Supporting Information

Synthesis and Magnetic Studies of Pentagonal Bipyramidal Metal Complexes of Fe, Co and Ni

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Table S1. Selected bond lengths (Å) and angles (deg) for complexes **1-3**.

1		**2**		**3**	
Fe(1)-N(1)	2.121(3)	Co(1)-N(1)	2.123(2)	Ni(1)-N(1)	1.982(4)
Fe(1)-N(2)	2.176(3)	Co(1)-N(2)	2.171(2)	Ni(1)-N(2)	2.109(3)
Fe(1)-N(3)$_{MeCN}$	2.165(3)	Co(1)-N(3)$_{MeCN}$	2.120(2)	Ni(1)-N(3)$_{MeCN}$	2.048(3)
Fe(1)-O(1)	2.300(2)	Co(1)-O(1)	2.273(2)	Ni(1)-O(1)	2.477(3)
N(1)-Fe(1)-N(2)	73.03(7)	N(3)-Co(1)-N(3)#1	173.21(8)	N(1)-Ni(1)-N(3)#1	95.37(7)
N(1)-Fe(1)-N(3)	93.88(7)	N(3)-Co(1)-N(1)	93.40(4)	N(1)-Ni(1)-N(3)	95.37(7)
N(3)-Fe(1)-N(2)	90.93(10)	N(3)#1-Co(1)-N(1)	93.40(4)	N(3)#1-Ni(1)-N(3)	169.26(15)
N(1)-Fe(1)-N(3)#1	93.87(7)	N(3)-Co(1)-N(2)	90.68(6)	N(1)-Ni(1)-N(2)	77.06(8)
N(3)#1-Fe(1)-N(3)	172.25(14)	N(3)#1-Co(1)-N(2)	91.34(6)	N(3)#1-Ni(1)-N(2)	91.77(11)
N(3)#1-Fe(1)-N(2)	91.34(10)	N(1)-Co(1)-N(2)	72.70(4)	N(3)-Ni(1)-N(2)	90.63(11)
N(1)-Fe(1)-N(2)#1	73.03(7)	N(1)-Co(1)-N(2)#1	72.70(4)	N(1)-Ni(1)-N(2)#1	77.06(8)
N(2)-Fe(1)-N(2)#1	146.05(15)	N(2)-Co(1)-N(2)#1	145.40(9)	N(2)-Ni(1)-N(2)#1	154.11(16)
N(1)-Fe(1)-O(1)	144.92(5)	N(3)-Co(1)-O(1)#1	89.88(6)	N(1)-Ni(1)-O(1)	147.81(5)
N(3)#1-Fe(1)-O(1)	89.80(9)	N(3)-Co(1)-O(1)	84.54(6)	N(3)#1-Ni(1)-O(1)	89.22(9)
N(3)-Fe(1)-O(1)	83.85(9)	N(1)-Co(1)-O(1)#1	145.07(3)	N(3)-Ni(1)-O(1)	81.67(9)
N(2)-Fe(1)-O(1)	72.02(9)	N(2)-Co(1)-O(1)#1	142.08(6)	N(2)-Ni(1)-O(1)	70.96(10)
N(2)#1-Fe(1)-O(1)	141.86(9)	N(3)#1-Co(1)-O(1)	89.89(6)	N(2)#1-Ni(1)-O(1)	134.86(9)
N(1)-Fe(1)-O(1)#1	144.92(5)	N(1)-Co(1)-O(1)	145.07(3)	N(3)-Ni(1)-O(1)#1	89.22(9)
N(3)-Fe(1)-O(1)#1	89.80(9)	N(2)-Co(1)-O(1)	72.46(6)	N(1)-Ni(1)-O(1)#1	147.82(7)
N(2)-Fe(1)-O(1)#1	141.86(9)	N(2)#1-Co(1)-O(1)	142.08(6)	N(2)-Ni(1)-O(1)#1	134.86(9)
O(1)-Fe(1)-O(1)#1	70.16(10)	O(1)#1-Co(1)-O(1)	69.86(7)	O(1)-Ni(1)-O(1)#1	64.37(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+1/2.

Table S2. Parameters fitted for **1** at 1500 Oe and **2** at 1200 Oe by a generalized Debye model.

1			**2**		
T / K	τ / s	α	T / K	τ / s	α
2.00	$1.71(6) \times 10^{-3}$	0.27(2)	2.00	$9.85(2) \times 10^{-2}$	0.27(2)
2.25	$1.42(3) \times 10^{-3}$	0.21(1)	2.50	$2.47(4) \times 10^{-2}$	0.15(2)
2.50	$1.18(2) \times 10^{-3}$	0.17(1)	3.00	$7.81(2) \times 10^{-3}$	0.087(5)
2.75	$9.50(7) \times 10^{-4}$	0.14(1)	3.50	$2.88(3) \times 10^{-2}$	0.063(5)
3.00	$7.46(6) \times 10^{-4}$	0.13(1)	4.00	$1.25(1) \times 10^{-2}$	0.049(3)
3.25	$5.72(4) \times 10^{-4}$	0.096(4)	4.25	$8.65(4) \times 10^{-4}$	0.044(2)
3.50	$4.02(2) \times 10^{-4}$	0.069(3)	4.50	$6.12(3) \times 10^{-4}$	0.043(3)
3.65	$3.05(2) \times 10^{-4}$	0.057(3)	4.75	$4.48(2) \times 10^{-4}$	0.033(3)
3.80	$2.22(1) \times 10^{-4}$	0.042(3)	5.00	$3.32(2) \times 10^{-4}$	0.029(2)
3.95	$1.49(2) \times 10^{-4}$	0.041(4)	5.25	$2.50(3) \times 10^{-4}$	0.024(3)
4.10	$9.41(2) \times 10^{-5}$	0.052(5)	5.50	$1.90(1) \times 10^{-4}$	0.023(2)
4.25	$5.95(3) \times 10^{-5}$	0.054(6)	5.75	$1.45(2) \times 10^{-4}$	0.019(2)
4.50	$2.89(3) \times 10^{-5}$	0.067(4)	6.00	$1.11(2) \times 10^{-4}$	0.016(3)
			6.25	$8.38(4) \times 10^{-5}$	0.019(3)

Table S3. The SH parameters extracted from fitting and *ab* initio calculations for complexes **1**–**3**.

	D / cm^{-1}	E/D	g_x	g_y	g_z
1	-19.7	0.02	2.13	2.17	2.65
2	+37.8	<0.01	2.30	2.28	2.04
3	-15.4	0.21	1.74	1.91	2.59

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

	1	**2**	**3**
$^4\Psi_0$	0.0	0.0	0.0
$^4\Psi_1$	5239.1	3078.2	6240.6
$^4\Psi_2$	7612.3	3122.0	7394.0
$^4\Psi_3$	9012.4	5282.6	8466.9
$^4\Psi_4$	10367.1	5813.2	12385.7
$^4\Psi_5$	11478.3	10392.2	12710.1
$^4\Psi_6$	11961.4	13131.0	13109.3
$^4\Psi_7$	24127.6	17262.0	28002.8
$^4\Psi_8$	25364.1	18418.1	28268.5
$^4\Psi_9$	27498.3	19842.2	29112.9

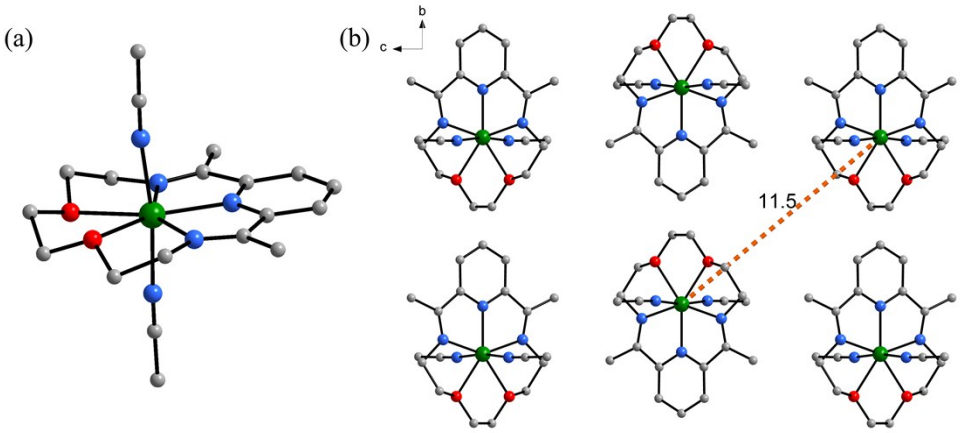

Figure S1. Molecular structure (a) and packing arrangement (b) of **1** along the crystallographic a axis; The dashed line shows the nearest intermolecular Fe···Fe separation (Å). Hydrogen atoms and counterions are omitted for clarity. Colour codes: Fe, green; C, grey; O, red; N, blue.

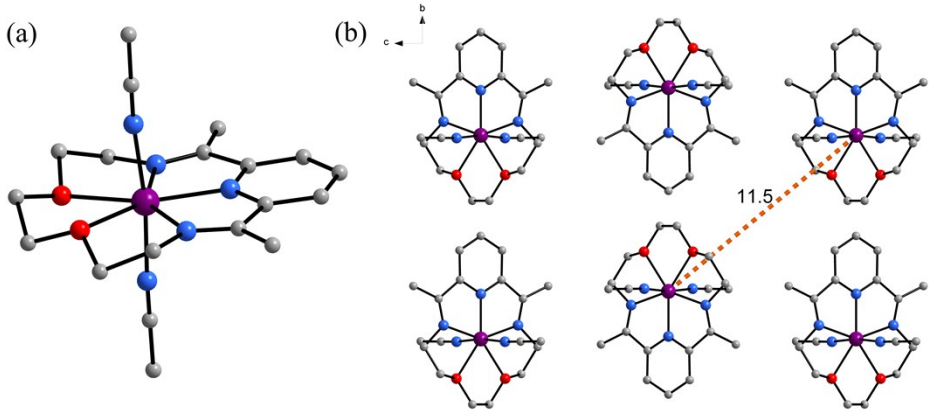

Figure S2. Molecular structure (a) and packing arrangement (b) of **2** along the crystallographic a axis; The dashed line shows the nearest intermolecular Co···Co separation (Å). Hydrogen atoms and counterions are omitted for clarity. Colour codes: Co, purple; C, grey; O, red; N, blue.

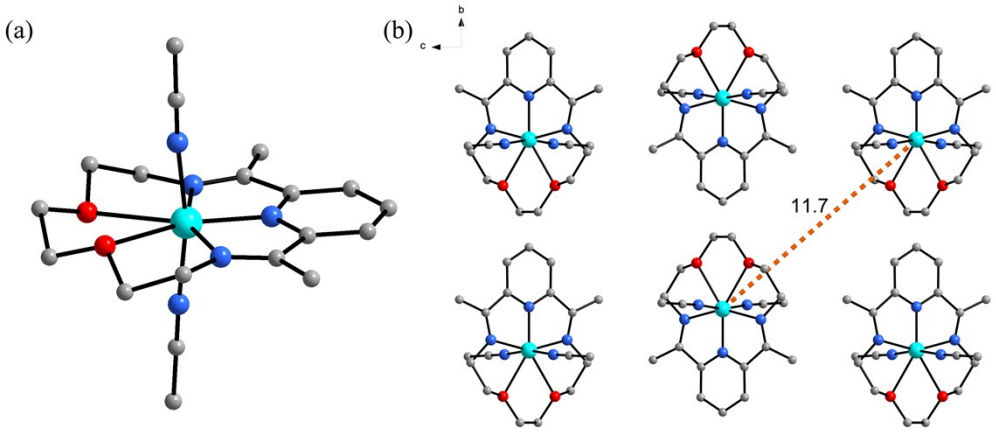

Figure S3. Molecular structure (a) and packing arrangement (b) of **3** along the crystallographic a axis; The dashed line shows the nearest intermolecular Ni···Ni separation (Å). Hydrogen atoms and counterions are omitted for clarity. Colour codes: Ni, green; C, grey; O, red; N, blue.

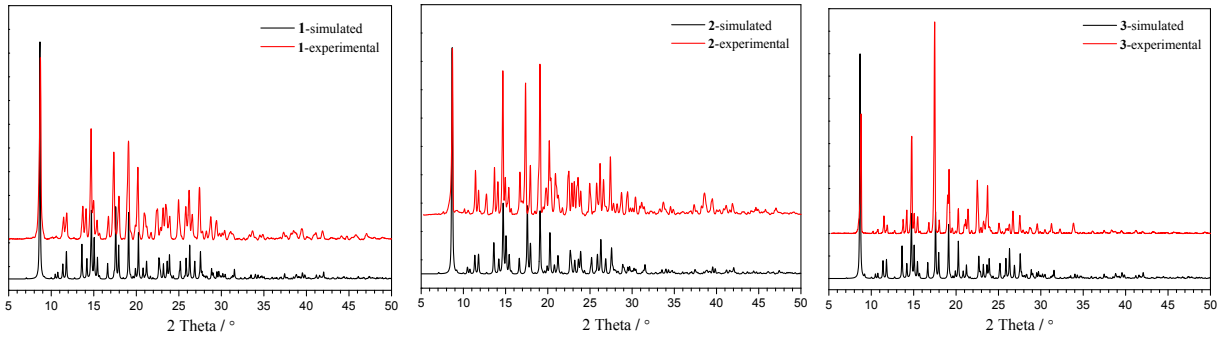

Figure S4. The powder X-ray diffractions for complexes **1**-**3**. The black curve is calculated from the single crystal data.

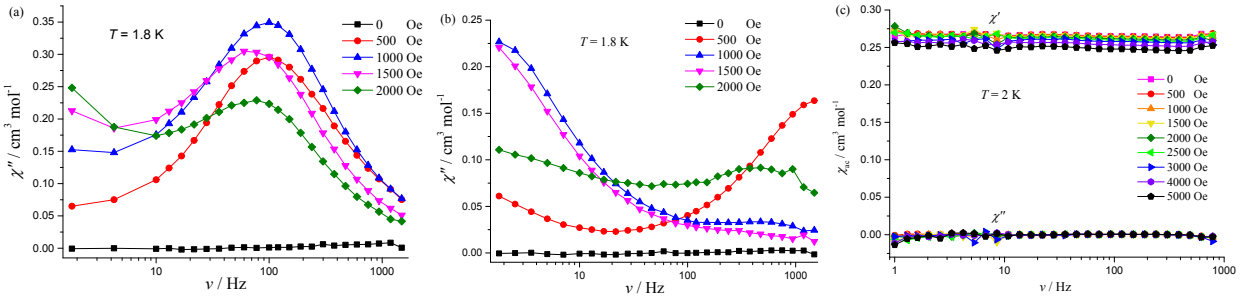

Figure S5. Frequency dependence of the ac susceptibility for **1**(a), **2**(b) and **3**(c) under different dc fields. The lines are guides to the eyes.

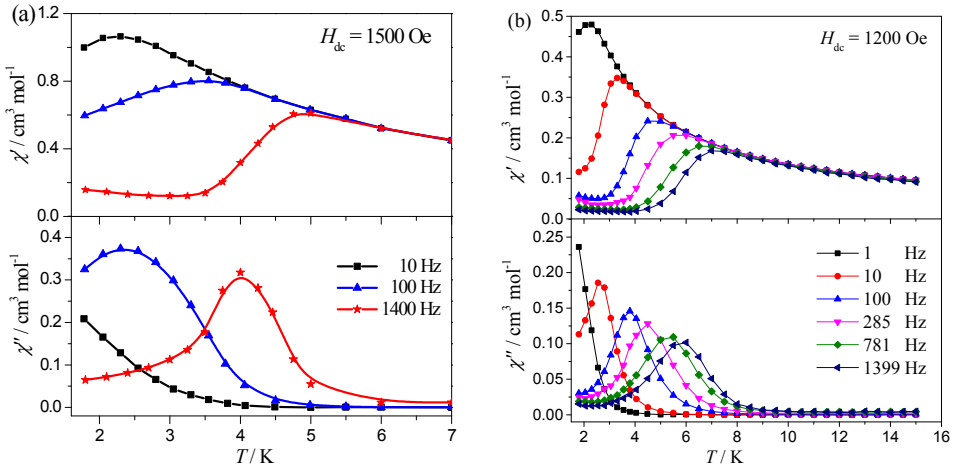

Figure S6. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility for **1**(a) and **2**(b) at indicated dc field. The lines are guides to the eyes.

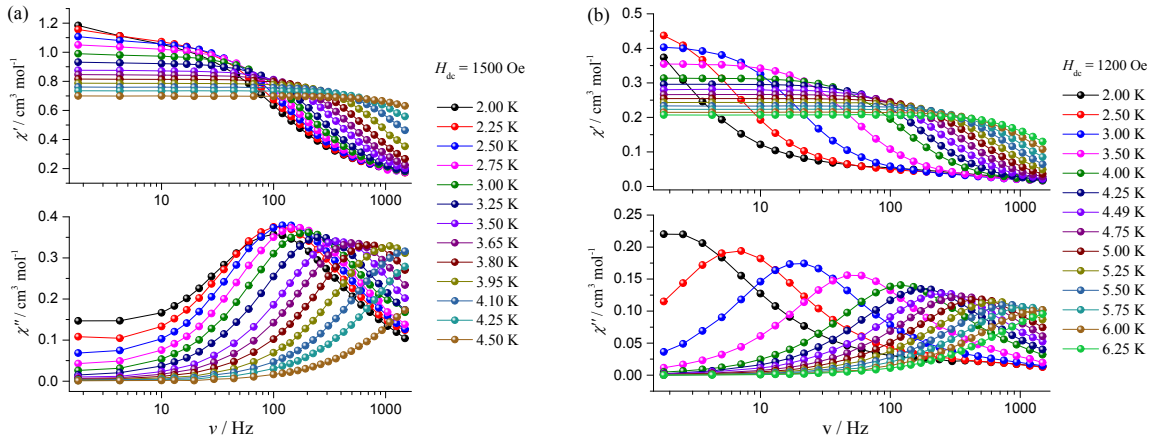

Figure S7. Frequency dependence of the in-phase χ' (top) and out-of-phase χ'' (bottom) components of the ac susceptibility for **1**(a) and **2**(b) at indicated dc field. The lines are guides to the eyes.

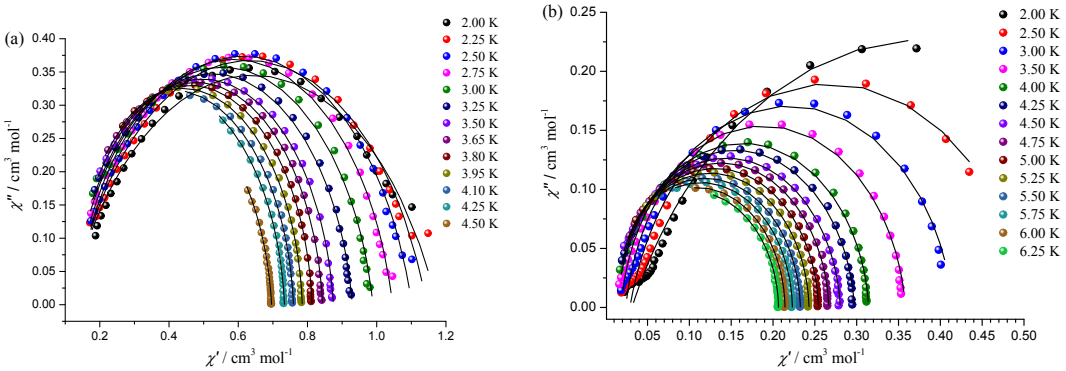

Figure S8. Cole-Cole plots for complexes **1**(a) and **2**(b). The solid lines represent the fit to the data.

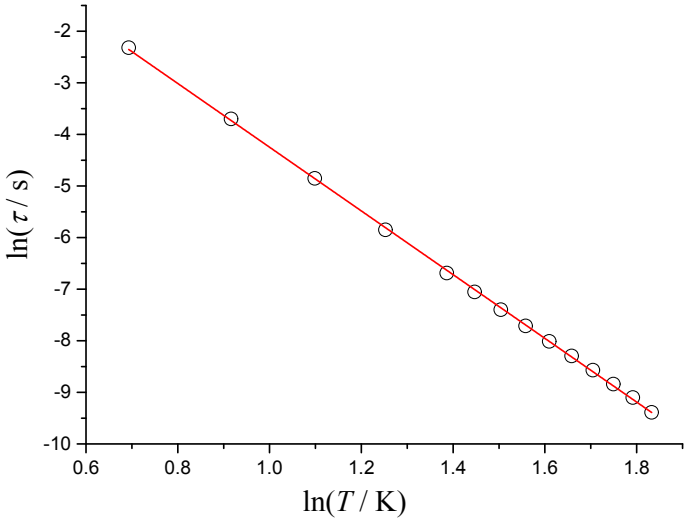

Figure S9. Power law analysis of complex **2** in the form ln(τ) vs ln(T). The solid line represents the best fits to the data.