

Supporting information

Stereoisomeric coordination polymers based on facial and meridional six-coordinate dysprosium(III)

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Table S1. Crystal data and structure refinement parameters for complexes **1-3**.

Complex	1	2	3
Empirical formula	C ₃₉ H ₃₆ Cl ₃ DyO ₃ P ₃ ·C _{1.75} H ₇ O _{1.75}	C ₃₉ H ₃₆ Cl ₃ DyO ₃ P ₃	C ₁₅₆ H ₁₄₄ Cl ₁₂ Dy ₄ O ₁₂ P ₁₂
Formula weight	970.51	914.44	3657.74
Temperature / K	100.0(2)	100.0 (2)	100.0 (2)
Crystal system	Triclinic	Triclinic	Trigonal
Space group	<i>P</i> -1	<i>P</i> -1	<i>R</i> -3
<i>a</i> / Å	12.7559(5)	11.9254(1)	35.6799(2)
<i>b</i> / Å	13.5242(6)	12.0637(1)	35.6799(2)
<i>c</i> / Å	14.6360(4)	15.1295(1)	21.4215(1)
α / °	105.698(3)	96.832(1)	90
β / °	97.442(3)	98.582(1)	90
γ / °	115.579(4)	115.438(1)	120
Volume / Å³	2102.43(15)	1902.29(3)	23617.2(3)
<i>Z</i>	2	2	6
Density / g·cm⁻³	1.533	1.596	1.543
μ / mm⁻¹	2.123	13.931	13.465
<i>F</i>(000)	975.0	912.0	10944.0
Radiation	Mo K α (λ = 0.71073 Å)	Cu K α (λ = 1.54184 Å)	Cu K α (λ = 1.54184 Å)
2θ range for data collection / °	4.05 to 59.178	6.036 to 152.91	4.954 to 153.8
Reflections collected	37423	46309	28652
Independent reflections	10482 [<i>R</i> _{int} = 0.0664, <i>R</i> _{sigma} = 0.0801]	7672 [<i>R</i> _{int} = 0.0622, <i>R</i> _{sigma} = 0.0292]	10478 [<i>R</i> _{int} = 0.0211, <i>R</i> _{sigma} = 0.0220]
Goodness-of-fit on <i>F</i>²	1.057	1.062	1.050
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0499 <i>wR</i> ₂ = 0.1090	<i>R</i> ₁ = 0.0313 <i>wR</i> ₂ = 0.0843	<i>R</i> ₁ = 0.0495 <i>wR</i> ₂ = 0.1190

Final R indexes [all data]	$R_1 = 0.0674$ $wR_2 = 0.1199$	$R_1 = 0.0339$ $wR_2 = 0.0865$	$R_1 = 0.0510$ $wR_2 = 0.1200$
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Table S2. Selected bond lengths (Å) and angles (°) for complexes **1-3**.

1		2	
Dy1-Cl1	2.6584(12)	Dy1-Cl1	2.6176(8)
Dy1-Cl2	2.5978(15)	Dy1-Cl2	2.6484(7)
Dy1-Cl3	2.6697(12)	Dy1-Cl3	2.6234(9)
Dy1-O1	2.233(4)	Dy1-O1	2.243(2)
Dy1-O2	2.225(4)	Dy1-O2	2.276(2)
Dy1-O3	2.271(4)	Dy1-O3	2.272(2)
Cl1-Dy1-Cl2	94.06(4)	Cl1-Dy1-Cl2	94.41(2)
Cl1-Dy1-O2	90.66(8)	Cl1-Dy1-O2	174.85(6)
Cl2-Dy1-O1	92.37(11)	Cl2-Dy1-O1	86.55(6)
Cl3-Dy1-O1	90.65(8)	Cl3-Dy1-O1	175.95(6)
O1-Dy1-O2	177.71(11)	O1-Dy1-O2	87.51(8)
Cl1-Dy1-Cl3	172.59(5)	Cl1-Dy1-Cl3	96.06(3)
Cl1-Dy1-O3	87.49(8)	Cl1-Dy1-O3	92.28(5)
Cl2-Dy1-O2	87.14(11)	Cl2-Dy1-O2	87.63(5)
Cl3-Dy1-O2	91.61(8)	Cl3-Dy1-O2	88.51(6)
O1-Dy1-O3	93.84(14)	O1-Dy1-O3	86.99(8)
Cl1-Dy1-O1	87.15(8)	Cl1-Dy1-O1	87.89(6)
Cl2-Dy1-Cl3	93.10(4)	Cl2-Dy1-Cl3	94.03(2)
Cl2-Dy1-O3	173.67(10)	Cl2-Dy1-O3	170.52(6)
Cl3-Dy1-O3	85.60(8)	Cl3-Dy1-O3	91.94(6)
O2-Dy1-O3	86.71(14)	O2-Dy1-O3	85.17(7)
Dy1(mer) of 3		Dy2(fac) of 3	
Dy1-Cl1	2.6322(18)	Dy2-Cl4	2.6214(11)
Dy1-Cl2	2.6126(14)	Dy2-Cl4 ^{#2}	2.6214(13)
Dy1-Cl3	2.6508(17)	Dy2-Cl4 ^{#1}	2.6214(12)
Dy1-O1	2.252(3)	Dy2-O4	2.273(3)
Dy1-O2	2.233(4)	Dy2-O4 ^{#2}	2.273(4)
Dy1-O3	2.232(3)	Dy2-O4 ^{#1}	2.273(4)
Cl2-Dy1-O1	96.14(10)	Cl4 ^{#2} -Dy2-Cl4 ^{#1}	94.47(4)
Cl2-Dy1-O1	96.14(10)	Cl4 ^{#2} -Dy2-O4 ^{#2}	82.58(10)
Cl2-Dy1-O2	174.59(10)	Cl4 ^{#2} -Dy2-O4 ^{#1}	167.09(10)
Cl2-Dy1-O2	174.59(10)	Cl4 ^{#1} -Dy2-O4 ^{#1}	82.58(9)
Cl2-Dy1-O3	83.68(8)	Cl4-Dy2-Cl4 ^{#2}	94.47(4)
Cl2-Dy1-O3	83.68(8)	Cl4-Dy2-Cl4 ^{#1}	94.47(4)
Cl3-Dy1-O1	88.10(12)	Cl4-Dy2-O4	82.58(9)
Cl3-Dy1-O1	88.10(12)	Cl4-Dy2-O4 ^{#2}	167.09(10)
Cl3-Dy1-O2	83.66(12)	Cl4-Dy2-O4 ^{#1}	98.28(10)
Cl3-Dy1-O2	83.66(12)	O4 ^{#2} -Dy2-Cl4 ^{#1}	98.28(10)
Cl3-Dy1-O3	90.90(10)	O4 ^{#2} -Dy2-O4 ^{#1}	85.40(14)

Cl3-Dy1-O3	90.90(10)	O4-Dy2-Cl4 ^{#2}	98.28(10)
O1-Dy1-O2	88.98(13)	O4-Dy2-Cl4 ^{#1}	167.09(10)
O1-Dy1-O3	178.96(15)	O4-Dy2-O4 ^{#2}	85.40(13)
O2-Dy1-O3	91.18(12)	O4-Dy2-O4 ^{#1}	85.40(13)

Symmetry code, ^{#1}: $-x + y, 1 - x, z$; ^{#2}: $1 - y, 1 + x - y, z$

Table S3. Continuous Shape Measures Calculations¹ results for Dy ions of **1-3**.

	Ideal structures	1 (mer)	2 (fac)	Dy1 (mer) of 3	Dy2 (fac) of 3
HP-6	D_{6h} Hexagon	33.52001	32.65284	31.71937	34.41366
PPY-6	C_{5v} Pentagonal pyramid	27.97370	28.27465	27.75832	24.88369
OC-6	O_h Octahedron	0.94148	0.88748	0.99352	1.75440
TPR-6	D_{3h} Trigonal prism	14.69981	16.38556	15.42735	11.30731
JPPY-5	C_{5v} Johnson pentagonal pyramid (J2)	30.58340	32.19463	30.52598	29.32199

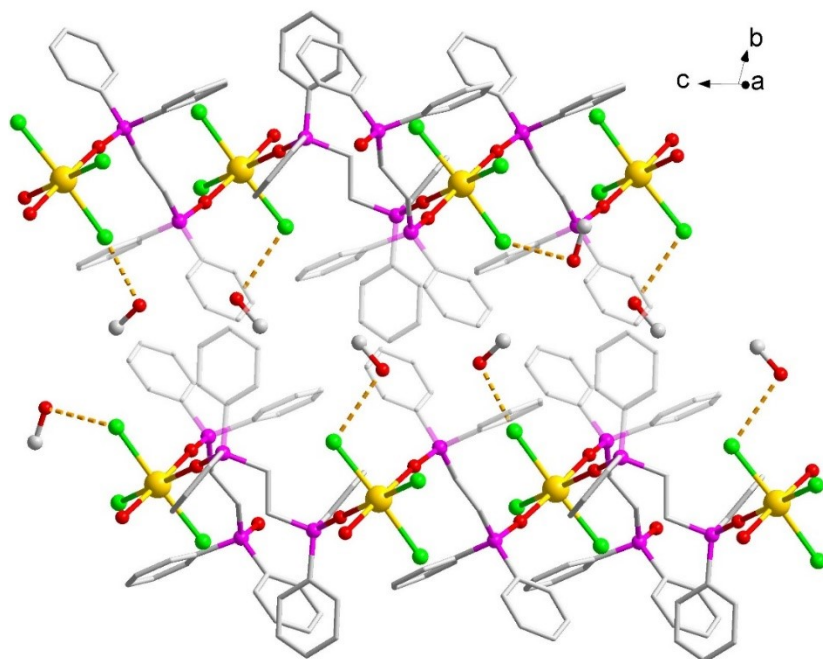


Figure S1. O-H...Cl hydrogen bonds in complex **1** among MeOH molecules and the 2D-layers.

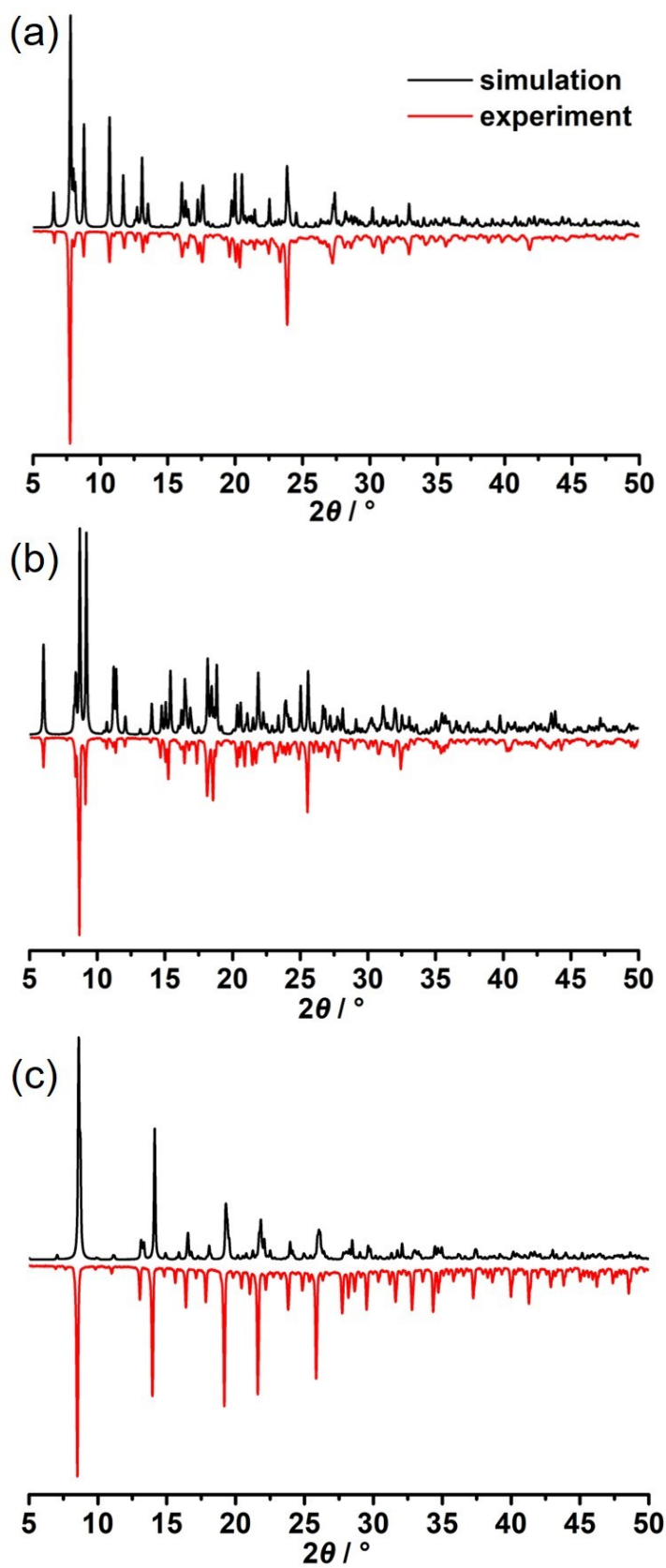


Figure S2. Experimental (red) and simulated (black) powder X-ray diffraction patterns of complexes **1(a)**, **2(b)** and **3(c)**.

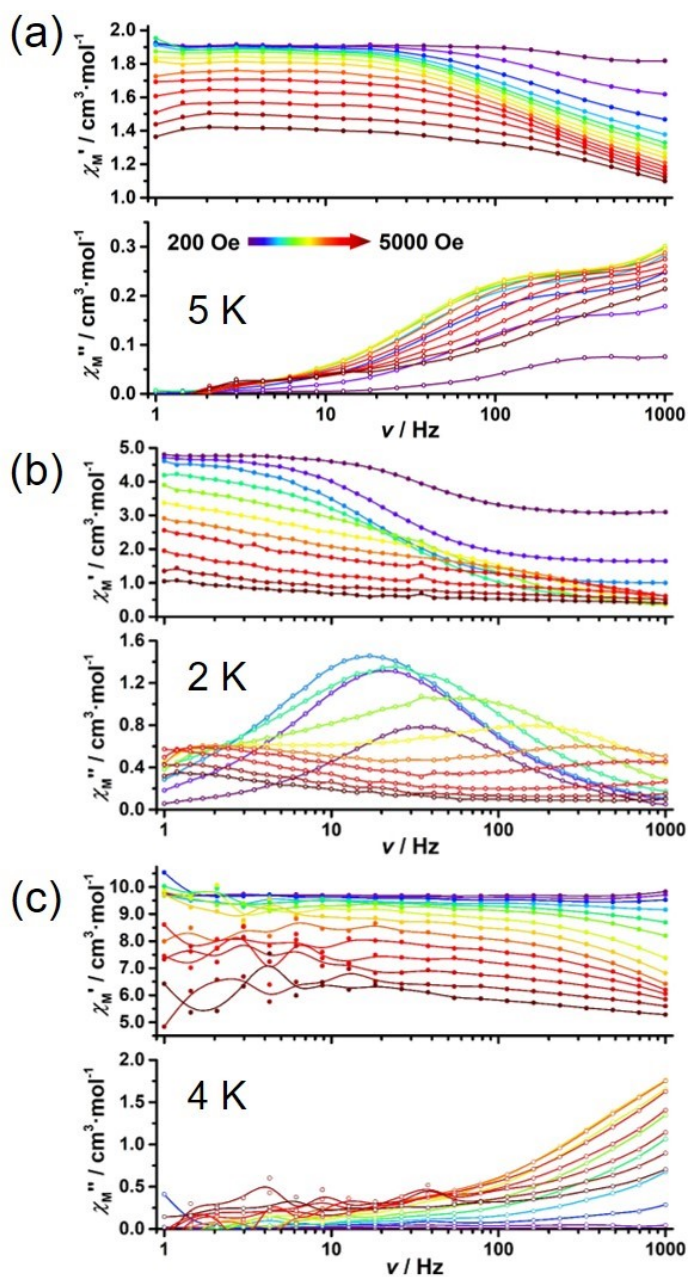


Figure S3. Frequency dependent in-phase (χ_M' , solid circles) and out-of-phase (χ_M'' , open circles) ac magnetic susceptibility for complex **1** (a), **2** (b) and **3** (c) under various dc fields at indicated temperatures. The chromatic solid lines represent the fitting results using generalized Debye model. The obtained optimal dc fields are 1600 Oe for **1**, 600 Oe for **2**, and 2000 Oe for **3**, respectively.

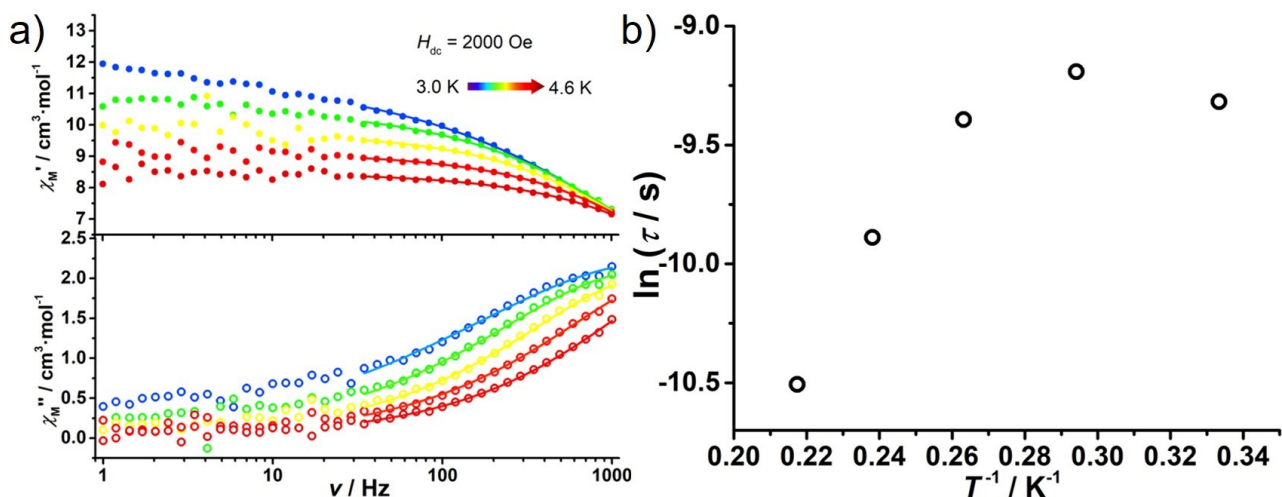


Figure S4. Frequency dependent in-phase (χ'_M , solid circles) and out-of-phase (χ''_M , open circles) ac magnetic susceptibility plots under a dc field of 2000 Oe, and temperature dependent relaxation time, for complex **3**. The circles and lines represent the experimental data and the fitting results, respectively. Although no peak of χ''_M can be observed under an external 2 kOe dc field, the relaxation times was extracted by fitting high-frequency section by modified Debye model.

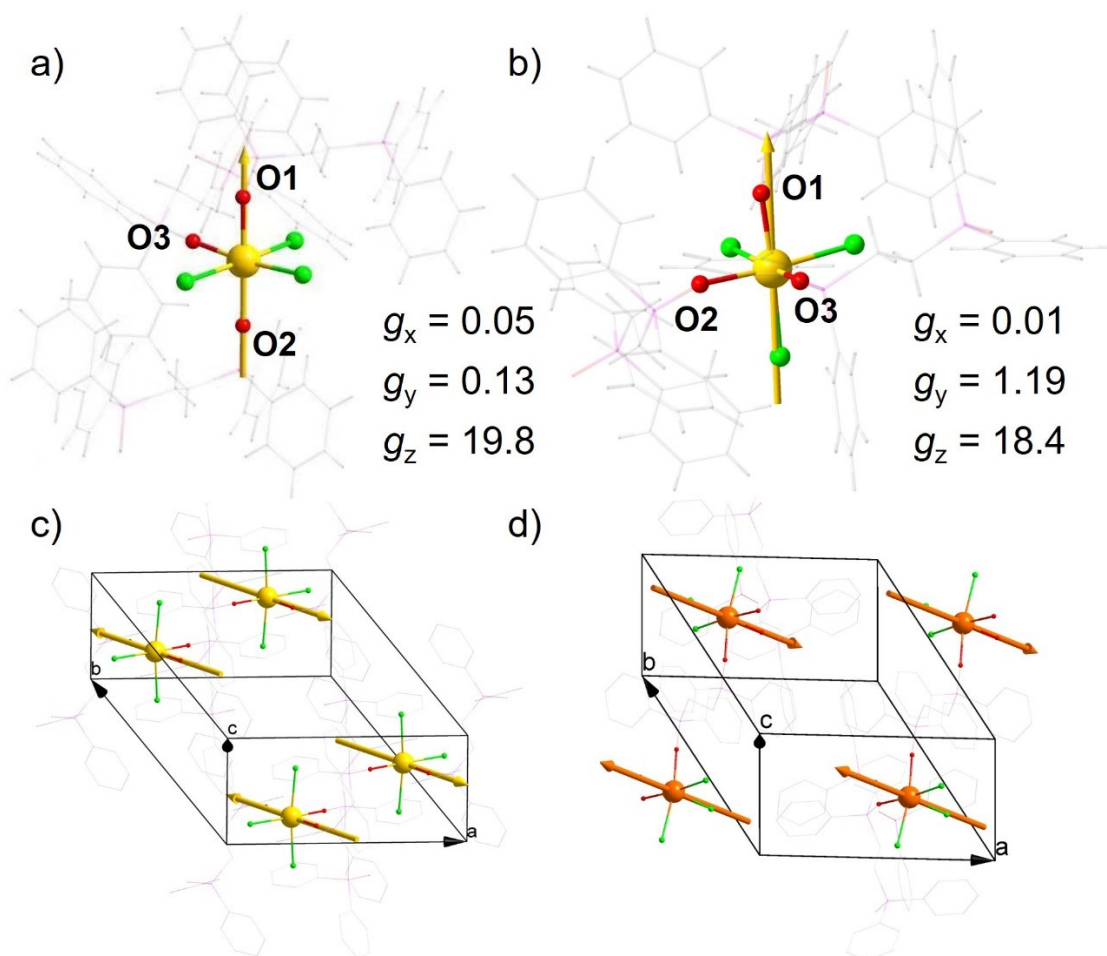


Figure S5. Orientation of the g_z -tensors of the ground state KDs for the Dy(III) ions in a single molecule (a for **1** and b for **2**) and in one unit cell (c for **1** and d for **2**). The ligands are transparented for clarity. The orientation of

the g_z -tensors for the Dy(III) ions in one unit cell is centrosymmetric because the nature the $P-1$ space group.

Table S4. CASSCF computed spin-free state energies for complex **1** and **2**.

Spin-free State Energies (cm ⁻¹) for 1	Spin-free State Energies (cm ⁻¹) for 2
0	0
15.53664	10.81137
98.70651	32.86216
238.46053	237.04643
395.22636	266.26262
401.88892	296.64506
441.11442	379.41457
491.84062	436.1085
550.68513	442.71902
581.22303	504.99708
629.90638	515.26477
7635.1648	7600.43584
7682.3591	7629.05551
7738.54179	7635.98922
7850.28529	7790.26221
7866.00108	7794.36233
7887.38704	7806.28239
7998.34004	7925.82981
34915.63105	34960.48018
35076.72608	35051.00587
35307.04338	35089.96672

Table S5. Calculated energy (cm⁻¹) and g -tensors of the lowest five Kramers doublets (KDs) for **1** and **2**.

KD	1		2		
	g -tensors	energy	g	g -tensors	energy
1	g_x	0.05064	0	g_x	0.0099
	g_y	0.13143		g_y	1.1875
	g_z	19.7715		g_z	18.412
2	g_x	0.8975	117.10	g_x	0.3308
	g_y	0.9673		g_y	1.2980
	g_z	18.785		g_z	17.298
3	g_x	1.5915	207.62	g_x	0.6254
	g_y	2.7529		g_y	1.2452
	g_z	13.632		g_z	17.792
4	g_x	3.4672	269.42	g_x	8.2308
	g_y	6.0692		g_y	7.6128
	g_z	12.704		g_z	5.9795
5	g_x	2.8717	382.32	g_x	3.1135
	g_y	4.0507		g_y	5.0209
	g_z	11.568		g_z	7.3012

Table S6. The transversal magnetic moment values of the lowest three KDs for **1** and **2**.

1		2	
1+ → 1-	0.0303	1+ → 1-	0.1996
1+ → 2+	0.8081	1+ → 2+	1.6294
1+ → 2-	0.3884	1+ → 2-	0.9323
1+ → 3+	1.5951	1+ → 3+	0.9856
1+ → 3-	0.0620	1+ → 3-	0.7514
2+ → 2-	2.3146	2+ → 2-	0.5022
2+ → 3+	1.3688	2+ → 3+	0.5333
2+ → 3-	1.1911	2+ → 3-	0.6324
3+ → 3-	0.7251	3+ → 3-	2.8876

Table S7. Wave functions with definite projection of the total moment $|m_J\rangle$ of the lowest three doublets for **1** and **2**.

KDs		Wave functions
1	1	98.3% $ \pm 15/2\rangle$
	2	44.0% $ \pm 1/2\rangle$ + 25.6% $ \pm 3/2\rangle$ + 14.0% $ \pm 5/2\rangle$ + 5.5% $ \pm 13/2\rangle$
	3	78.7% $ \pm 13/2\rangle$ + 7.1% $ \pm 5/2\rangle$ + 5.8% $ \pm 1/2\rangle$ + 5.0% $ \pm 3/2\rangle$
2	1	88.8% $ \pm 15/2\rangle$ + 4.0% $ \pm 7/2\rangle$
	2	42.2% $ \pm 1/2\rangle$ + 23.5% $ \pm 3/2\rangle$ + 13.0% $ \pm 5/2\rangle$ + 6.4% $ \pm 15/2\rangle$
	3	36.8% $ \pm 1/2\rangle$ + 29.1% $ \pm 3/2\rangle$ + 15.3% $ \pm 5/2\rangle$ + 7.4% $ \pm 13/2\rangle$

1. S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llonell and D. Avnir, Shape maps and polyhedral interconversion paths in transition metal chemistry, *Coord. Chem. Rev.*, 2005, **249**, 1693–1708.