Supporting Information

"Normal" and "reverse" spin crossover induced by two different structural events in iron(II) coordination polymer.

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Experimental

Materials and methods. Acetonitrile (Honeywell LC-MS), used to synthesis of the complex, was distilled over the calcium hydride (Aldrich). 1,4-di(5-ethyl-1,2,3-triazol-1yl)butane (ebbtr) was synthesized according to previously described method.^[1] Iron(II) trifluoromethanesulfonate hexahydrate was prepared in reaction of powdered iron metal (Merck) with aqueous solution of trifluoromethanesulfonic acid (Aldrich).^[2] IR spectra of 1 were recorded with the Jasco FT/IR-6700 spectrometer in the range 400-4000 cm⁻¹ in nujol mull. Elemental analyses for carbon, hydrogen and nitrogen were performed on Vario El Cube elemental analyzer. Temperature dependent measurements of the magnetic susceptibility of complexes were carried out with a Quantum Design SQUID MPMS-XL-5 magnetometer in the 10-300 K under 1T applied magnetic field with temperature scan rate 0.1, 1 and 3 K/min. The measurements were carried out for samples placed in the sealed glass tubes. Magnetic data were corrected for signal of glass tube and for the diamagnetic contributions of the sample, estimated from Pascal's constants. Mössbauer spectra (~10mCi ⁵⁷Co/Rh source) were measured with transmission geometry on POLON spectrometer controlled by MOSIEK software. The sample was transferred (under nitrogen atmosphere) into the plastic container. Sealed container, positioned between beryl windows, was mounted on a cold finger of ARS DMX-20 helium cryostat. PIECUCH software (Elektronika) and Lakeshore 200 device were used to control a temperature. Deconvolution of Mössbauer spectra was carried by least-square fitting using Lorentzian functions (MOS software). The isomer shifts δ and quadrupole splitting ΔE_Q were calculated in relation to α -iron. DSC measurements were carried out with Mettler Toledo DSC 3 at 10 K min⁻¹.

X-ray data collection and structure determination. Single crystals of 1 were prepared according with synthesis procedure and preselected using the stereoscopic Zeiss microscope. For the X-ray measurements they were placed on the loops in the drop of oil. Structural studies were performed with a four-circle SuperNova X-ray diffractometer with microfocus X-ray tube, optimized multi-layer optics for Mo-K α ($\lambda = 0.71073$ Å) radiation and an Atlas CCD detector. The controlling of the measurement procedure and data reduction were performed by CrysAlisPro software.^[3] The same program was used to determine and refine the lattice parameters. Low temperatures were achieved with a stream of cold nitrogen gas using an Oxford Cryosystem cooling device. The temperature stability was 0.1 K. The crystal structures of 1 were solved using the SHELXS-2013 program and refined with the SHELXL-2014/7 program.^[4] Non-hydrogen atoms of the 2D net of 1 were refined with anisotropic

displacement parameters. Hydrogen atoms were introduced to the structure by appropriate rigid body constraints (AFIX 23, AFIX 43 or AFIX 137) with temperature factors Uiso(H) equal to 1.2Ueq(C) excepting methyl hydrogen atoms for which Uiso(H) = 1.5Ueq(C). Because of disordering of triflate anions, their geometry was restrained to be similar to that of the major one using a SAME instruction. Some of the atoms in anions were refined isotropically to avoid undesirable displacement ellipsoids.

CCDC 1905014-1905023 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Synthesis of $[Fe(ebbtr)_2(MeCN)_2](CF_3SO_3)_2 \cdot 4MeCN$ (1). Syntheses of 1 was performed under nitrogen using standard Schlenk techniques. 46.2 mg of $Fe(CF_3SO_3)_2 \cdot 6H_2O$ (0.10 mmol) dissolved in 2.0 mL of acetonitrile was added to a solution of 24.8 mg ebbtr (0.10 mmol) in 2.0 mL acetonitrile. The resulting colorless reaction mixture was transferred into a Schlenk flask and a stream of nitrogen was passed over the solution. After the reduction of the solution by half of the starting volume, the Schlenk was closed. After two weeks the colorless crystalline product was filtered off, washed with acetonitrile and dried in a stream of nitrogen. 1 was isolated with yield of 31.0 % (17.0 mg). Elementary analysis for $C_{38}H_{58}N_{18}FeS_2F_6O_6$ (1096.95 g/mol): calcd (%). C 41.6, H 5.3, N 23.0; found (%) C 41.6, H 5.2, N 22.9. FTIR: See Fig. S13 for IR spectrum.
 Table S1a. Crystallographic data for crystal structures of 1 determined at different temperatures.

Structure number	1	2	5	6	7	10			
т [К]	270 K (cooling)	225 K (cooling)	160 K (cooling)	100 K (cooling)	195 K (heating)	270 K (heating)			
CCDC number	<mark>1905014</mark>	<mark>1905015</mark>	<mark>1905018</mark>	<mark>1905019</mark>	<mark>1905020</mark>	<mark>1905023</mark>			
	HT(HS)	HT(HS/LS)	LT(LS)	LT(LS)	LT(LS)	HT(HS)			
Chemical formula			C ₂₈ H ₄₆ Fe N ₁₄ , 2(C	F ₃ S O ₃), 4(C ₂ H ₃ N)					
Formula mass		1096.99							
Crystal system, space group			Triclin	ic, P-1					
Z				L					
a [Å]	11.910(3)	11.8046(17)	11.8402(6)	11.7464(5)	11.9565(5)	11.890(2)			
b [Å]	12.104(2)	12.092(2)	11.9712(7)	11.8983(7)	12.0756(8)	12.0986(19)			
c [Å]	12.368(3)	12.2737(18)	11.8910(7)	11.7776(7)	11.9872(8)	12.349(2)			
α[°]	66.30(2)	67.293(15)	69.846(6)	70.253(5)	69.006(7)	66.416(17)			
β[°]	65.36(3)	64.866(14)	62.779(6)	62.681(5)	62.644(6)	65.468(17)			
γ [°]	61.05(3)	60.571(16)	61.129(6)	61.357(5)	60.642(6)	61.180(17)			
V [ų]	1372.4(7)	1346.0(4)	1295.84(16)	1268.75(14)	1319.85(17)	1370.6(5)			
Absorption coefficient [mm ⁻¹]	0.429	0.437	0.454	0.464	0.446	0.429			
No. of measured reflections	11541	11302	10706	10412	10945	5696			
No. of independent reflections	5608	5496	5290	5170	5372	3197			
Theta range for data collection [°]	3.054 to 26.371	3.027 to 26.368	3.335 to 26.372	3.371 to 26.371	2.990 to 26.371	3.339 to 24.451			
Index ranges	$-14 \le h \le 14$	-14 ≤ <i>h</i> ≤14	-14 ≤ <i>h</i> ≤14	-14 ≤ <i>h</i> ≤14	-14 ≤ <i>h</i> ≤14	-13 ≤ <i>h</i> ≤13			
	$-14 \le k \le 15$	$-14 \le k \le 15$	$-14 \le k \le 14$	$-14 \le k \le 14$	-14 ≤ <i>k</i> ≤ 15	$-12 \le k \le 11$			
	-14 ≤ <i>l</i> ≤ 15	-14 ≤ <i>l</i> ≤ 15	-14 ≤ <i>l</i> ≤ 14	-14 ≤ <i>l</i> ≤ 14	-14 ≤ <i>l</i> ≤ 14	-12 ≤ <i>l</i> ≤ 12			
R _{int}	0.0320	0.0295	0.0247	0.0259	0.0257	0.0545			
Final R_1 values ($l > 2\sigma(l)$)	0.1029	0.0990	0.0412	0.0382	0.0434	0.1131			
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.3082	0.2938	0.1070	0.1000	0.1110	0.3039			
Final R ₁ values (all data)	0.1361	0.1388	0.0521	0.0455	0.0595	0.1451			
Final wR(F ²) values (all data) ^b	0.3575	0.3482	0.1156	0.1059	0.1224	0.3468			
Goodness-of-fit on F ²	1.227	1.158	1.034	1.037	1.030	1.235			
Largest diff. peak and hole [eÅ-3]	0.801 and -0.635	0.651 and -0.670	0.620 and -0.418	0.914 and -0.466	0.405 and -0.413	0.796 and -0.526			

 Table S1b. Crystallographic data for crystal structures of 1 determined at different temperatures in the intermediate phase.

Structure number	3	4	8	9					
т [К]	215 K (cooling)	195 K (cooling)	210 K (heating)	225 K (heating)					
CCDC number	1905016	1905017	1905021	1905022					
	IP(HS)	IP(HS)	IP(HS)	IP(HS)					
Chemical formula	ormula C ₈₄ H ₁₃₈ Fe ₃ N ₄₂ , 6(C F ₃ S O ₃), 12(C ₂ H ₃ N)								
Formula mass		3290.97							
Crystal system, space group		Triclir	nic, P-1						
Z			1						
a [Å]	12.0469(11)	12.0056(8)	12.0929(8)	12.1229(15)					
b [Å]	18.2982(13)	18.3067(8)	18.3605(11)	18.3542(18)					
c [Å]	20.582(2)	20.6014(14)	20.6682(14)	20.670(3)					
α[°]	64.984(8)	64.898(5)	64.854(6)	64.830(11)					
β[°]	75.059(9)	74.873(6)	74.914(6)	74.777(11)					
γ [°]	85.411(7)	85.388(4)	85.364(5)	85.360(9)					
V [Å ³]	3970.2(7)	3955.8(5)	4008.6(5)	4014.0(9)					
Absorption coefficient [mm ⁻¹]	0.445	0.446	0.440	0.440					
No. of measured reflections	33599	33464	16882	17025					
No. of independent reflections	16207	16147	9397	9433					
Theta range for data collection [°]	2.971 to 26.373	3.036 to 26.372	3.133 to 24.545	3.130 to 24.558					
Index ranges	$-15 \le h \le 14$	-15 ≤ <i>h</i> ≤14	-13 ≤ <i>h</i> ≤14	-13 ≤ <i>h</i> ≤14					
	-22 ≤ <i>k</i> ≤ 22	-21 ≤ <i>k</i> ≤ 22	-20 ≤ <i>k</i> ≤ 21	-20 ≤ <i>k</i> ≤ 21					
	-25 ≤ <i>l</i> ≤ 25	-25 ≤ <i>l</i> ≤ 25	-20 ≤ <i>l</i> ≤ 20	-20 ≤ <i>l</i> ≤ 20					
R _{int}	0.1107	0.0745	0.0424	0.0540					
Final R_1 values ($l > 2\sigma(l)$)	0.0885	0.0801	0.0640	0.0703					
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.1833	0.2048	0.1650	0.1787					
Final R_1 values (all data) ^a	0.2418	0.1330	0.1000	0.1135					
Final wR(F ²) values (all data) ^b	0.2804	0.2570	0.2002	0.2225					
Goodness-of-fit on F ²	0.949	1.009	1.028	1.032					
Largest diff. peak and hole [eÅ-3]	1.157 and -0.534	1.531 and -0.923	0.668 and -0.472	0.631 and -0.432					

Structure number	1	2	3	4	5	6	7	8	9	10
т [К]	270 K (cooling)	225 K (cooling)	215 K (cooling)	195 K (cooling)	160 K (cooling)	100 K (cooling)	195 K (heating)	210 K (heating)	225 K (heating)	270 K (heating)
Fe1-N3 [Å]	2.148(4)	2.151(5)			2.0742(17)	2.0036(15)	2.1573(18)			2.155(6)
Fe1-N13 [Å]	2.190(3)	2.185(4)			2.0610(17)	1.9912(15)	2.1440(17)			2.183(6)
Fe1-N23 [Å]	2.190(5)	2.164(5)			2.020(2)	1.9292(16)	2.133(2)			2.192(9)
Average Fe-N [Å]	2.176(4)	2.167(4)			2.0518(18)	1.9747(15)	2.1448(19)			2.177(7)
N3-Fe1-N13 [°]	88.27(14)	88.74(16)			91.23(6)	91.76(6)	90.72(7)			87.9(2)
N3-Fe1-N23 [°]	91.25(17)	90.25(18)			90.14(7)	90.26(6)	90.33(7)			91.4(3)
N13-Fe1-N23 [^o]	91.94(15)	91.32(15)			89.32(7)	89.63(6)	89.26(7)			92.0(2)
ΣFe1	19.68	11.31			8.21	9.56	7.16			22
Fe1-N3 [Å]			2.159(5)	2.162(3)				2.176(4)	2.176(5)	
Fe1-N33 [Å]			2.162(5)	2.151(3)				2.165(4)	2.168(5)	
Fe1-N43 [Å]			2.167(5)	2.163(3)				2.174(4)	2.176(4)	
Fe1-N63 [Å]			2.180(5)	2.184(3)				2.193(4)	2.183(4)	
Fe1-N24 [Å]			2.166(7)	2.166(4)				2.173(6)	2.180(7)	
Fe1-N25 [Å]			2.180(7)	2.183(4)				2.201(6)	2.210(7)	
Average Fe-N [Å]			2.169(6)	2.168(4)				2.180(5)	2.182(5)	
N33-Fe1-N24 [°]			91.0(2)	91.48(13)				91.35(17)	91.24(19)	
N3-Fe1-N24 [°]			91.8(2)	91.60(14)				91.63(17)	91.70(19)	
N3-Fe1-N43 [°]			90.36(18)	90.45(11)				91.63(17)	90.41(16)	
N33-Fe1-N43 [°]			88.73(18)	88.64(12)				88.55(15)	88.23(16)	
N24-Fe1-N43 [°]			90.6(2)	91.02(13)				90.95(17)	90.94(19)	
N3-Fe1-N25 [°]			87.1(2)	86.81(13)				91.18(16)	87.09(18)	
N33-Fe1-N25 [°]			90.2(2)	90.15(13)				89.20(15)	90.03(19)	
N43-Fe1-N25 [°]			91.3(2)	90.99(13)				91.18(16)	91.17(18)	
N3-Fe1-N63 [°]			89.04(18)	89.21(12)				89.20(15)	89.36(16)	
N33-Fe1-N63 [°]			91.91(18)	91.71(12)				91.88(15)	92.00(16)	
N24-Fe1-N63 [°]			88.6(2)	88.75(13)				88.94(17)	88.99(18)	
N25-Fe1-N63 [°]			89.5(2)	89.23(12)				88.93(16)	88.91(18)	
Σ Fe1			14.2	14.76				16.67	14.91	
Fe2-N13 [Å]			2.157(5)	2.157(3)				2.169(4)	2.173(4)	
Fe2-N53 [Å]			2.168(4)	2.165(3)				2.172(4)	2.173(4)	
Fe2-N23 [Å]			2.189(6)	2.179(4)				2.190(6)	2.196(6)	
Average Fe-N [Å]			2.172(5)	2.167(3)				2.177(4)	2.180(5)	
N13-Fe2-N53 [°]			91.01(18)	91.32(11)				91.25(15)	91.0(2)	
N13-Fe2-N23 [^o]			88.9(2)	89.03(13)				89.16(16)	89.39(18)	
N53-Fe2-N23 [^o]			89.7(2)	89.56(13)				89.84(16)	89.80(18)	
Σ Fe2			9.63	10.94				9.03	7.04	
Fe1-N23-C23 [°]	177.0(5)	177.2(5)			178.12(18)	179.07(15)	177.12(19)			177.5(8)
Fe2-N23-C23 [°]			171.3(6)	171.7(3)				171.6(4)	171.2(5)	
Fe1-N24-C24 [^o]			172.2(6)	171.5(4)				172.0(5)	172.4(5)	
Fe1-N25-C25 [°]			176.6(6)	176.5(3)				176.4(5)	176.1(6)	

 Table S2a. Fe-N distances (Å), N-Fe-N and Fe-N-C angles (°) at different temperatures.

1	Table S2b. Selected Fe···	·Fe, donor	atom…donor atom ($N \cdots N$) interator	nic distances a	nd torsion ang	les (°) at differ	rent temperatur	es.
									(

Structure number 1 2 3 4 5 6 7 8 9	10
T [K] 270 K (cooling) 225 K (cooling) 215 K (cooling) 195 K (cooling) 160 K (cooling) 100 K (cooling) 195 K (heating) 210 K (heating) 225 K (h	g) 270 K (heating)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	13.113(3) *=[1+x,y,-1+z]
N3···N3* [Å] 9.690(9) 9.40(1) 8.804(4) 8.804(3) 8.750(4)	9.68(1) *=[2 x y z]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-[2-x,-y,-2]
Oshicical 765(3) 775(2) 600(3)	78(6)
C5-N1-C1-C2b [9] 100 5(6) 100 5(6)	111(1)
N1-C1-C2-C2* [⁰] 66.1(3) 66.0(3)	
*=[1-x,2-y,-z] *=[1-x,2-y,-z] *=[1-x,2-y,-z]	
N1-C1-C2a-C2a* [°] 56(6) 64(2) *-[2x,y,-z] *-[2x,y,-z]	62(9) *-[2-x -x -7]
N1_C1_C2b_C2b* [9] -175_4[6] -175_7[7]	-[2-x,-y,-2]
$\begin{array}{c} 1 & 1 & 1 & 3 & -3 & -3 & -3 & -3 & -3 $	*=[2-x -y -7]
$\frac{(1-r_{1})^{2}}{(1-r_{1})^{2}} = \frac{(1-r_{1})^{2}}{(1-r_{1})^{2}} = (1$	-169.7(9)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	()
N13-033 [Å] 8.669(7) 8.668(5) 8.699(
C15-N11-(21/21)	
N11-C11-C12-C32 [⁰]67.8(7) -70.4(5)69.5(6) -69.7(7)	
C11-C12-C32-C31 [⁰] -179.6(6) -179.1(4) -179.4(4) -179.4(4) -179.4(4) -179.4(5)	
C12-C32-C31-N31 [⁰] 69.1(7) 69.3(5) 68.8(6) 68.2(7)	
C32-C31-N31-C35 [7] 79.8(8) 79.4(5) 78.5(7) 80.4(8	
C17-C16-C15-N11 [°] -169.9(7) -169.8(5) -169.8(6) -169.8(6) -169.8(6)	
C37-C36-C35-N31 [°] 161.6(8) 161.6(5) 159.9(7) 162.2(°	
Fe1…Fe1[1-x, 2-y, 1-z] [Å]	
N3···N3[1-x, 2-y, 1-2] [Å] 9.654(6) 9.674(8) 9.680(
C5-N1-C1-C2 [⁰] -99.5(7) -100.3(5) -98.4(6) -99.1(7	
N1-C1-C2-C2[1-x, 2-y, 1-z] ^{[0}]	
C7-C6-C5-N1 [°] -73.4(9) -72.1(6) -71.9(7) -72.6(8)	
Fe1…Fe1* [Å] 12.104(2) 12.092(2) 11.9712(7) 11.8983(7) 12.0756(8)	12.0986(19)
*=[x,1+y,2] *=[x,-1+y,2] *=[x,-1+y,2] *=[x,-1+y,2]	*=[x, 1+y, z]
N13···N13* [Å] 8.599(7) 8.598(7) 8.651(3) 8.678(3) 8.633(3)	8.59(1)
*=[1-x,1-y,1-z] *=[1-x,1-y,1-z] *=[-x,1-y,1-z] *=[-x,1-y,1-z]	*=[1-x, 1-y, 1-z]
C15-N11-C11-C12 [°] 77.5(7) 78.6(6) -77.6(3) -75.6(2) -79.5(3)	78(1)
N11-C11-C12-C12* ^[0] 69.9(8) 69.1(7) -67.8(3) -68.0 (3) -68.3(3)	70 (1)
*=[1-x,1-y,1-z] *=[1-x,1-y,1-z] *=[1-x,1-y,1-z] *=[-x,1-y,1-z] *=[*=[1-x, 1-y,1-z]
C17-C16-C15-N11 [*] 149.2(8) 151.2(6) -152.4(2) -151.06(19) -153.8(3)	149(1)
reimet [1.915(2) 11.8987(12) 11.9375(16) 11.949	
N43-:N43[1-x, 1-y, 1-z] [A] 8.465(9) 8.463(6) 8.477(8) 8.493(2)	
C45-N41-C41-C42[1] 82.5(9) 82.9(5) 82.9(5) 82.9(7) 82.	
N41-C41-C42-C42[1-X, 1-Y, 1-2][*] 61[1] 61.8(b) 62.6(9) 62.6(9) C47_C44_1C4_2(1-X, 1-Y, 1-2)[*] 61.1 61.8(b) 62.6(1-X) 62.6(1-X)	
$(47-(46-(45-84) 1)^2)$ $(-168.8(5))$ $(-169.7(7))$ $(-168.8(5))$ $(-169.7(7))$ $(-168.8(5))$ $(-169.7(7))$ $(-169.8(5))$ $(-169.7(7))$ $(-169.8(5))$ $(-169.7(7))$ $(-169.8(5))$ $(-169.7(7))$ $(-169.8(5))$ $(-169.7(7))$ $(-169.8(5))$ $(-169.7(7))$ $(-169.8(5))$ $(-16$	
Fe2Fe1x, -1+y,z] [A] 12.2/5/(15) 12.2//9(9) 12.3107(12) 12.309(12)	
N53-Wb3 [A] 8.500(7) 8.598(4) 8.621(6) 8.627(6)	
C55-N51-C51-C52 [*] 81.0(8) 81.1(5) 81.3(6) 82.3(7) NF4 GF2 CF3 [0] C64 (7) C73 (7) C73 (7) C73 (7)	
N51-C51-C52-C52 [] 55.7(5) 55.	
C51-C52-C62-L61 [0] 1//.0(5) 1/8.5(3) 1/8.9(4) 1/8.7(4) C52-C62-C61 Me1 [0] 62.2(6) 62.2(6) 62.2(7) 62.2(7)	<u> </u>
C2-C2-C2-C3-F001 -03.2(6) -02.2(5) -03.5(6)	
Concentration -00.0(a) -7.5.0(b)	<u> </u>
C67-C66-C65-N61 [°] -176.9(7) -176.4(4) -176.2(5) -176.2(5)	

Structure number	1			2	6	
т [к]	270 K (cooling)		225K (cooling)		100K (cooling)	
. [17]						
	D····A [A]	D - H…A [*]	D····A [A]	D - H…A [°]	D···A [A]	D - H…A [°]
С6-Н6А	3.38(3)	169	3.27(3)	154		
С11-Н11В…О1В	3.55(3)	137	3.41(2)	131		
C12-H12B…O1B[-x+1, -y+1, -z+1]	3.46(2)	143	3.341(14)	137		
C231-H23A…F3B[x, y-1, z]	3.30(3)	140	2.92(3)	163		
C88-H88B…O2B[x+1, y, z]	3.07(3)	152	3.16(2)	160		
С98-Н98С…О1В	3.08(3)	127	3.22(3)	127		
С98-Н98С…ОЗВ	3.47(3)	146	3.30(3)	132		
C1-H1B…O3B[1-x,1-y,-z]	3.26(2)	160	3.17(2)	162		
C2B-H2B2···O2A[1+x,-1+y,z]	3.300(11)	166	3.15(1)	175		
C17-H17C…F3B[x,-1+y,1+z]	3.40(3)	151	3.57(4)	153		
C17-H17C…F1B[x,-1+y,1+z]	4.11(4)	165	3.97(3)	156		
C2A-H2A…F2A[x+1, y-1, z]	3.45(5)	173	3.498(15)	164		
C88-H88B…O2A[x+1, y, z]	3.159(13)	173	3.252(11)	146		
C88-H88C…N89[-x+2, -y+1, -z+1]	3.31(3)	142	3.432(13)	132		
C16-H16A…N99[-x+1, -y+1, -z+1]	3.517(12)	128	3.421(12)	135		
C17-H17C…F2A[x,-1+y,1+z]	3.462(16)	166	3.423(11)	158		
C14-H14…N2*	3.213(6)	115	3.233(6)	117	3.116(2)	116
C221 U22A C2A*	*=[1-x,-y,1-z]	110	*=[1-x,-y,1-z]	120	*=[x,y,z]	125
C231-H23A····O3A	3.380(13) *=[x1+y.7]	110	3.303(11) *=[x1+v.7]	129	3.132(3) *=[x-1.y.7]	135
C11-H11B…O1A*	3.019(12)	120	3.003(8)	121	3.127(3)	123
	*=[x,y,z]		*=[x,y,z]		*=[-x+1,-y+1,-z+1]	
C1-H1A…N99*	3.435(13)	129	3.399(13)	133	3.236(3)	122
C4 H4O2A*	*=[x,y,z]	171	*=[x,y,z]	172	*=[x,γ+1,z]	172
C4-H4OSA	5.452(11) *=[-x+1,-y+1,-z+1]	1/1	*=[-x+1,-y+1, -z+1]	1/5	5.415(2) *=[-x+1,-y+2,-z+1]	172
C1-H1B…F1A[-x+1, -y+2, -z]					3.500(2)	161
C231-H23B…F1A[-x+1, -y+2, -z]					3.355(2)	152
C231-H23B…F3A[-x+1, -y+2, -z]					3.343(3)	133
C231-H23C…N89[x-1, y+1, z]					3.463(3)	171
C98-H98A…O1A[x-1, y, z]					3.321(3)	135
C88-H88B…O2A					3.223(3)	176
C2-H2A…O2A					3.449(3)	133
С7-Н7С…ОЗА					3.363(3)	124

Table S3. Selected C-H…N and C-H…O interatomic contacts [Å] and angles [°] for **1** at 270 K, 225 K and 100 K. D-H…A distances longer than 3.5 Å were included to facilitate comparison of changes.

Structure number	3			
т [К]	215 K (cooling)			
. []	HS (IP)			
	D…A [Å]	D - H…A [°]		
C51-H51A…N99[x-1, y, z]	3.356(11)	133		
C51-H51B…O11[x-1, y, z]	3.398(9)	169		
C52-H52B…O23[-x+1, -y+1, -z]	3.339(14)	136		
С12-Н12В…О21	3.322(16)	133		
C14-H14…N52	3.267(8)	120		
C16-H16A…N59	3.447(12)	153		
C231-H23A…O11[x-1, y, z]	3.473(10)	167		
C231-H23C…F31[-x, -y+1, -z+1]	3.380(19)	149		
C231-H23C…F33[-x, -y+1, -z+1]	3.151(18)	123		
C241-H24A…F23	2.967(15)	135		
C241-H24B…N69	3.337(17)	168		
C251-H25C…N79[x-1, y, z]	3.500(16)	141		
C31-H31B…O31[-x, -y+1, -z+1]	2.957(12)	130		
C36-H36BN99[-x+1, -y+1, -z]	3.328(13)	146		
C41-H41B…O33	3.449(14)	176		
C42-H42A…O32[-x+1, -y+1, -z+1]	3.434(16)	140		
C44-H44…O21	3.438(14)	155		
C1-H1A…O12[x, y+1, z]	3.309(8)	148		
C2-H2B…O12[-x+1, -y+1, -z+1]	3.432(9)	144		
C4-H4…N42	3.153(8)	122		
C6-H6A…N89[-x+1, -y+1, -z+1]	3.456(12)	158		
C6-H6B…F31	3.537(16)	154		
C62-H62A…O13[x-1, y, z]	3.332(9)	133		
C98-H98A…O22[-x+1, -y+1, -z]	2.987(14)	129		
C98-H98C…O11	3.430(11)	153		
C78-H78A…O32[-x+1, -y+1, -z+1]	3.311(17)	161		
C78-H78B…N69	3.47(2)	136		
C68-H68C…O13[x, y+1, z]	3.278(11)	174		
C48-H48A…N49[-x+1, -y+1, -z+2]	3.36(2)	147		
C48-H48B…O23[x, y, z+1]	3.262(15)	160		
C41-H41A…N59	3.387(10)	125		
C47-H47A…O21	3.424(13)	152		
C51-H51B…O13 [-1+x,y,z]	3.435(8)	130		
C58-H58B…O33 [-x,1-y,1-z]	3.398(15)	132		
C66-H66B…O13 [-1+x,y,z]	3.408(9)	128		

Table S4. Selected C-H…N and C-H…O interatomic contacts [Å] and angles [°] for IP structure of **1** at 215 K involving only components of disordered anions with the highest value of the occupancy.



Figure S1. A comparison of anion orientations in 1 at 270 K (a, HT(HS) structure), 225 K (b, HT(HS/LS) structure), 215 K (c, IP(HS) structure) and 100 K (d, LT(LS) structure). Anions are presented in relation to the same orientation of the polymeric skeleton. Dark green color denotes iron(II) atoms (balls). Hydrogen atoms were omitted for clarity. Please note that plot (c) corresponds to IP(HS) structure and differs from plots (a), (b) and (d) which are very similar to each other.





Figure S2. Temperature dependences of occupancy factors of triflate anions in cooling (a) and heating (b) mode.

Intermolecular contacts in 1.

In HT(HS) structure of **1** triflate anions form numerous intermolecular contacts. They participate in formation of intermolecular contacts C_{alkyl} -H····O, C_{ring} -H···O with ebbtr molecules as well as $C_{nitrile}$ -H···O with noncoordinated and coordinated acetonitrile molecules (Fig. S3a, Table S3). Noncoordinated acetonitrile molecules form C_{alkyl} -H···N contacts too. Lowering of temperature from 270 K to 225 K (HT(HS,LS) structure) does not involve changes of intermolecular contacts. Formation of IP structure is associated with presence of three anion sides. It causes differentiation of intermolecular contacts, however, the anions still interact with ebbtr as well as coordinated and non-coordinated acetonitrile molecules (Table S4, Fig. S3c). IP(HS) \rightarrow LT(LS) transition triggers reconstruction of network of intermolecular contacts which results in increase of a number of contacts in relation to HT structure. In particular, it concerns coordinated acetonitrile molecules (Fig. S3b, Table S3).





Figure S3. A comparison of the networks of intermolecular contacts in **1** at 270 K (a, HT(HS) structure), at 100 K (b, LT(LS) structure) and at 215 K (c, IP(HS) structure) showing their rebuilding. Intermolecular contacts are marked by black dashed lines. Intermolecular contacts involving minor components (a) are marked by thin pale blue dashed lines. Intermolecular contacts presented on (c) involve only components of disordered anions of the greatest occupancy. Dark green color denotes iron atoms.



Figure S4. $\chi_M T(T)$ dependence for 1 recorded at different temperature scan rates.



Figure S5. The temperature dependences of $\chi_M T(T)$ (triangles) derived from SQUID measurement (at scan rate 1 Kmin⁻¹) and relative areas of HS form (A_{HS}/(A_{HS}+A_{LS}); where A – peak area) derived from Mössbauer spectra (open circles) in cooling (blue) and heating (red) mode.



Figure S6. Selected Mössbauer spectra recorded for **1** in cooling (left column) and heating (right column) mode. Experimental data are marked by crossed points, fitted spectrum by black line, HS component by blue line and LS component by red line.



Figure S7. Temperature dependence of average Fe-N distances in 1.



Figure S8. Temperature dependence of unit cell parameters for 1 in cooling (blue) and heating (red) mode (average structure was used for IP phase).

Temperature dependence of unit cell volume in 1

The temperature dependence of the unit cell volume shows that the change of crystal packing remains in contradiction with direction of the change of spin state from LS to HS. Namely, increasing of the average unit cell volume, which is expected during formation of the IP(HS) structure, has not been observed. Instead, one can observe a reduction of the average unit cell volume (Fig. S9). Thus, the crystal lattice properties rather do not create conditions which are conducive for stabilization of HS form of the complex. Although, the factor favoring HS form can be a geometry of the first coordination spheres of Fe1 and Fe2 ions which differ in relation to the one for HT structure because of slight reduction of Fe-N-C(CH₃CN) angles (Table S2). Studies on spin crossover in one-dimensional coordination polymer [Fe(ebtz)₂(C₂H₅CN)₂](ClO₄)₂ (ebtz = 1,2-di(tetrazol-2-yl)etane) have shown that an increase of Fe-N-C(nitrile) angle corresponds to stabilization of HS form of the complex which is associated with occurrence of wide hysteresis loop.^[5] Thus, a greater bending of Fe-N-C(nitrile), while maintaining a similar values of Σ parameters for [FeN₆] chromophore (Table S2), may be a factor stabilizing HS form of iron(II) in the IP structure.



Figure 89. Temperature dependence of the unit cell volume for 1 in cooling (blue) and heating (red) modes. Inset (a) shows only reduction of unit cell volume during HT(HS/LS) \rightarrow IP(HS) transition. Average structure was used for IP phase.



a)



b)

Figure S10. Temperature dependence of Fe...Fe distances between bridged iron(II) ions in cooling (a) and heating (b).



b)

Figure S11. View along t-t/t-g (a) and t-g (b) linking directions showing non-collinear arrangement of bridged iron(II) ions in IP structure of 1 at 215 K. Dark green color denotes iron atoms.

Differential scanning calorimetry studies of 1.

Results of differential scanning calorimetry (DSC) measurements (Fig. S12) carried out in cooling mode show presence of two exothermic peaks at temperatures (onset) 220 K ($\Delta H =$ 2.5 kJmol⁻¹, $\Delta S = 11.4$ Jmol⁻¹K⁻¹) and 190 K ($\Delta H = 4.4$ kJ mol⁻¹, $\Delta S = 23.0$ Jmol⁻¹K⁻¹). According to results of magnetic and single crystal X-ray diffraction studies, presence of these peaks corresponds to consecutive structural phase transitions $HT(HS/LS) \rightarrow IP(HS)$ and then IP(HS) \rightarrow LT(LS). It is worth noticing that the phase transition occurred during cooling at 220 K corresponds to exothermic effect instead of endothermic one expected for LS→HS transition. It means that thermal effect, associated with structural reorganization, is dominant in relation to change of the spin state of ca. 5% of iron(II) ions (an expected ΔH value for change of spin state in iron(II) complexes equals 10-20 kJmol⁻¹). It stays in line with earlier finding, that in spite of occurrence of HT(HS/LS) → IP(HS) transition, associated with increase of [FeN₆] coordination octahedron volume, structural reorganization leading to formation of IP structure prevails the spin crossover effect which results in reduction of lattice cell volume (Fig. S9). During the heating cycle there are present two endothermic peaks. The peak found at 200 K ($\Delta H = -2.9$ kJ mol⁻¹, $\Delta S = -14.6$ Jmol⁻¹K⁻¹) corresponds to structural phase transition LT(LS) \rightarrow IP(HS), whereas the presence of the second one at 238 K (Δ H = -4.2 kJ mol⁻¹, $\Delta S = -17.9$ Jmol⁻¹K⁻¹) is associated with IP(HS) \rightarrow HT(HS/LS) transition. Thus, structural phase transitions are shifted to higher temperatures in relation to the corresponding ones recorded during cooling which confirms the presence of two hysteresis loops.



Figure S12. DSC curve for 1 recoded at 10 K/min in cooling and heating mode.



Figure S13. FTIR spectrum of 1 (nujol) (room temperature).

The existence of unique area of stable IP(HS) phase has interesting consequences because it makes possible to choose which sequence of spin transitions we want to perform. Thus, reaching of area of high spin form stability followed then by reversal of change of temperature allows to carry out independent cooling/heating cycles resulting exclusively in "normal" or "reverse" hysteresis loops (Fig. S14).



Figure S14. "Reverse" and "normal" hysteresis loops resulted from carried out independently HT&IP (a) or IP< (b) transitions. In (a) sample was cooled from 300 to 200 K (blue triangles) and then heated from 200 to 300 K (red triangles). In (b) sample was initially cooled from 300 to 10 K, and then heated from 10 to 225 K (red circles) and cooled from 225 to 10 K (blue circles).

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