Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Rationalization of single-molecule magnet behavior in a three-coordinate Fe(III) complex with high-spin state (S = 5/2)

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Table S1. ZFS parameters in high spin Fe (III) complexes based on Magnetic Measurements (MM), Electron Paramagnetic Resonance (EPR), Inelastic Neutron Scattering (INS) and Far-Infrared Magnetic Resonance (FIMR).

Complex	D(cm^{-1})	E(cm^{-1})	E / D	g	Experimenta	cn[a]	Ref.
Fe^{III} in Ferrichrome-A	-0.27		-0.25	2	FIMR	6	1
$[Fe^{III}(S_2CNR_2)_3]$, NR_2 =							
pyrrolidyl	-2.14		-0.1		FIMR	6	1
$[Fe^{III}(Pydtc)_3$	-2.14				MM	6	2
$[Fe^{III}\{L_2NNOO\}Cl(H_2O)]$	7.2	2.4		2	MM	6	3
Fe doped in Al_2O_3	0.1683	0		2.003	EPR	6	4
Fe(III)-EDTA	0.8	0.27			EPR	6	5
Fe in $PbTiO_3$	1.176	0		2.002	EPR	6	6
Fe in Al_2O_3-hercynite	0.185	0.0015		2.002	EPR	6	7
$[Fe(DMSO)_6](NO_3)_3$	0.197	0.017	0.086		EPR	6	8
$ET_4[AIFe(C_2O_4)_3]\cdot G$,							
AI/G = H_3O/PhF	0.31			1.965	MM	6	9
AI/G =H_3O/PhCl	0.65			2.024	MM	6	9
AI/G =H_3O/PhBr	0.52			2.001	MM	6	9
(OEP)Fe(η^2-ON(t-Bu)NO)	3.89		0.07	2	EPR	6	10
(TPP)Fe(η^2-ON(t-Bu)NO)	3.89		0.07	2	EPR	6	10
[Fe(Ln)X]	0.5				MM	6	11
$TBA_7H_{10}[(A\text{-}\alpha\text{-}XW_9O_{34})_2Fe$							
II^X, X = Ge	-1.26	-0.476			MM	6	12
II^X, X = Si	-1.22	-0.248			MM	6	12
$[Fe^{III}(DP)(OMe)]$	4.65				FIMR	5	13
$[Fe^{III}(DP)(OPh)]$	5.45				FIMR	5	13
$[Fe^{III}(DP)(ac)]$	6.9				FIMR	5	13
$[Fe^{III}(daDP)Cl]$	7.89				FIMR	5	13
$[Fe^{III}(DP)F]$	5.55				FIMR	5	1
$[Fe^{III}(DP)Cl]$	8.95				FIMR	5	1
$[Fe^{III}(DP)Br]$	11.8				FIMR	5	1
$[Fe^{III}(DP)I]$	16.4				FIMR	5	1
$[Fe^{III}(DP)N_3]$	7.32		0.036		FIMR	5	1
$[Fe^{III}(PP)F]$	5				FIMR	5	1
$[Fe^{III}(PP)Cl]$	6.95				FIMR	5	1
$[Fe^{III}(PP)N_3]$	9.1		0.085		FIMR	5	1
Met-hemoglobin	10.7			1.95	EPR	5	14
Fe(salen)BzO			0.31		EPR	5	15
Met-myoglobin	9-9.5			1.98	EPR	5	16
$[Fe^{III}\{L_1NNOO\}Cl]\cdot CH_3CN$	10.2	3.4		2	MM	5	3
$[Fe^{III}H_3buea(O)]^{2-}$	-0.7		0.005	2	EPR	5	17
$[Fe^{III}H_3buea(OH)]^{-}$	-2.4		0.157	2.010	EPR	5	17
[Fe(TPP)X], H_2TPP = tetraphenylporphyrin)							
X = F	4.49				INS	5	18
X = Cl	6.33				INS	5	18
X = Br	8.8	0.1			INS	5	18
X = I	13.4	0.3			INS	5	18
$(^{Ar}L)Fe(NAd)$	1		0.01	2	MM	3	19

[a] cn = Coordination number

Table S2. Crystal data and structure refinement for 1

	1
formula	$C_{18}H_{54}FeN_3Si_6$
Molecular weight /g mol^{-1}	537.02
Crystal system	Trigonal
Space group	*P*-31*c*
a, Å	16.1834(6)
b, Å	16.1834(6)
c, Å	8.4220(3)
α, deg	90
β, deg	90
λ, deg	120
V, Å^3	1910.23(16)
Z	2
D_{cal}/g cm^{-3}	0.934
temperature, K	150
2θ range/^{o}	5.644 to 51.038
completeness	98.6%
residual map, e Å^{-3}	0.966/-0.338
Goodness-of-fit on F^2	1.094
Final indices[I>2σ(I)]	R_1 = 0.0398, wR_2 = 0.1160
R indices (all data)	R_1 = 0.0446, wR_2 = 0.1219

Table S3. Selected bond lengths (Å) and angles (^{o}) for complex **1**

Bonds	Å	Angles	^{o}
Fe(1)-N(1)#1	1.907(1)	N(1)#1-Fe(1)-N(1)	120.0(1)
Fe(1)-N(1)#2	1.907(1)	N(1)#1-Fe(1)-N(1)#2	120.0(1)
Fe(1)-N(1)	1.907(1)	N(1)-Fe(1)-N(1)#2	120.0(1)
Si(1)-N(1)	1.749(3)	N(1)-Si(1)-C(3)	109.9(2)
Si(1)-C(3)	1.865(5)	N(1)-Si(1)-C(1)	112.5(2)
Si(1)-C(1)	1.877(5)	N(1)-Si(1)-C(2)	112.4(2)
Si(1)-C(2)	1.872(5)	C(3)-Si(1)-C(1)	108.5(3)
N(1)-Si(1)#3	1.749(3)	C(3)-Si(1)-C(2)	106.2(3)
		C(2)-Si(1)-C(1)	107.1(3)
		Si(1)-N(1)-Fe(1)	119.7(2)
		Si(1)#3-N(1)-Fe(1)	119.7(2)
		Si(1)#3-N(1)-Si(1)	120.6(3)

Symmetry transformations used to generate equivalent atoms:

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

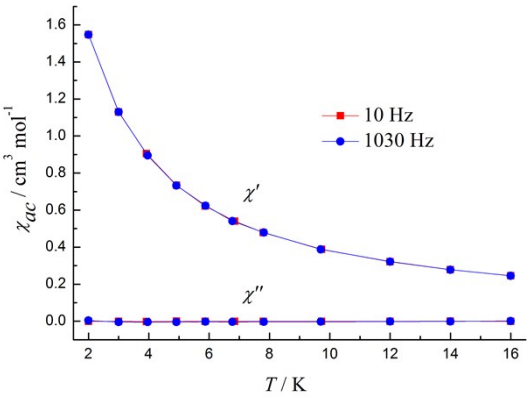

Fig. S1. Temperature-dependent in-phase (χ') and out-of-phase (χ'') ac susceptibility for **1** in the zero applied field. The lines are guides to the eyes.

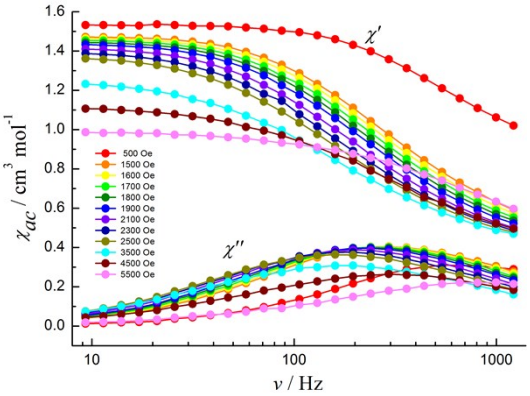

Fig. S2. Frequency-dependent in-phase (χ') and out-of-phase (χ'') ac susceptibility for **1** at 2 K under various dc fields. The lines are guides to the eyes.

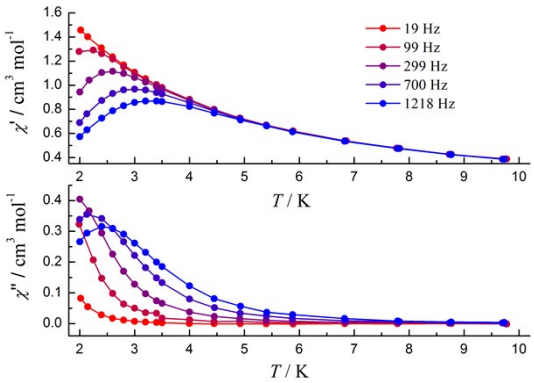

Fig. S3. Temperature-dependent in-phase (χ') and out-of-phase (χ'') ac susceptibility for **1** under 1600 Oe applied field. The lines are guides to the eyes.

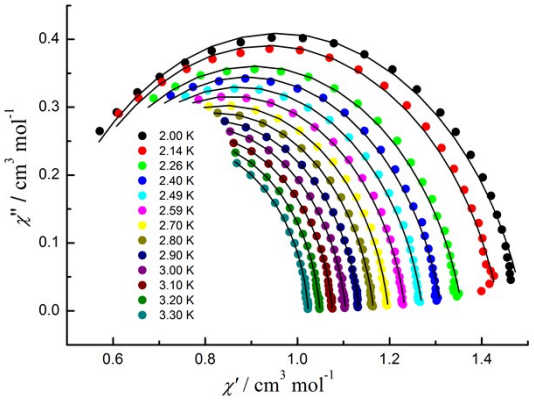

Fig. S4. Cole-Cole plots for **1** at 1600 Oe dc field. The solid lines represent a fit to the data.

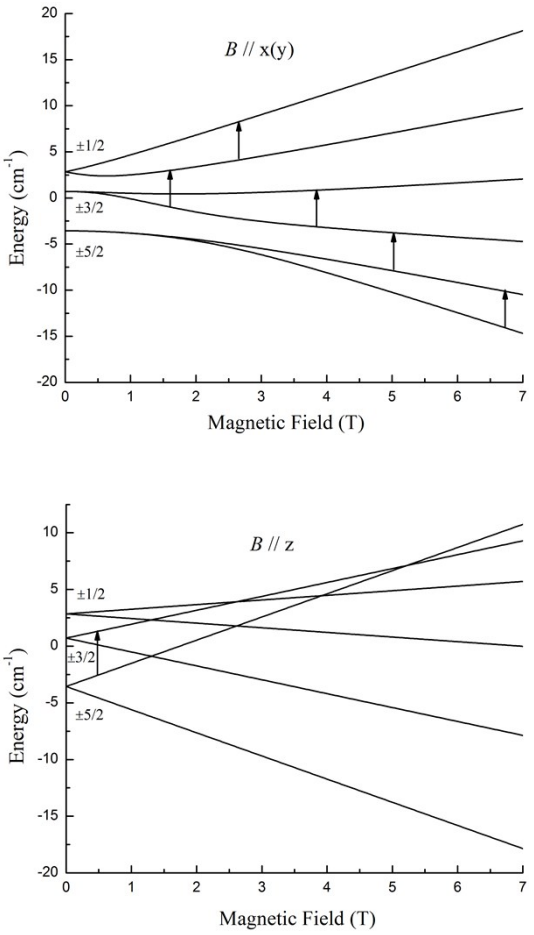

Fig. S5. Magnetic field dependent energy levels in the three canonical orientations of the field relative to the principal zfs axis calculated for **1**. Top: Arrows stand for EPR transitions along x(y) orientation in 120 GHz; Bottom: Arrows stand for EPR transitions along z orientation in 120 GHz.

Table S4. The relative energies of ground and low-lying quartet spin eigenstates (cm^{-1}).

$^6\Psi_0$	0.0
$^4\Psi_0$	15782
$^4\Psi_1$	20021

$^4\Psi_2$	21348
$^4\Psi_3$	33547
$^4\Psi_4$	39944
$^4\Psi_5$	42145
$^4\Psi_6$	46743
$^4\Psi_7$	56723
… …	

Table S5. The relative energy of d-orbitals for **1**. (cm^{-1}).

d_z^2	0
d_{xz}	3734
d_{yz}	4912
d_{xy}	13836
$d_{x^2-y^2}$	16143

Table S6. Individual contribution to *D*-tensor calculated by CASSCF/NEVPT2 (cm^{-1})

Multiplicity	Root	*D*
6	0	0
4	1	-1.47
	2	0.51
	4	-0.49
	5	0.11
	…	…
2	-	0[b]

[b] Only D values with > 0.1 are given in this table.

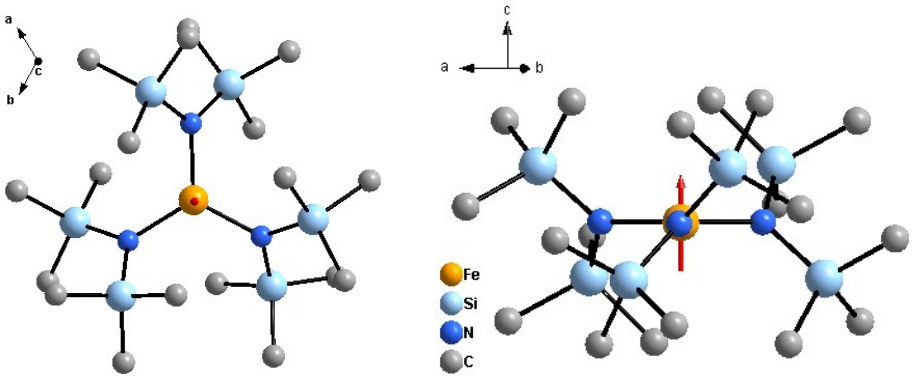

Fig. S6. Orientation of the main axis of the g tensor viewed from top (left) and side (right) for the ground state KD of complex **1**.

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