies, (b) clearly shows the transition at 240 K and 270 K in the dielectric losses of **1** at 1 MHz.

Table S1 Crystallographic data from $Mo(K\alpha)$ and synchrotron X-ray diffraction

Parameters	Compound 1 [Fe ^{III} (H-5-Cl-thsa-Me)(5-Cl-thsa-Me)] \cdot H ₂ O					
	$C_{18}H_{19}Cl_2FeN_6O_3S_2$					
	X-ray			Synchrotron		
T/K	110 K	260 K	293 K	100 K	260 K	300 K
λ, Å	0.71073	0.71073	0.71073	0.68880	0.68880	0.68880
Formula weight	558.26	558.26	558.26	558.26	558.26	558.26
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Cc</i> (No. 9)	<i>Cc</i> (No. 9)	<i>Cc</i> (No. 9)	<i>Cc</i> (No. 9)	<i>Cc</i> (No. 9)	<i>Cc</i> (No. 9)
a/Å	8.9434(18)	8.9606(18)	8.9480(18)	8.9235(10)	8.9440(14)	8.930(2)
$b/{ m \AA}$	22.298(5)	22.354(5)	22.429(5)	22.248(2)	22.338(4)	22.346(5)
$c/{ m \AA}$	11.270(2)	11.337(2)	11.469(2)	11.2506(12)	11.3409(18)	11.428(3)
$eta/^\circ$	91.301(3)	91.20(3)	91.28(3)	91.422(2)	91.314(3)	91.306(4)
$V/\text{\AA}^3$	2246.9(8)	2270.4(8)	2301.2(8)	2232.9(4)	2265.3(6)	2279.9(9)
Ζ	4	4	4	4	4	4
$D_{\rm c}/{ m g~cm}^{-3}$	1.650	1.633	1.611	1.661	1.637	1.626
μ/mm^{-1}	1.129	1.118	1.103	1.032	1.017	1.011
GOF	1.03	1.13	0.96	0.978	1.022	0.993
R_1^{a}/wR_2^{b}	0.0486/0.1191	0.0786/0.1743	0.0837/0.2389	0.0497/0.1111	0.0577/0.1410	0.0520/0.1274
Flack parameter	0.01(2)	0.03(5)	0.00(5)	0.008(13)	0.07(3)	0.07(3)
Completeness/%	0.997	0.999	1.000	0.990	1.000	1.000

studies of compound 1 at variable temperatures.



 $\label{eq:Scheme S1} Schematic illustration for the deprotonation of the ligand.$

	110 K		260 K		293 К	
Fe–N	Fe1-N1	1.933(5)	Fe1-N1	1.999(8)	Fe1-N1	2.111(10)
	Fe1-N4	1.948(5)	Fe1-N4	2.016(9)	Fe1-N4	2.124(9)
Fe–O	Fe1-O1	1.940(4)	Fe1-O1	1.910(9)	Fe1-O1	1.916(9)
	Fe1-O2	1.933(4)	Fe1-O2	1.940(10)	Fe1-O2	1.937(9)
Fe–S	Fe1-S1	2.2389(15)	Fe1-S1	2.308(4)	Fe1-S1	2.391(4)
	Fe1-S2	2.2566(16)	Fe1-S2	2.338(4)	Fe1-S2	2.453(4)
С-О	C1-O1	1.328(6)	C1-O1	1.349(14)	C1-O1	1.324(16)
	C10-O2	1.336(6)	C10-O2	1.327(15)	C10-O2	1.339(16)
C–N _{amide}	C8-N3	1.343(6)	C8-N3	1.349(14)	C8-N3	1.354(17)
	C17-N6	1.325(6)	C17-N6	1.324(15)	C17-N6	1.315(16)
C-N _{azomethyne}	C8-N2	1.316(6)	C8-N2	1.301(14)	C8-N2	1.325(17)
	C17-N5	1.334(6)	C17-N5	1.339(14)	C17-N5	1.344(17)
C–S	C8-S1	1.752(5)	C8-S1	1.731(10)	C8-S1	1.731(13)
	C17-S2	1.712(5)	C17-S2	1.703(11)	C17-S2	1.707(12)

Table S2 Bond distances of compound 1 selected for $Mo(K\alpha)$ X-ray diffraction.

$Table \ S3 \ Bond \ distances \ for \ 1 \ from \ synchrotron \ X-ray \ diffraction \ at \ different$

temperatures.

	100 K		260 K		300 K	
Fe–N	Fe1-N1	1.937(2)	Fe1-N1	2.034(4)	Fe1-N1	2.111(4)
	Fe1-N4	1.946(2)	Fe1-N4	2.030(4)	Fe1-N4	2.135(5)
Fe–O	Fe1-O1	1.9281(18)	Fe1-O1	1.920(4)	Fe1-O1	1.927(4)
	Fe1-O2	1.9282(18)	Fe1-O2	1.924(5)	Fe1-O2	1.949(4)
Fe–S	Fe1-S1	2.2364(7)	Fe1-S1	2.3051(16)	Fe1-S1	2.3933(17)
	Fe1-S2	2.2531(7)	Fe1-S2	2.3465(16)	Fe1-S2	2.4536(17)
С-О	C1-O1	1.323(3)	C1-O1	1.323(8)	C1-O1	1.324(7)
	C10-O2	1.324(3)	C10-O2	1.332(8)	C10-O2	1.325(7)
C–N _{amide}	C8-N3	1.329(3)	C8-N3	1.342(7)	C8-N3	1.331(7)
	C17-N6	1.312(3)	C17-N6	1.298(7)	C17-N6	1.317(7)
C-N _{azomethyne}	C8-N2	1.319(3)	C8-N2	1.304(7)	C8-N2	1.319(7)
	C17-N5	1.342(3)	C17-N5	1.344(7)	C17-N5	1.348(7)
C–S	C8-S1	1.750(2)	C8-S1	1.742(5)	C8-S1	1.732(5)
	C17-S2	1.712(2)	C17-S2	1.705(5)	C17-S2	1.685(6)

Table S4 Hydrogen bond distances of compound 1 at variable temperatures (Å and $^{\circ}$)

Temperature	D–H···A	d(D—H)	$d(H \cdots A)$	$d(D \cdots A)$	∠(DHA)
100 K	N(5)-H(5N)O(1W)#1	0.88	2.03	2.845(3)	154.2
	N(6)-H(6A)O(2)#2	0.88	1.84	2.706(3)	167.0
	N(3)-H(3B)O(1)#3	0.88	1.94	2.815(6)	173.9
	O(1W)-H(1W)N(2)#2	0.85	2.50	3.234(3)	145.6
	O(1W)-H(1W)O(1)#4	0.85	2.57	3.131(3)	124.8
260 K	N(5)-H(5N)O(1W)#1	0.86	2.07	2.857(7)	152.6
	N(6)-H(6A)O(2)#2	0.86	1.93	2.774(7)	168.7
	N(3)-H(3B)O(1)#3	0.86	2.03	2.890(7)	174.6
	O(1W)-H(1W)N(2)#2	0.86	2.44	3.190(7)	147.3
	O(1W)-H(1W)O(1)#4	0.86	2.61	3.145(8)	121.3
300 K	N(5)-H(5N)O(1W)#1	0.86	2.06	2.839(6)	150.2
	N(6)-H(6A)O(2)#2	0.86	1.97	2.812(6)	166.5
	N(3)-H(3B)O(1)#3	0.86	2.08	2.933(6)	172.9
	O(1W)-H(1W)N(2)#2	0.86	2.37	3.134(7)	148.3
	O(1W)-H(1W)O(1)#4	0.86	2.63	3.116(6)	117.3
	1				

from synchrotron X-ray diffraction.

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z+1/2 #2 x+1/2,-y+1/2,z+1/2

#3 x+1/2,-y+1/2,z-1/2 #4 x+1,y,z

Variable-temperature IR spectroscopy studies on **1** were carried out between 300 K and 80 K. The shifted and split peaks around 1500 cm⁻¹ and 1280–1300 cm⁻¹ are ascribed to the vibration of C–O that is formed by the N_{amide}–H…O hydrogen bond, which should be assigned to the thermal modification of the ligand (Fig. S1, top). The vibrational bands around 810-830 cm⁻¹ should be assigned to v(C=S) stretching vibration, indicating the coordination environment was changing with the thermal treatment (Fig. S1, bottom).



Fig. S1 Variable-temperature IR for compound 1 at 110 K, 260 K and 300 K.



Fig. S2 Packing diagram for **1** along *c* axis.



Fig. S3 Differentiation of the magnetic data, showing the transition temperatures.



Fig. S4 Experimental and calculated powder XRD pattern at room temperature.



Fig. S5 Plot of $\delta \chi T / \delta T$ versus temperature indicating *T*(LIESST) value of 40 K at the minimum.



Fig. S6 Mössbauer spectra at 110 K (top), 260 K (middle) and 300 K (bottom), respectively.

For the high temperature phase at 300 K, one quadrupole doublet is observed with an isomer shift $\delta = 0.297$ (relative to the metallic iron at 293 K) and quadrupole splitting $\Delta E_Q = 0.592$ mm s⁻¹, which is characteristic of HS Fe(III) species (area fraction

100%). When the temperature is decreased to 260 K, the δ is 0.091 and the quadrupole splitting ΔE_Q equals 2.694 mm s⁻¹ for LS (area fraction 42.4%, green line) and $\delta = 0.326$ and $\Delta E_Q = 0.823$ mm s⁻¹ for HS (area fraction 57.6%, blue line). As the temperature is decreased to 110 K, the LS fraction ($\delta = 0.148$ and $\Delta E_Q = 2.735$ mm s⁻¹) reaches a value of 100%, which is consistent with the results of the magnetic studies and suggests that a complete spin transition occurs. The results of the Mössbauer spectra are in accord with the nature of the two-step spin transition process as characterized by the crystallographic and magnetic studies.



Fig. S7 DSC results for **1**, showing two anomaly peaks consistent with spin transition and dielectric anomalies.







(b)

Fig. S8 (a) The dielectric losses of **1** at different frequencies, (b) clearly shows the transition at 240 K and 270 K in the dielectric losses of **1** at 1 MHz.

Experimental Section and Measurements

The Schiff base ligand 5-Cl-thsa-Me (2 mmol, 0.548 g) and DMA (4 mmol, 0.45 g in MeOH) were reacted in 50 mL of methanol and 5 mL of water at 80°C and 1 mmol $Fe(NO_3)_3 \cdot 9H_2O$ was slowly added to the refluxing mixture. After 8 h, the reaction was cooled to room temperature and left to stand overnight. The resulting black precipitate was collected and washed with acetone/water and then dried under vacuum for 4 h. Single crystals suitable for X-ray diffraction had deposited in the bottom of flask. Yield is ~ 92%. Elemental analysis (%) for compound **1**: Calc. (found) for $C_{18}H_{19}O_3N_6S_2Cl_2Fe: C 38.73\%$ (38.45%), H 3.43% (3.33%), N 15.05% (15.00%).

For the photoirradiation experiment, we directed 532 nm light into the magnetometer cavity via an optical fiber. The powdered sample was spread on a commercial transparent adhesive tape and placed on the edge of the optical fiber. The residual magnetic signal of the tape, which had been determined previously, was found to be the same magnitude as the instrumental magnetization noise; therefore, the raw data were not corrected for the diamagnetic correction.

Magnetic susceptibility data under an applied magnetic field of 0.5 T were collected using a Quantum Design MPMS-5S SQUID magnetometer. Variable-temperature infrared spectra were recorded as fine powder spread on a KBr plate with a JASCO FT/IR-600 Plus spectrometer in the 400–4000 cm⁻¹ region. Variable temperature IR data were collected using a model 331 temperature controller (Lakeshore) operating between 80 and 300 K.

The complex permittivity was measured using a Tonghui TH2828A LCR meter with an AC voltage of 1 V. The pressed pellets deposited with silver conducting glue were used for dielectric studies.

The single-crystal XRD experiments for 1 were performed on a Bruker Apex-II

diffractometer with Mo(K α) radiation at variable temperatures using the same single crystal. The structures were solved by a direct method and refined by full-matrix least squares on F^2 using the SHELX program with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were added geometrically and refined using the riding model. CCDC-936362 (110 K), CCDC-936361 (260 K) and CCDC-936360 (293 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction was performed on Rigaku RINT-TTR III powder diffractometer at room temperature.

The synchrotron X-ray diffraction experiments were conducted at the Advanced Light Source, Lawrence Berkeley National Lab, on Beamline 11.3.1. The data collection was performed on a modified Bruker Apex-II diffractometer with synchrotron radiation (0.68880 Å). The sample was mounted on a MiTeGen Kapton pin for data collection at 100 K, 260 K and 300 K. The same crystal was used for all three temperatures with re-centering between datasets to account for thermal expansion of the Kapton pin. The cell constants were indexed from reflections obtained from 36 frames with an exposure time of 1 s/frame. A full sphere (2400 frames at 5 cm detector distance) was collected with scan widths of 0.30° in ω and an exposure time of 1 s/frame. Data reduction and cell refinement for all temperatures were performed with SAINT.¹ SADABS was used to obtain absorption corrected data.² The space group was uniquely determined to be *Cc* (No. 9). The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the Bruker SHELXTL package.³ All non-hydrogen atoms were refined anisotropically.

riding model. The amino and water hydrogen atoms were found in the difference map and their distances to their respective N and O atoms were restrained; however, the coordinates were allowed to refine. CCDC-936357 (100 K), CCDC-936358 (260 K) and CCDC-936359 (300 K).

 SAINT frame integration software, v. 8.27B, Bruker AXS, Inc. Madison, WI, 2012.
 G. M. Sheldrick, SADABS, Program for Absorption Correction of Area Detector Frames, Bruker AXS, Inc. Madison, Wi., 2008.

3 G. Sheldrick, Acta Crystallographica Section A, 2008, 64, 112–122.