Supporting Information for

Single-Ion Magnet Behavior in Heptacoordinated Fe(II) Complexes: On the Importance of Supramolecular Organization

Arun Kumar Bar,[ab] Céline Pichon,[ab] Nayanmoni Gogoi,[ab] Carine Duhayon,[ab]
S. Ramasesha,[c] and Jean-Pascal Sutter[*,ab]

[a] CNRS, LCC, 205 Route de Narbonne, F-31077 Toulouse, France.
[b] Université de Toulouse, UPS, INPT, LCC, F-31007 Toulouse, France.
[c] Indian Institute of Science, Bangalore 560012, India
E-mail : sutter@lcc-toulouse.fr

Experimental Section

Materials and methods:

All reagents and solvents used for the syntheses were used as received from commercial sources. All the solvents used in the air-sensitive reactions were distilled under anaerobic condition and degased by following the freeze and thaw method prior to use. The organic ligand H_2DAPBH[1] was synthesized following reported procedures. Fourier transform infrared (FT-IR) spectroscopy was performed with a Perkin–Elmer spectrum GX 2000 FT-IR spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 series II instrument.

Magnetic susceptibility measurements were carried out with a Quantum Design MPMS-5S SQUID susceptometer. The magnetic measurements were performed on freshly filtered polycrystalline materials. The polycrystalline powders were mixed with grease and put in gelatin capsules. All the magnetic samples associated with Fe(II) metal ion were prepared under N_2 atmosphere. dc measurements were conducted from 300 to 2 K at 1 kOe and the data were corrected for the diamagnetic contribution of the sample holder, grease and sample by using Pascal's tables.[2] The field dependences of the magnetization were measured at several temperatures between 2 and 10 K with dc magnetic field up to 5 T. Preliminary ac susceptibility experiments for **1** and **2** were performed at various frequencies ranging from 1 to 1500 Hz with an ac field amplitude of 3 Oe. ac susceptibility was investigated under an oscillating ac field of 3 Oe over the frequency range of 1 to 1500 Hz. High frequency ac experiments were carried out on a Quantum Design PPMS under an oscillating ac field of 3 Oe over the frequency range of 100 to 10000 Hz.

Mössbauer measurements were recorded at 80 K using an MD 306 Oxford cryostat on a constant acceleration conventional spectrometer with a 50 mCi source of ^{57}Fe (Rh matrix).

---

[1] T. J. Giordano, G. J. Palenik, R. C. Palenik, D. A. Sullivan, *Inorg. Chem.,* 1979, **18**, 2445.
[2] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.

The absorber was a powdered sample enclosed in a 20 mm diameter cylindrical, plastic sample holder, the size of which had been determined to optimize the absorption. A least-squares computer program was used to fit the Mössbauer parameters and determine their standard deviations (given in parentheses). Isomer shift values (δ) are relative to iron foil at 293 K.

X-ray crystallographic studies: Single crystals suitable for X-ray diffraction were coated with paratone oil and mounted onto the goniometer. The X-ray crystallographic data were obtained at low temperature from a Gemini Oxford Diffraction (CuKα radiation source) or an Apex2 Bruker diffractometer (MoKα radiation source) and equipped with an Oxford Cryosystem. The structures have been solved by direct methods using Shelxs or Superflip and refined by means of least-square procedures on F using the PC version of the program CRYSTALS.[3] The scattering factors for all the atoms were used as listed in the International Tables for X-ray Crystallography.[4] Absorption correction was performed using a multi-scan procedure. All non-hydrogen atoms were refined anisotropically. When it was possible, the H atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry and U~iso~(H) (in the range 1.2-1.5 times U~eq~ of the parent atom), after which the positions were refined with riding constraints. Structures **1** and **3** were disordered. For compound **1**, three F atoms were disordered on 2 sites (0.5 : 0.5 occupancy). Moreover, for structure **3** restraints (using the command SAME) were applied for the two parts of the disordered phenyl (0.55 : 0.45 occupancy). For compound **2**, the detected electron densities suggested the presence of a half occupancy methanol molecule with high thermal motion The molecule appears disordered over several positions that can be approximated by 4 oxygen positions with occupancies 0.3, 0.3, 0.3, and 0.1. Tentative refinement of the MeOH molecule lead to odd C-O distances, therefore we decided to remove this residual density using the SQUEEZE facility from PLATON.

Computational studies: Single point energy and spin density distribution were computed for **1** and **2** using TD-DFT on GAUSSIAN-09[5] platform utilizing hybrid UB3LYP[6] basis functions with mixed basis sets: 6-31G*[7] for all non-metal elements and the small-core Hay-Wadt pseudopotential (indicated in the Gaussian code as LANL2DZ)[8] for Fe. The mixing of d and p as well as HOMO and LUMO orbitals were allowed. The crystallographic coordinates of the di-cationic moiety $[Fe(H_2DAPBH)(H_2O)(MeOH)]^{2+}$ for **1** and of the neutral moiety $[Fe(H_2DAPBH)Cl_2]$ for **2** were used for the calculations (Table SI11-12). The S**2

---

[3] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.

[4] *International Tables for X-ray Crystallography, Vol. IV*, Kynoch Press, Birmingham, England, 1974.

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. B. Rendell, J. C., S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09; Gaussian, Inc., Wallingford CT*, 2009.

[6] A. D. J. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

[7] T. H. J. Dunning, P. J. Hay, *In Modern Theoretical Chemistry; Schaefer, H. F., III, Ed.; Plenum: New York,* 1976; **Vol. 3**.

[8] P. J. Hay, R. J. Wadt, *Chem. Phys. Chem.*, 1985, **82**, 299.

values in the output files after normal termination were cross-checked. The S**2 values after annihilations are found to be 6.0000 for 1 and 6.0002 for 2 and thus excluding the spin contaminations. The estimated spin densities are Mulliken atomic spin densities (Table SI13-14). The spin density maps were drawn using GassView4.1 software[9] and are presented in 4×10^{-4} μ_B Å^3 isosurface (Figure SI5).

---

[9] A. E. Frisch, R. D. Dennington, T. A. Keith, J. Millam, A. B. Nielsen, A. J. Holder, J. Hiscocks, *Gaussian, Inc., Wallingford CT*, 2003.

Synthesis:

$[Fe(H_2DAPBH)(H_2O)(MeOH)]\cdot 2MeOH\cdot 2BF_4$, **1:** The reaction was carried out at room temperature under N_2 atmosphere using standard Schlenk line technique. In a 50 mL round bottom Schlenk flask, 675 mg (2 mmol) of $Fe(BF_4)_2.6H_2O$ was dissolved in 20 mL of degased MeOH yielding a colorless solution. In a 100 mL Schlenk tube, 2 mmol of the corresponding organic ligand H_2DAPBH (800 mg) in 60 mL of degased MeOH gave a milky slurry. The methanol solution of Fe(II) was then slowly added with a syringe into the slurry. The deep blue solution was stirred at room temperature for 6 h followed by filtering through a frit under N_2 atmosphere into a 250 mL Schlenk tube. The filtrate was concentrated under vacuum to ~150 mL and *ca.*100 mL of degased diethyl ether was layered over it for slow diffusion. The whole set up was kept undisturbed under inert atmosphere for 10−14 days until the complex crystallized out rendering the mother liquor almost colorless. The polycrystalline solid was filtered off the solvent mixture through frit under N_2 atmosphere, washed twice with 10 mL portions of degased diethyl ether and finally dried under low vacuum to obtain polycrystalline dark blue solid (905 mg; 67 %). Good quality single crystals suitable for X-ray diffraction were picked up before filtering off the crystalline material. IR (cm^{-1}): $\upsilon_{C=O}$ = 1627 (vs) and 1578 (s); $\upsilon_{C=N}$ = 1522 (vs). Elemental analysis (%) calcd. for $C_{24}H_{27}N_5O_4B_2F_8Fe$: C 42.46; H 4.01; N 10.31; found: C 41.96; H 4.07; N 10.22. Mössbauer: one symmetric doublet: δ = 1.289(12) mm/s; Δ = 3.0728(23) mm/s.

$[Fe(H_2DAPBH)Cl_2]\cdot 0.5MeOH$, **2: (**Adapted from a reported procedure[10]) In a 50 mL round bottom Schlenk flask, 397.7 mg (2 mmol) of $FeCl_2.4H_2O$ was dissolved in 20 mL of degased MeOH yielding a greenish yellow solution. In a 100 mL Schlenk tube 2 mmol of the corresponding organic ligand (800 mg of H_2DAPBH) in 60 mL of degased MeOH gave a milky slurry. The methanol solution of $FeCl_2$ was then slowly added with a syringe into the slurry. The deep blue solution was stirred at room temperature for 6 h followed by filtering through a frit under N_2 atmosphere into a 250 mL Schlenk tube. The filtrate was concentrated under vacuum to ~150 mL and ~100 mL of degased diethyl ether was layered over it for slow diffusion. The whole set up was kept undisturbed under inert atmosphere for 10−14 days until the complex crystallized out rendering the mother liquor almost colorless followed by filtration off the solvent mixture through frit under N_2 atmosphere. The isolated solid was washed twice with 10 mL portions of degased diethyl ether followed by drying under low vacuum to obtain polycrystalline dark blue solid; mass (yield): 810 mg (73 %). Good quality single crystals suitable for X-ray diffraction were picked up before filtering off the crystalline material. IR (cm^{-1}): $\upsilon_{C=O}$ = 1624 (vs) and 1579 (s); $\upsilon_{C=N}$ = 1522 (vs). Elemental analysis (%) calcd. for $C_{23}H_{21}N_5O_2Cl_2Fe$: C 52.50; H 4.02; N 13.31; found: C 52.60; H 4.07; N 13.28. Mössbauer: one symmetric doublet: δ = 1.27657(87) mm/s; Δ = 1.6687(17) mm/s.

$[Fe(H_2DAPBH)\{Ni(CN)_4\}]_\infty$, **3:** A 100 mL columnar Schlenk tube was charged with 241 mg (1 mmol) of $K_2Ni(CN)_4$ in 15 mL of water under N_2 atmosphere. Additional 5 mL of water was layered over the aqueous solution of $K_2Ni(CN)_4$, and finally a methanol solution of 1

---

[10] A. S. M. Al-Shihri, J. R. Dilworth, S. D. Howe, J. Silver, R. M. Thompson, J. Davies, D. C. Povey, *Polyhedron,* 1993, **12**, 2297.

mmol (558 mg) of the complex **2** was slowly layered on top. The whole set up was kept undisturbed under N_2 atmosphere. Slow interdiffusion of these two solutions resulted in pale blue crystals. After 2−3 days, the whole reaction mixture was mechanically stirred and was filtered off through frit under N_2 atmosphere followed by drying under vacuum to obtain a polycrystalline dark blue solid (557 mg; 90 %). Desirable single crystals required for the X-ray data collections were picked up from these crystals prior to mechanical stirring. IR (cm^{-1}): $\upsilon_{C=O}$ = 1631 (vs) and 1579 (m); $\upsilon_{C=N}$ = 1526 (vs); υ_{CN} = 2134 (s). Elemental analysis (%) calcd. for $C_{27}H_{21}N_9O_2FeNi$: C 52.47; H 3.42; N 20.40; Found: C 52.34; H 3.49; N 20.18. Mössbauer: single symmetric doublet; site population 100 %; δ = 1.2138(19) mm/s; Δ = 2.2889(38) mm/s.

Table SI1. Characteristic Infra-Red stretching bands of the ligands and complexes

Ligand/Complex	$\upsilon_{C=O}$(cm^{-1})	$\upsilon_{C=N}$(cm^{-1})	$\upsilon_{C\equiv N}$(cm^{-1})
H_2DAPBH	1662 (vs), 1604 (s)	1567 (s)	−
$K_2[Ni(CN)_4]$	−	−	2119 (s)
$[Fe(H_2DAPBH)(H_2O)(MeOH)](BF_4)_2$•2MeOH (**1**)	1627 (vs), 1578 (s)	1522 (vs)	
$[Fe(H_2DAPBH)Cl_2]$•MeOH (**2**)	1624 (vs), 1579 (s)	1522 (vs)	−
$[Fe(H_2DAPBH)]_n[Ni(CN)_4]_n$ (**3**)	1631 (vs), 1579 (m)	1526 (vs)	2134 (vs)
vs = very strong; s = strong; m = medium; w = weak and b = broad			

Table SI2. Selected crystallographic data and refinement parameters of the complexes **1−3**

	1	**2**	**3**
Formula	$C_{26}H_{35}B_2F_8FeN_5O_6$[a]	$C_{23}H_{21}Cl_2FeN_5O_2$	$C_{27}H_{21}Fe_1N_9Ni_1O_2$
MW (g mol^{-1})	743.05	526.20	618.08
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C\ 2/c$
T (K)	100	180	100
a (Å)	7.7688(4)	8.6132(4)	17.3572(6)
b (Å)	8.5125(4)	13.1321(6)	15.1852(4)
c (Å)	24.4247(11)	22.5986(10)	10.1318(2)
α (°)	82.716(2)	-	-
β (°)	85.057(2)	108.557(2)	91.117(2)
γ (°)	84.926(2)	-	-
V (Å^3)	1591.34(13)	2423.22(19)	2669.96(13)
Z	2	4	4
$\rho_{calcd.}$ (g.cm^{-3})	1.551	1.442	1.538
μ (mm^{-1})	0.569	0.873	5.598
Collected reflections	78089	103992	13075
Unique reflections	7192	10233	2550
R_{int}	0.022	0.022	0.038
Final R_1, wR_2 ($I \geq 3\sigma$)[b, c]	0.0646	0.0275, 0.0327	0.0604,0.0618
R_1, wR_2 (all data)	0.0700	0.0370,0.0436	0.0689, 0.0648
GOF on F[d]	1.086	0.961	1.131

[a] Including co-crystallized solvant molecules. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [c] $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma\ ([w(F_o^2)^2]^{1/2}$ where $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$ with $P = (2F_c^2 + \max(F_o^2,0))/3$. [d] GOF $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters.

Figure SI1. View of the crystal packing of **1** along the crystallographic *b* axis. Color codes: yellow = Fe; green = F, red = O; blue = N, dark grey = C and pink = B. The H atoms and interstitial solvent molecules are omitted for clarity. Some of the F atoms of the BF_4^- ions have thermal disorder. Only one position of the disordered F atoms is shown for clarity.

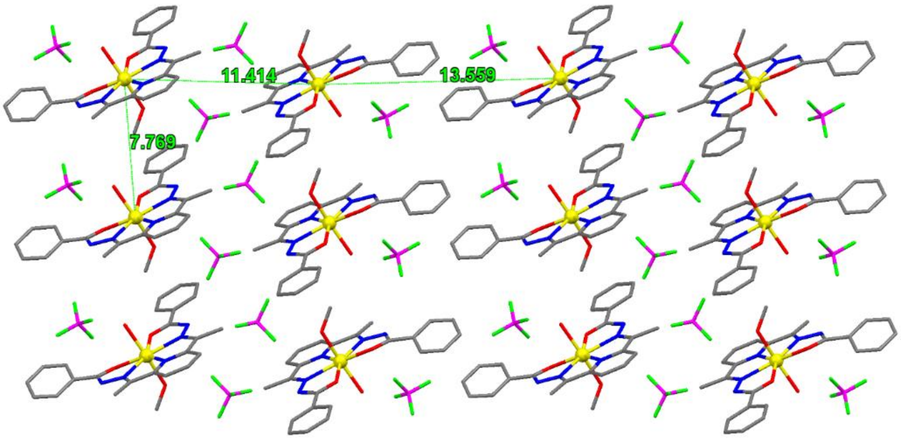

Figure SI2. Intermolecular interactions in the solid state packing of **1**. The atoms found by DFT to bear noticeable spin density (see Fig.SI5), and therefore likely to mediate intermolecular interactions, are highlighted in ball-and-stick model. Color codes: yellow = Fe; green = F, red = O; blue = N, dark grey = C and pink = B. The H atoms and interstitial solvent molecules are omitted for clarity.

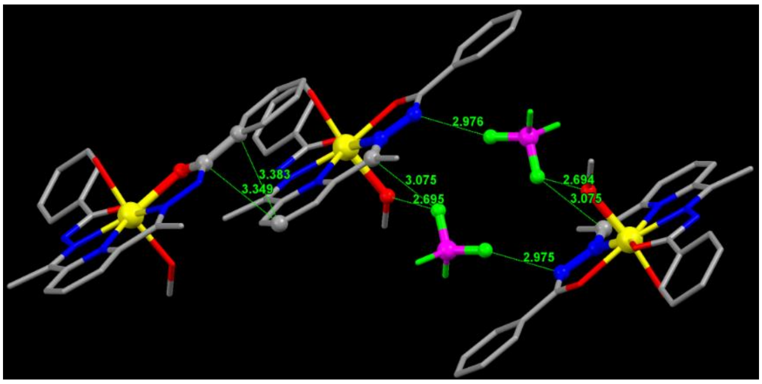

Table SI3. Selected bond lengths (Å) of **1**.

Fe1—N1	2.2312(18)	Fe1—N2	2.222(3)	C18—C19	1.396(5)
Fe1—N5	2.236(2)	C18—C23	1.403(4)	Fe1—O1	2.2158(16)
C19—C20	1.384(6)	Fe1—O2	2.202(2)	Fe1—O30	2.140(2)
C20—C21	1.383(5)	Fe1—O40	2.151(2)	C1—C2	1.404(3)
C21—C22	1.379(6)	C1—C10	1.470(5)	C1—N1	1.347(3)
C22—C23	1.377(6)	C2—C3	1.367(5)	C3—C4	1.394(4)
C24—O30	1.424(3)	C4—C5	1.398(3)	C5—C6	1.489(3)
C25—O6	1.423(5)	C5—N1	1.326(4)	C6—C7	1.476(5)
C6—N2	1.294(3)	C26—O5	1.415(7)	C8—C12	1.488(3)
C8—N32	1.359(3)	N2—N32	1.370(2)	C8—O1	1.231(4)
N5—N42	1.365(4)	C9—C18	1.474(5)	C9—N42	1.367(3)
C9—O2	1.242(4)	C10—C11	1.502(4)	C10—N5	1.296(3)
C12—C13	1.396(4)	C13—C14	1.394(3)	C14—C15	1.383(5)
C15—C16	1.388(4)	C16—C17	1.396(3)		

Table SI4. Selected bond angles (°) of **1**

N1—Fe1—N2	69.08(8)	N1—Fe1—N5	69.56(9)
N2—Fe1—N5	138.59(7)	N1—Fe1—O1	139.31(9)
N2—Fe1—O1	70.46(7)	N5—Fe1—O1	150.35(9)
N1—Fe1—O2	139.77(8)	N2—Fe1—O2	150.69(6)
N5—Fe1—O2	70.62(7)	O1—Fe1—O2	80.92(7)
N1—Fe1—O30	92.31(8)	N2—Fe1—O30	86.77(8)
N5—Fe1—O30	96.78(8)	O1—Fe1—O30	89.63(7)
O2—Fe1—O30	86.84(8)	N1—Fe1—O40	98.62(7)
N2—Fe1—O40	96.60(8)	N5—Fe1—O40	87.59(8)
O1—Fe1—O40	81.75(7)	O2—Fe1—O40	85.15(8)
O30—Fe1—O40	169.06(7)	Fe1—N1—C1	119.4(2)
Fe1—N1—C5	120.20(14)	Fe1—N2—C6	123.80(16)
Fe1—N2—N32	115.58(16)	Fe1—N5—C10	122.8(2)
Fe1—N5—N42	115.12(13)	Fe1—O1—C8	118.66(15)
Fe1—O2—C9	117.26(15)	Fe1—O30—C24	127.9(2)

Figure SI3. View of the crystal packing of **2** along the crystallographic *a* axis. Color codes: yellow = Fe; green = F, red = O; blue = N, dark grey = C and pink = B. The H atoms and interstitial solvent molecules are omitted for clarity.

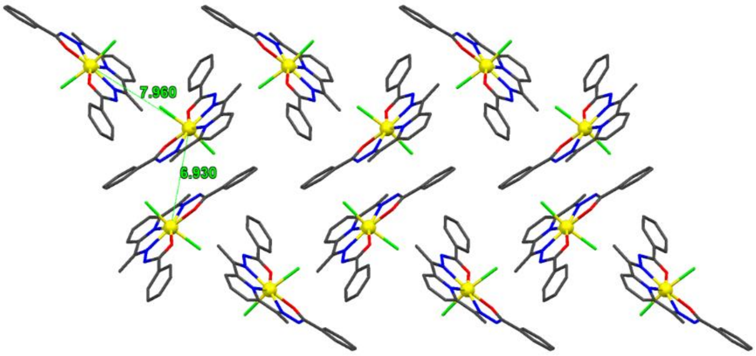

Figure SI4. Intermolecular interactions in the solid state packing of **2**. The atoms found by DFT to bear noticeable spin density (see Fig.SI5), and therefore likely to mediate intermolecular interactions, are highlighted in ball-and-stick model. Color codes: yellow = Fe; green = Cl, red = O; blue = N; dark grey = C and light grey = H.

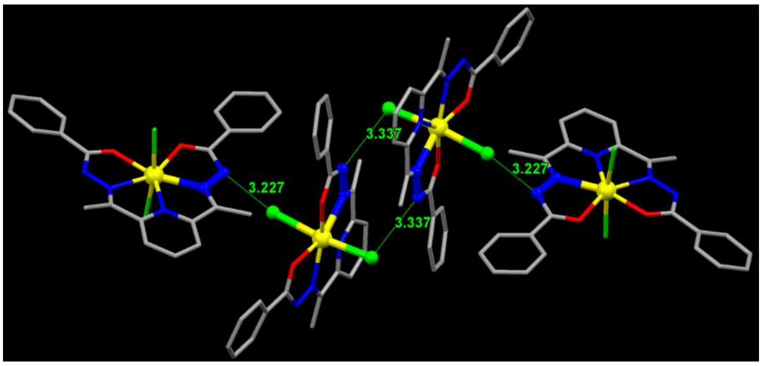

Table SI5. Selected bond lengths (Å) of **2**

Fe1—Cl1	2.4847(3)	Fe1—Cl2	2.4865(3)	C8—C12	1.4837(15)
Fe1—O1	2.2318(8)	C9—C18	1.4813(14)	Fe1—O2	2.2667(8)
Fe1—N5	2.2307(9)	O1—C8	1.2374(12)	C12—C13	1.3932(15)
N1—C5	1.3393(13)	C13—C14	1.3883(17)	N2—N3	1.3690(13)
N2—C6	1.2886(13)	C14—C15	1.380(2)	N3—C8	1.3678(13)
C15—C16	1.384(2)	N4—N5	1.3656(12)	C16—C17	1.3952(19)
N4—C9	1.3604(13)	N5—C10	1.2898(13)	C18—C19	1.3928(15)
C1—C2	1.3974(14)	C18—C23	1.3953(15)	C1—C10	1.4759(14)
C19—C20	1.3903(16)	C2—C3	1.3860(17)	C20—C21	1.3843(19)
C3—C4	1.3882(17)	C21—C22	1.388(2)	C4—C5	1.3954(14)
C5—C6	1.4801(15)	C22—C23	1.3919(17)	C6—C7	1.4869(16)
O3—C24	1.294(5)	Fe1—N1	2.2290(7)	Fe1—N2	2.2637(7)

Table SI6. Selected bond angles (°) of **2**

Cl1—Fe1—Cl2	170.398(12)	Cl1—Fe1—O1	87.17(3)
Cl2—Fe1—O1	83.23(2)	Cl1—Fe1—O2	92.35(2)
Cl2—Fe1—O2	86.52(2)	O1—Fe1—O2	83.21(3)
Cl1—Fe1—N1	92.15(2)	Cl2—Fe1—N1	95.06(2)
O1—Fe1—N1	138.63(3)	O2—Fe1—N1	138.10(3)
Cl1—Fe1—N2	92.53(2)	Cl2—Fe1—N2	84.13(2)
O1—Fe1—N2	69.48(3)	O2—Fe1—N2	151.96(3)
N1—Fe1—N2	69.23(3)	Cl1—Fe1—N5	88.71(3)
Cl2—Fe1—N5	99.78(3)	O1—Fe1—N5	152.11(3)
O2—Fe1—N5	69.41(3)	N1—Fe1—N5	69.07(3)
N2—Fe1—N5	138.30(3)	Fe1—O1—C8	118.87(7)
Fe1—O2—C9	117.97(7)	Fe1—N1—C1	120.34(7)
Fe1—N1—C5	120.35(7)	Fe1—N2—N3	116.07(6)
Fe1—N2—C6	121.37(7)	Fe1—N5—N4	117.51(6)
Fe1—N5—C10	123.29(7)		

Figure SI5: Electron density from spin SCF density (blue = positive spin density presented in 4×10^{-4} μ_B Å^3 isosurface; green = negative spin density presented in -4×10^{-4} μ_B Å^3 isosurface) of the complexes **1** *(left)* and **2** *(right)* estimated from UB3LYP[6] DFT calculations employing mixed basis sets with Gaussian 09 program.[5] The basis set for all non-metal atoms is 6-31G*,[7] while LANL2DZ[8] basis set was used for Fe atoms. Analyses revealed that the Mulliken atomic spin densities are 3.784843 (**1**) and 3.742484 (**2**) μ_B on Fe atoms; 0.095831 and 0.083779 μ_B on Cl atoms; 0.031137 and 0.020545 μ_B on axially coordinated O atoms; and 0.005471 and 0.004426 μ_B on the amide N atoms for **1** and 0.001568 and -0.000452 μ_B on the amide N atoms for **2** (See Table S13-14).

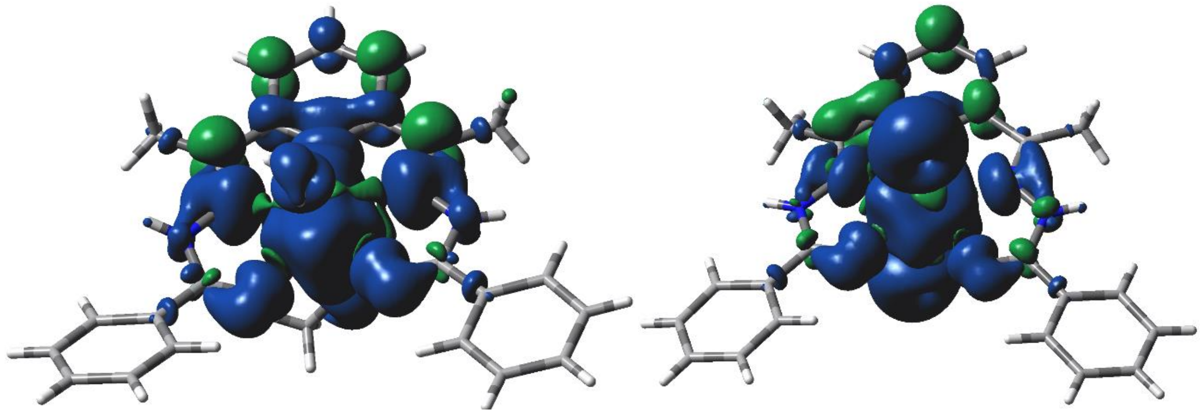

Table SI7. Selected bond lengths (Å) of **3**

Fe1—O1^{i}	2.195(2)	C8—C90	1.489(4)	Fe1—N4^{i}	2.256(3)
C8—C9	1.528(4)	Fe1—N1^{i}	2.139(4)	N4—N5	1.368(4)
Fe1—N1	2.139(4)	Fe1—N3	2.209(4)	C90—C100	1.463(4)
Fe1—N4	2.256(3)	C90—C140	1.322(4)	Fe1—O1	2.195(2)
C100—C110	1.386(4)	Ni1—C1^{ii}	1.866(4)	Ni1—C2^{ii}	1.858(3)
C110—C120	1.416(4)	Ni1—C1	1.866(4)	Ni1—C2	1.858(3)
C120—C130	1.333(5)	C1—N1	1.144(5)	C2—N2	1.149(5)
C130—C140	1.412(4)	C3—C4^{i}	1.385(4)	C3—C4	1.385(4)
C9—C10	1.418(4)	C4—C5	1.398(4)	C9—C14	1.331(4)
C10—C11	1.389(4)	C5—C6	1.481(4)	C5—N3	1.341(4)
C11—C12	1.413(4)	C6—C7	1.507(4)	C6—N4	1.287(4)
C12—C13	1.342(5)	C13—C14	1.404(4)	C8—N5	1.368(5)
C8—O1	1.237(4)				

Table SI8. Selected bond angles (°) of **3**

O1^{i}—Fe1—N4^{i}	70.21(9)	O1^{i}—Fe1—N1^{i}	87.55(11)
N4^{i}—Fe1—N1^{i}	93.72(11)	Fe1—N1—C1	167.6(3)
O1^{i}—Fe1—N1	88.15(11)	Fe1—N3—C5^{i}	120.06(19)
N4^{i}—Fe1—N1	88.25(11)	Fe1—N3—C5	120.06(19)
N1^{i}—Fe1—N1	174.36(15)	O1^{i}—Fe1—N3	139.73(6)
Fe1—N4—C6	122.4(2)	N4^{i}—Fe1—N3	69.58(7)
Fe1—N4—N5	115.7(2)	N1^{i}—Fe1—N3	92.82(8)
N1—Fe1—N3	92.82(8)	O1^{i}—Fe1—N4	150.57(10)
N4^{i}—Fe1—N4	139.16(14)	N1^{i}—Fe1—N4	88.25(11)
Fe1—O1—C8	119.4(2)	N1—Fe1—N4	93.72(11)
N3—Fe1—N4	69.58(7)	O1^{i}—Fe1—O1	80.54(13)
N4^{i}—Fe1—O1	150.57(10)	N1^{i}—Fe1—O1	88.15(11)
N1—Fe1—O1	87.55(11)	N3—Fe1—O1	139.73(6)
N4—Fe1—O1	70.21(9)	C1^{ii}—Ni1—C2^{ii}	88.64(15)
C1^{ii}—Ni1—C1	179.994	C2^{ii}—Ni1—C1	91.36(15)
C1^{ii}—Ni1—C2	91.36(15)	C2^{ii}—Ni1—C2	179.994
C1—Ni1—C2	88.64(15)	Ni1—C1—N1	178.4(3)
Ni1—C2—N2	177.5(3)		

(i) 1-x, y, 1.5-z; (ii) 1.5-x, 0.5-y, 1-z.

Figure SI6. Representation of the relative orientation of the Fe^{II} heptacoordinate planes (shown in yellow) in **3**. The green lines indicate the N$_{C\equiv N}$–Fe–N$_{C\equiv N}$ axes. Color codes: yellow = Fe, cyan = Ni, blue = N, dark grey = C and red = O. H atoms are omitted for clarity.

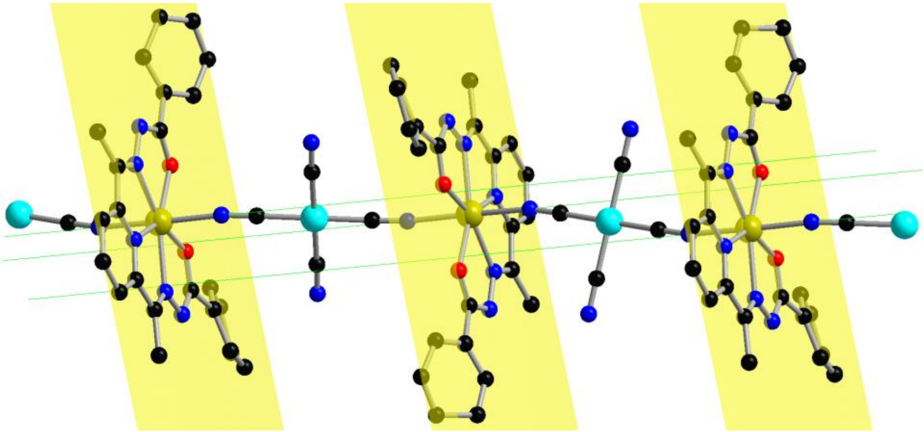

Figure SI7. View of the crystal packing of **3** emphasizing shortest inter-chain and intra-chain Fe···Fe distances. Color codes: yellow = Fe, cyan = Ni, blue = N, dark grey = C and red = O. H atoms are omitted for clarity.

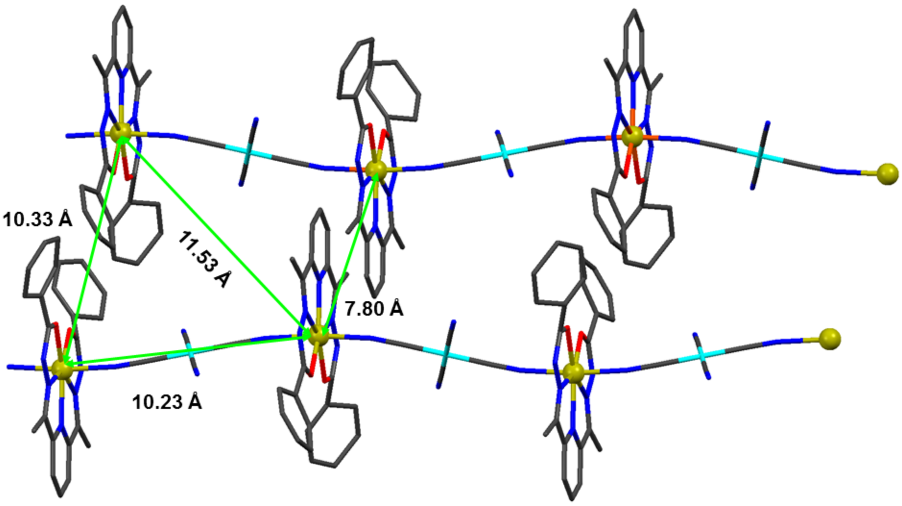

Table SI9. Results of Continuous Shape Measures calculation using SHAPE[11] with the closest geometries for each Fe metal center highlighted in blue.

```
-------------------------------------------------------------------------------
  S H A P E   v2.1       Continuous Shape Measures calculation
 (c) 2013  Electronic Structure Group, Universitat de Barcelona
--------------------------------------------------------------------------------
```

HP-7	1 D_{7h}	Heptagon
HPY-7	2 C_{6v}	Hexagonal pyramid
PBPY-7	3 D_{5h}	Pentagonal bipyramid
COC-7	4 C_{3v}	Capped octahedron
CTPR-7	5 C_{2v}	Capped trigonal prism
JPBPY-7	6 D_{5h}	Johnson pentagonal bipyramid J13
JETPY-7	7 C_{3v}	Johnson elongated triangular pyramid J7

	HPY-7	BPY-7	PBPY-7	COC-7	CTPR-7	JPBPY-7	JETPY-7
1_Fe1	32.228,	20.918	0.733	6.908	4.879	3.697	19.889
2_Fe1	33.519	23.011	0.912	6.906	5.295	6.209	20.961
3_Fe1	33.738	22.914	0.344	7.635	5.706	3.313	21.785

Table S10. ZFS parameters of compounds **1-3** from the best fits using the PHI code[12]

Compound	*D* (cm^{-1})	*E* (cm^{-1})	*g*
2	-13.3	0.017	2.31
3	-10.7	0.12	2.22

---

[11] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, 2.1 ed., University of Barcelona, Barcelona, 2013. D. Casanova, P. Alemany, J. M. Bofill, S. Alvarez, *Chem. Eur. J.*, 2003, 9, 1281.

[12] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34**, 1164

Figure SI8. Experimental powder X-ray diffractogram of complex **2** measured in a capillary tube at room temperature (blue line) and diffractogram calculated from the single crystal structure data measured at 100 K (red line).

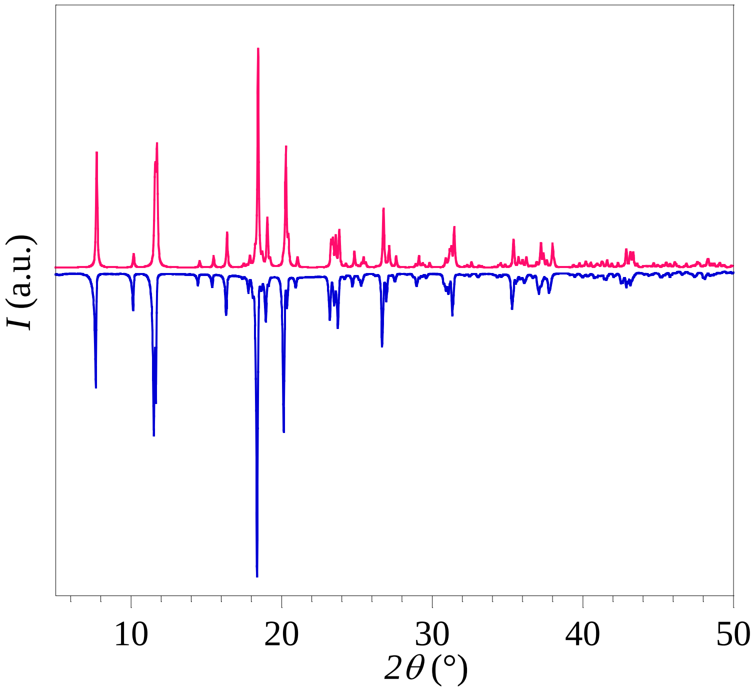

Figure SI9. Solid-state ^{57}Fe Mössbauer spectra of **1**–**3** measured at 80 K shown with circle markers along with the best spectral fits for a high spin Fe^{II} site for the parameters indicated in the text.

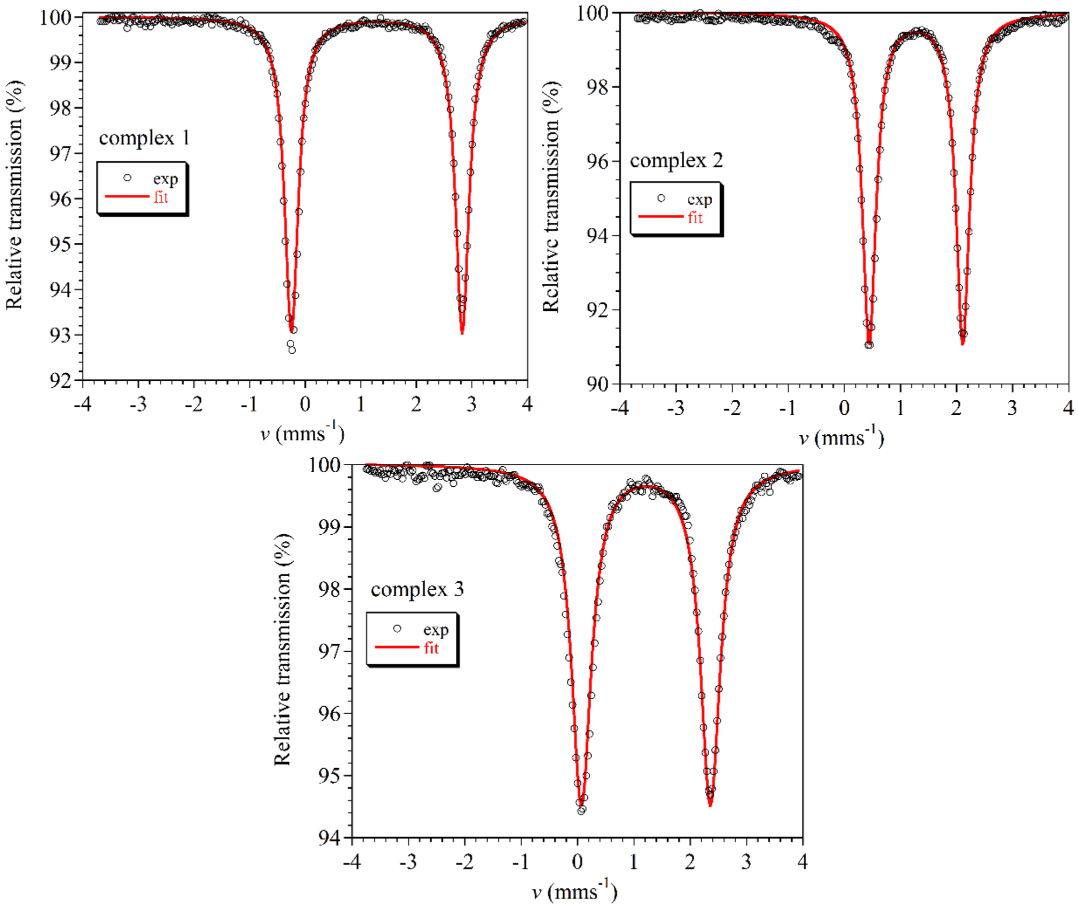

Figure SI10. Temperature dependence of the $\chi_M T$ products of **1** (red circles), **2** (blue circles) and **3** (green circles) recorded at 1 kOe along with the best fits (solid lines) for the parameters indicated in the text.

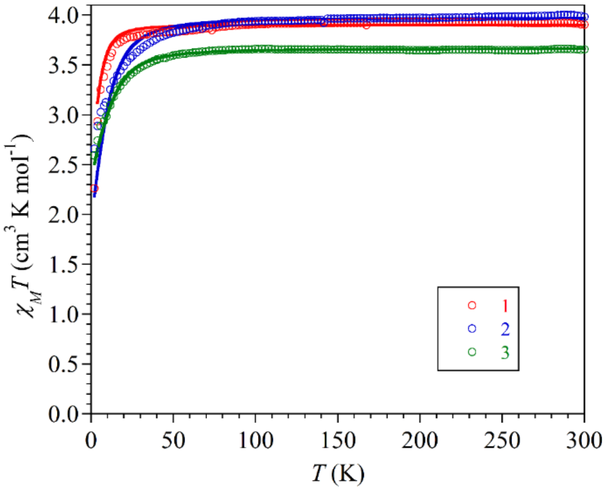

Figure SI11. ***(a)*****:** *M vs. H* isotherms; ***(b)***: reduced *M vs. H/T* isotherms measured between 0−5 T at several temperatures ranging from 2 to 10 K and ***(c)*****:** temperature dependence of the in-phase (χ_M') and out-of-phase (χ_M'') ac signals recorded at different dc fields with a 3 Oe ac field oscillating at 1000 Hz for **1**. The solid lines are guides for the eyes only.

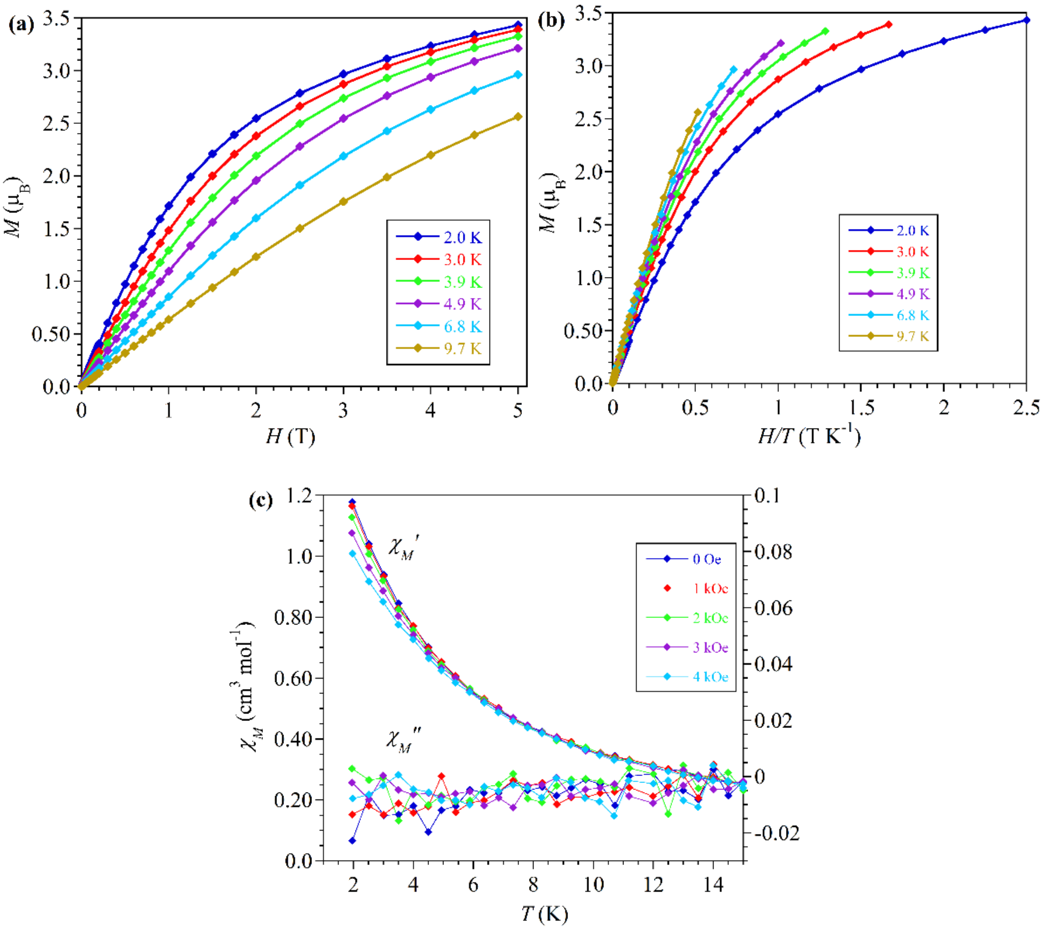

Figure SI12. *M vs. H* (left) and reduced *M vs. H/T* isotherms (right) for **2** measured between 0−5 T at several temperatures ranging from 2 to 10 K. The solid lines are the best fits for the parameters indicated in the text.

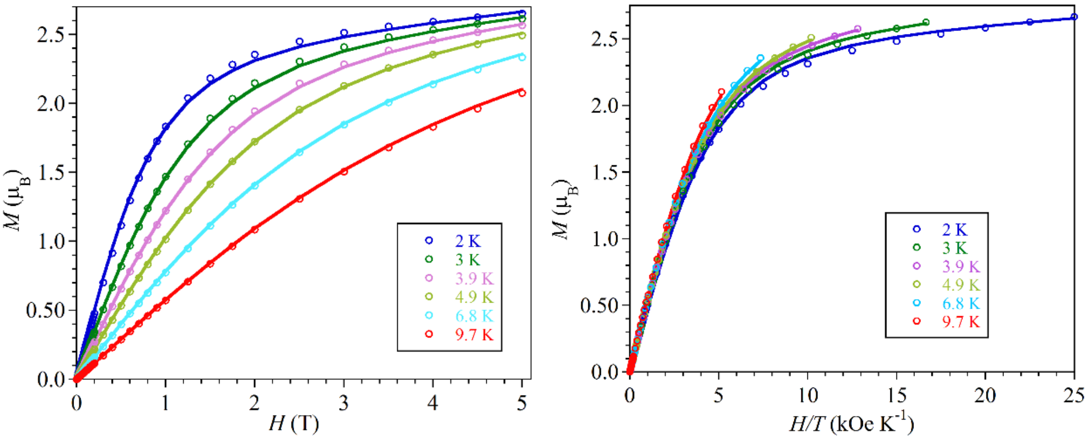

Figure SI13. Compound **2**: **(a)** DC field dependence of the in-phase (χ_M') and out-of-phase (χ_M'') ac signals (H_{ac} = 3 Oe ac, Frq: 1000 Hz); **(b)** frequency-dependence of the in-phase (χ_M'), and out-of-phase (χ_M'') ac signals as a function of the temperature recorded between 2.2 and 8.0 K at different frequencies with a 3 Oe ac field oscillating between 100 and 10000 Hz under an applied dc field of 3000 Oe ;**(c)** τ *vs.* T^{-1} plot. The solid lines are guides for the eyes only.

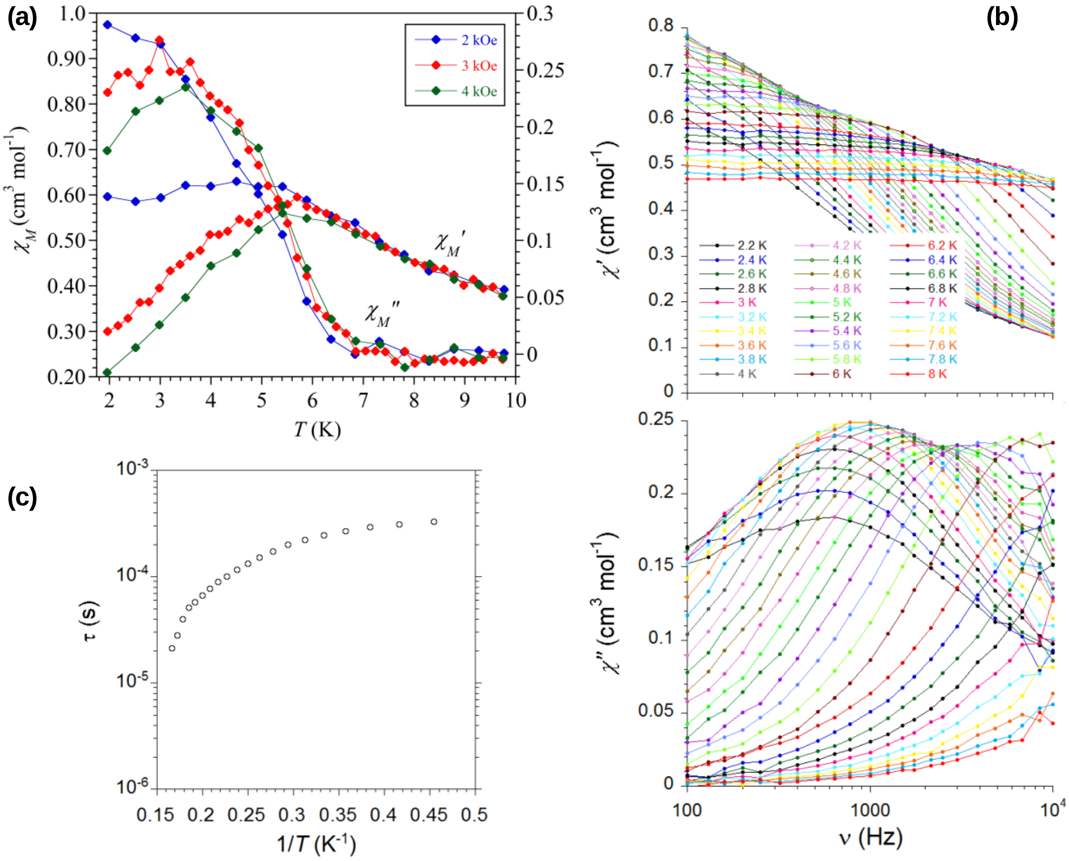

Figure SI14. Compound **3**: (left) *M vs. H* isotherms (circles) measured between 0−5 T at several temperatures ranging from 2 to 10 K with the best fits (solid lines) and (right) temperature dependence of the in-phase (χ_M') and out-of-phase (χ_M'') ac signals recorded at different dc fields with a 3 Oe ac field oscillating at 1000 Hz for **3**. The solid lines (right) are eye guides only.

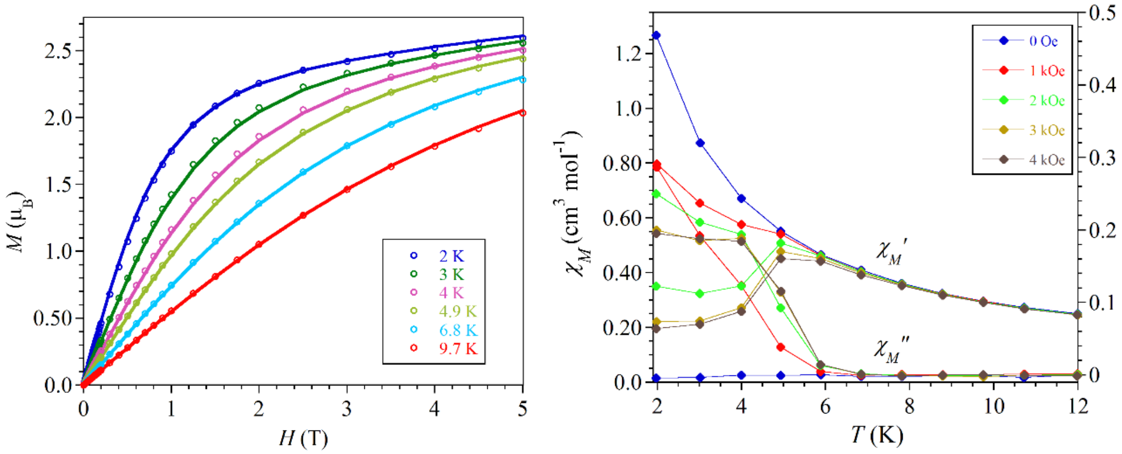

Figure SI15. Compound **3**: Frequency-dependence of the in-phase (χ_M') ac signals as a function of the temperature recorded between 2 and 6 K at different frequencies with a 3 Oe ac field oscillating between 100 and 10000 Hz under an applied dc field of 3000 Oe. The solid lines are guides for the eyes only.

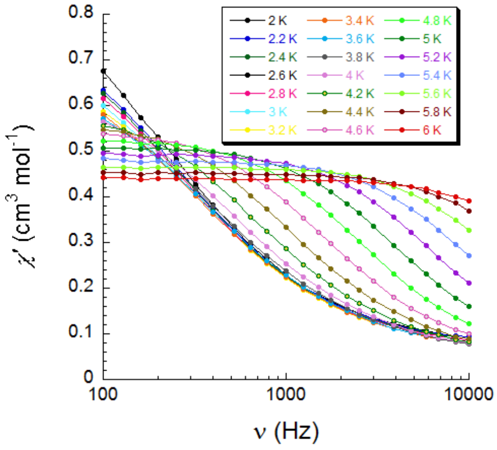

Figure SI16. Cole-Cole plots of **2** (left) between 2.2 and 6.0 K and **3** (right) between 2 and 5.6 K. The solid lines are the best fits for the parameters indicated in the text.

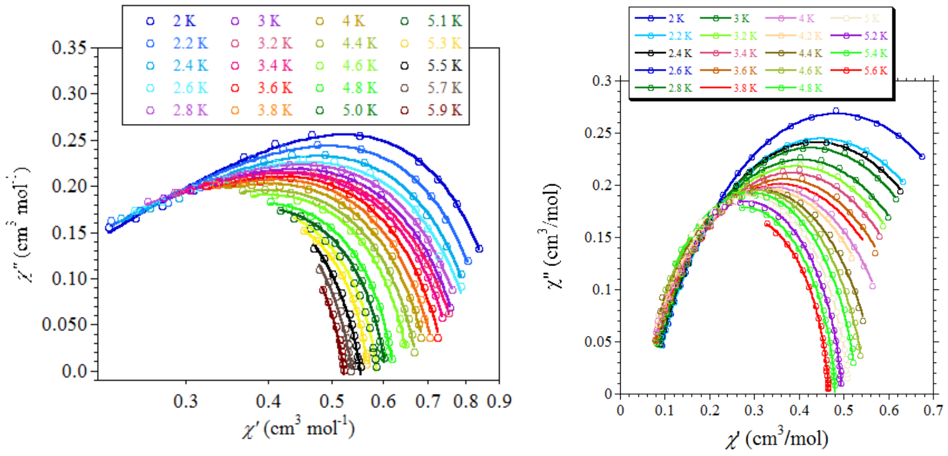

Table SI11: The crystallographic coordinates of the moiety $[Fe(H_2DAPBH)(H_2O)(MeOH)]^{2+}$

Fe	6.06070000	7.61970000	17.39890000
C	5.35680000	10.62790000	16.95150000
C	5.25960000	11.86870000	16.30170000
C	5.69210000	11.97950000	15.01000000
C	6.22400000	10.87070000	14.35330000
C	6.29790000	9.66760000	15.06170000
C	6.88240000	8.42520000	14.48520000
C	7.30770000	8.34850000	13.07350000
C	7.52100000	5.36140000	16.05310000
C	5.08760000	7.42620000	20.21110000
C	4.92850000	10.38770000	18.33700000
C	4.39410000	11.51040000	19.17910000
C	8.18570000	4.05860000	15.78350000
C	8.12350000	3.10400000	16.80130000
C	8.68800000	1.84550000	16.60340000
C	9.29350000	1.53700000	15.39870000
C	9.36430000	2.48580000	14.38890000
C	8.82120000	3.75710000	14.58820000
C	4.98510000	6.95450000	21.60410000
C	4.20820000	7.60810000	22.56310000
C	4.19740000	7.14980000	23.87030000
C	4.94780000	6.04490000	24.22780000
C	5.70160000	5.38210000	23.28330000
C	5.71570000	5.81590000	21.97680000
C	2.96770000	6.78310000	17.11650000
N	5.87680000	9.56090000	16.31450000
N	6.95470000	7.48260000	15.36890000
N	5.09430000	9.15530000	18.70540000
N	7.48800000	6.26510000	15.03870000
N	4.83650000	8.75010000	19.98260000
O	7.00650000	5.63300000	17.13850000
O	5.40460000	6.67360000	19.27550000
O	4.26030000	6.86170000	16.52540000
O	7.89510000	8.01120000	18.45100000
H	4.91750000	12.61040000	16.74860000
H	5.63070000	12.80070000	14.56470000
H	6.53190000	10.93350000	13.47040000
H	6.83910000	8.97880000	12.54270000
H	7.14170000	7.48440000	12.72870000
H	8.23800000	8.52810000	13.00170000
H	5.10070000	12.10380000	19.43010000
H	3.72650000	11.99710000	18.68120000
H	3.97930000	11.16190000	19.97120000
H	7.71250000	3.31500000	17.61340000
H	8.64190000	1.21490000	17.29210000
H	9.66890000	0.69840000	15.25810000
H	9.79480000	2.28660000	13.58390000
H	8.88940000	4.40200000	13.89800000
H	3.69680000	8.36750000	22.32900000
H	3.67760000	7.60000000	24.51530000
H	4.94820000	5.75250000	25.11200000
H	6.20120000	4.62170000	23.53690000
H	6.21160000	5.35400000	21.32650000
H	2.75070000	5.90190000	17.37430000
H	2.92130000	7.34850000	17.88640000
H	2.31990000	7.09600000	16.49980000
H	4.24550000	6.87600000	15.70500000
H	7.67650000	6.05250000	14.22410000
H	7.90600000	8.62160000	18.98320000

H	8.16630000	7.34970000	18.90590000
H	4.87440000	9.30790000	20.63320000

Table SI12: The crystallographic coordinates of the moiety [Fe(H_2DAPBH)Cl_2]

Fe	1.63070000	7.17710000	7.42720000
Cl	2.54390000	8.79680000	9.07540000
Cl	0.89980000	5.26640000	6.01400000
O	2.58360000	5.56850000	8.64620000
O	3.58590000	7.09660000	6.28310000
N	-0.31450000	8.26060000	7.31420000
N	0.15440000	6.33440000	8.92250000
N	0.56330000	5.22460000	9.61170000
H	0.04290000	4.77220000	10.12480000
N	2.84580000	8.89990000	5.14470000
H	2.96880000	9.52470000	4.56750000
N	1.70260000	8.78500000	5.88270000
C	-0.45850000	9.30860000	6.49240000
C	-1.63300000	10.06480000	6.45600000
H	-1.71520000	10.80510000	5.88940000
C	-2.67810000	9.70490000	7.29220000
H	-3.45240000	10.19180000	7.27980000
C	-2.54760000	8.59260000	8.11230000
H	-3.24560000	8.32180000	8.68300000
C	-1.33870000	7.89610000	8.09660000
C	-1.08440000	6.68920000	8.91480000
C	-2.21160000	5.97770000	9.57360000
H	-2.02260000	5.03880000	9.57850000
H	-3.01820000	6.13140000	9.09860000
H	-2.30940000	6.26930000	10.47400000
C	1.87610000	4.89870000	9.40880000
C	3.77480000	7.93890000	5.39770000
C	0.70410000	9.55730000	5.61790000
C	0.66500000	10.56070000	4.52100000
H	0.97440000	11.38550000	4.83320000
H	-0.23590000	10.67380000	4.19470000
H	1.25310000	10.27190000	3.80270000
C	2.42040000	3.70300000	10.09850000
C	3.79590000	3.49680000	10.01810000
H	4.33240000	4.10770000	9.55490000
C	4.38420000	2.40070000	10.63450000
H	5.32480000	2.30070000	10.58330000
C	3.59800000	1.48960000	11.31150000
H	3.97580000	0.74070000	11.72300000
C	2.22890000	1.67490000	11.38730000
H	1.71130000	1.04400000	11.83870000
C	1.62840000	2.78260000	10.78810000
H	0.70620000	2.91270000	10.84040000
C	4.97430000	7.93700000	4.52850000
C	6.06920000	7.16190000	4.90300000
H	6.02500000	6.64090000	5.70080000
C	7.21950000	7.14310000	4.12260000
H	7.93000000	6.63700000	4.38540000
C	7.27570000	7.89120000	2.95900000
H	8.02820000	7.89500000	2.43800000
C	6.17910000	8.64290000	2.56080000
H	6.22230000	9.12810000	1.75460000
C	5.02700000	8.66850000	3.34140000
H	4.29210000	9.18980000	3.07860000

Table SI13: The Mulliken atomic spin densities (μ_B) for $[Fe(H_2DAPBH)(H_2O)(MeOH)]^{2+}$

1	Fe	3.784843	2	C	0.010041	3	C	-0.014703	4	C	0.009646
5	C	-0.016017	6	C	0.009848	7	C	-0.028413	8	C	0.003366
9	C	-0.006974	10	C	-0.005696	11	C	-0.027188	12	C	0.003456
13	C	0.003383	14	C	-0.001176	15	C	0.000420	16	C	-0.000752
17	C	0.000433	18	C	-0.000501	19	C	0.001740	20	C	0.000530
21	C	-0.000030	22	C	0.000693	23	C	-0.000338	24	C	0.000396
25	C	0.000181	26	N	0.039648	27	N	0.048694	28	N	0.045267
29	N	0.005471	30	N	0.004426	31	O	0.038875	32	O	0.035969
33	O	0.031137	34	O	0.020545	35	H	0.001473	36	H	-0.000580
37	H	0.001562	38	H	-0.000015	39	H	-0.000440	40	H	-0.001214
41	H	-0.000870	42	H	-0.000580	43	H	-0.000106	44	H	0.000144
45	H	-0.000022	46	H	0.000050	47	H	0.000033	48	H	0.000025
49	H	-0.000031	50	H	0.000024	51	H	-0.000043	52	H	0.000019
53	H	0.000009	54	H	0.000347	55	H	0.000833	56	H	0.000250
57	H	-0.000301	58	H	0.001035	59	H	-0.000324	60	H	0.000165
61	H	0.001338									

Table SI14: The Mulliken atomic spin densities (μ_B) for $[Fe(H_2DAPBH)Cl_2]$

1	Fe	3.742484	2	Cl	0.095831	3	Cl	0.083779	4	O	0.030264
5	O	0.026432	6	N	0.032022	7	N	0.021661	8	N	0.001568
9	H	0.001603	10	N	-0.000452	11	H	0.001853	12	N	0.023622
13	C	-0.012667	14	C	0.006107	15	H	0.000247	16	C	-0.022304
17	H	0.001512	18	C	0.010797	19	H	-0.000078	20	C	-0.018424
21	C	-0.016149	22	C	0.002657	23	H	-0.000288	24	H	0.000120
25	H	-0.000991	26	C	-0.007624	27	C	-0.009124	28	C	0.001410
29	C	0.001248	30	H	-0.000102	31	H	0.000195	32	H	0.000015
33	C	0.003425	34	C	-0.001241	35	H	0.000128	36	C	0.000484
37	H	-0.000025	38	C	-0.000906	39	H	0.000065	40	C	0.000569
41	H	0.000019	42	C	-0.000886	43	H	0.000038	44	C	0.003272
45	C	-0.001405	46	H	0.000156	47	C	0.000556	48	H	-0.000030
49	C	-0.001110	50	H	0.000077	51	C	0.000659	52	H	0.000007
53	C	-0.001124	54	H	0.000050						