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High Temperature Spin Crossover in [Fe(pyrazine){Ag(CN)$_2$}$_2$] and its Solvate

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SUPPLEMENTARY INFORMATION

Experimental details

Magnetic susceptibility measurements. Magnetic susceptibility measurements were carried out with a Quantum-Design MPMS-XL-5 SQUID magnetometer equipped with a 5 T magnet and a MPMS sample space oven over the temperature range 306–420 K with a heating and cooling rate of 2 K min^{-1}, and a magnetic field of 0.5 T. Diamagnetic correction for the molecule was derived from the Pascal's constants.

Mössbauer measurements. Room-temperature ^{57}Fe-Mössbauer spectra were recorded in transmission geometry with a ^{57}Co source in a rhodium matrix using a conventional constant-acceleration Mössbauer spectrometer. 3 K spectra were recorded at ESRF using the Synchrotron Mössbauer Source. Isomer shifts are given relatively to an α-Fe foil at ambient temperature. Fits of the experimental Mössbauer data were performed using the Recoil software (Lagarec and Rancourt, Ottawa University).

IR spectroscopy. IR spectra were recorded using a Nicolet Nexus spectrometer fitted with a Golden Gate attenuated total reflection accessory (Thermo Nicolet). Spectra were recorded at 4 cm^{-1} resolution, averaging 16 scans.

Thermal analysis. Thermal analysis was performed with DTG-60H Simultaneous TGA/DTA in air flow of 100 ml min^{-1} within a temperature range 273-873 K.

Powder XRD. The samples were analysed with a Siemens D5000 powder diffractometer using Cu-K$_\alpha$ radiation.

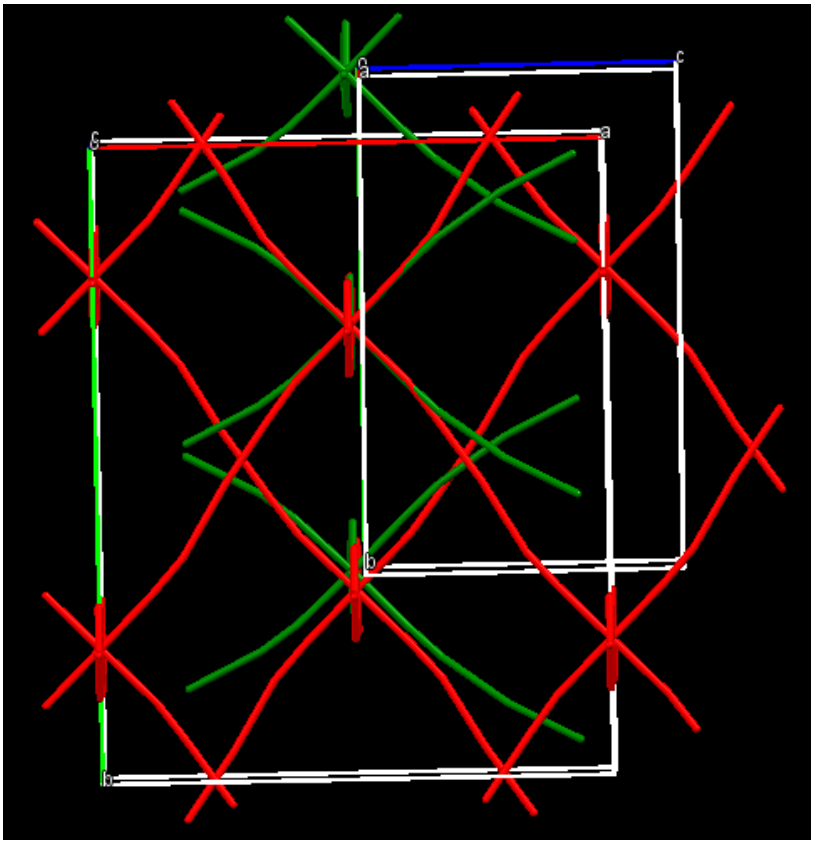

Figure S1. Comparison of the network of **1·MeCN** (green) and of the complex reported by Real et al. (red).

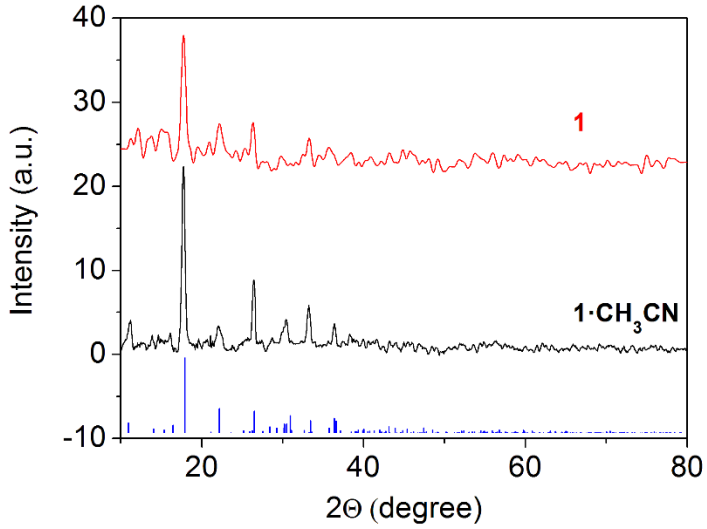

Figure S2. PXRD of **1** (red), **1·MeCN** (black) and theoretical patterns simulated from the single crystal structure of **1·MeCN** (blue).

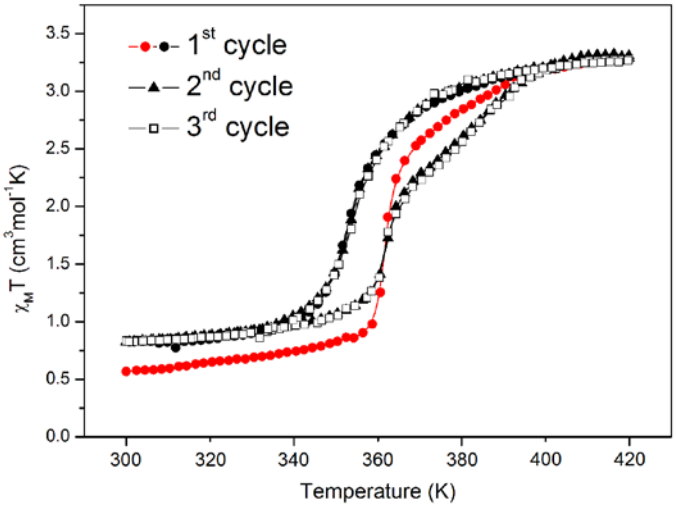

Figure S3. Reproducibility of magnetic properties (different batch). Temperature dependent magnetic measurements of the complex in three consequent thermal cycles.

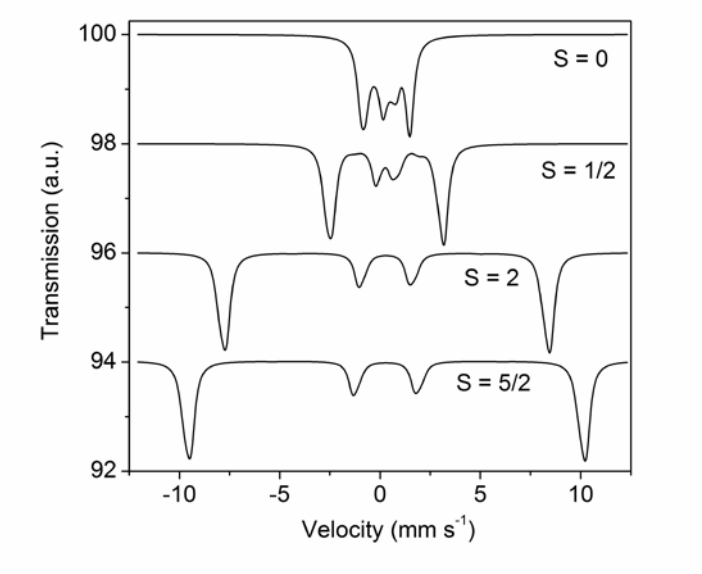

Figure S4. Simulated influence of the iron spin state on Mössbauer spectra in magnetic field for the high quadrupole doublet of **1** (δ = 0.3 mm s^{-1}, ΔE_Q = -0.74 mm s^{-1}, B = 6.0 T, Γ = 0.23 mm s^{-1}, θ = 0°).

Table 1 Crystal data and structure refinement.

Empirical formula	$C_{10}H_7Ag_2FeN_7$
Formula weight	496.82
Temperature/K	296.15
Crystal system	monoclinic
Space group	Cm
a/Å	6.728(3)
b/Å	12.521(5)
c/Å	8.320(3)
α/°	90
β/°	106.478(8)
γ/°	90
Volume/$Å^3$	672.1(5)
Z	2
$\rho_{calc}g/cm^3$	2.455
μ/mm^{-1}	3.948
F(000)	472.0
Crystal size/mm^3	0.1 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.106 to 55.548
Index ranges	$-8 \le h \le 8$, $0 \le k \le 16$, $-10 \le l \le 10$
Reflections collected	1399
Independent reflections	1399 [R_{sigma} = 0.0659]
Data/restraints/parameters	1399/2/60
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0965, wR_2 = 0.2412
Final R indexes [all data]	R_1 = 0.1041, wR_2 = 0.2473
Largest diff. peak/hole / e $Å^{-3}$	5.64/-2.77
Flack parameter	0.19(14)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Fe1	-10477(6)	-5000	-10411(5)	6.9(8)
N2	-11160(30)	-6068(13)	-12180(20)	8.7(13)
C1	-9350(40)	-3270(20)	-7660(30)	24(5)
N1	-9860(30)	-3902(13)	-8730(20)	8.7(13)
C2	-11710(30)	-6590(15)	-13320(30)	8.7(13)
N4	-13400(40)	-5000	-10380(30)	8.7(13)
N3	-7520(30)	-5000	-10470(30)	8.7(13)
C3	-6540(30)	-5886(15)	-10370(30)	8.7(13)
C4	-14390(30)	-5901(15)	-10360(20)	8.7(13)
C6	-6800(100)	-5000	-4530(60)	48(6)
C5	-5560(110)	-5000	-5710(70)	48(6)
N5	-4600(90)	-5000	-6580(50)	48(6)
Ag1	-8045(4)	-2331.6(13)	-5599(4)	27.6(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	6.2(15)	2.9(15)	11(2)	0	1.2(15)	0
N2	9(3)	5(3)	10(3)	1(3)	0(3)	3(3)
C1	25(12)	28(12)	17(12)	-3(9)	4(10)	-8(9)
N1	9(3)	5(3)	10(3)	1(3)	0(3)	3(3)
C2	9(3)	5(3)	10(3)	1(3)	0(3)	3(3)
N4	9(3)	5(3)	10(3)	1(3)	0(3)	3(3)
N3	9(3)	5(3)	10(3)	1(3)	0(3)	3(3)
C3	9(3)	5(3)	10(3)	1(3)	0(3)	3(3)
C4	9(3)	5(3)	10(3)	1(3)	0(3)	3(3)
C6	80(19)	23(9)	34(13)	0	6(13)	0
C5	80(19)	23(9)	34(13)	0	6(13)	0
N5	80(19)	23(9)	34(13)	0	6(13)	0
Ag1	33.4(10)	27.1(10)	18.4(9)	-10.2(11)	1.1(7)	2.1(13)

Table 4 Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	N2[1]	1.942(17)	N4	C4[1]	1.31(2)
Fe1	N2	1.942(18)	N4	C4	1.31(2)
Fe1	N1	1.923(18)	N3	C3[1]	1.28(2)
Fe1	N1[1]	1.923(18)	N3	C3	1.28(2)
Fe1	N4	1.98(2)	C3	C4[3]	1.45(2)
Fe1	N3	2.00(2)	C4	C3[4]	1.45(2)
N2	C2	1.13(3)	C6	C5	1.46(9)
C1	N1	1.16(3)	C5	N5	1.10(8)
C1	Ag1	2.06(3)	Ag1	C2[5]	2.08(2)
C2	Ag1[2]	2.08(2)			

[1]+X,-1-Y,+Z; [2]-1/2+X,-1/2+Y,-1+Z; [3]1+X,+Y,+Z; [4]-1+X,+Y,+Z; [5]1/2+X,1/2+Y,1+Z

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Fe1	N2[1]	87.0(10)	C2	N2	Fe1	171.3(17)
N2	Fe1	N4	89.2(7)	N1	C1	Ag1	170(2)
N2[1]	Fe1	N4	89.2(7)	C1	N1	Fe1	175(2)
N2[1]	Fe1	N3	90.3(8)	N2	C2	Ag1[2]	170.2(18)
N2	Fe1	N3	90.3(8)	C4	N4	Fe1	120.7(13)
N1	Fe1	N2	177.8(8)	C4[1]	N4	Fe1	120.7(13)
N1[1]	Fe1	N2	90.9(6)	C4[1]	N4	C4	119(3)
N1[1]	Fe1	N2[1]	177.8(8)	C3	N3	Fe1	119.6(13)
N1	Fe1	N2[1]	90.9(6)	C3[1]	N3	Fe1	119.6(13)
N1[1]	Fe1	N1	91.2(10)	C3[1]	N3	C3	120(3)
N1	Fe1	N4	90.1(7)	N3	C3	C4[3]	120.4(19)
N1[1]	Fe1	N4	90.1(7)	N4	C4	C3[4]	119.9(19)
N1	Fe1	N3	90.3(7)	N5	C5	C6	179(7)
N1[1]	Fe1	N3	90.3(7)	C1	Ag1	C2[5]	171.4(9)
N4	Fe1	N3	179.3(11)				

[1]+X,-1-Y,+Z; [2]-1/2+X,-1/2+Y,-1+Z; [3]1+X,+Y,+Z; [4]-1+X,+Y,+Z; [5]1/2+X,1/2+Y,1+Z

Table 6 Torsion Angles.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	N4	C4	C3[1]	-179.1(14)	C3[3]	N3	C3	C4[2]	-8(4)
Fe1	N3	C3	C4[2]	-178.3(15)	C4[3]	N4	C4	C3[1]	2(4)

[1]-1+X,+Y,+Z; [2]1+X,+Y,+Z; [3]+X,-1-Y,+Z

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3).

Atom	*x*	*y*	*z*	U(eq)
H3	-7221	-6525	-10295	10
H4	-13705	-6548	-10337	10
H6A	-8248	-5000	-5146	71
H6B	-6493	-4374	-3843	71
H6C	-6493	-5626	-3843	71

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2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.