Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

SMM behaviour of heterometallic dinuclear $Cu^{II}Ln^{III}$ (Ln = Tb and Dy) complexes derived from N_2O_3 donor unsymmetrical ligands

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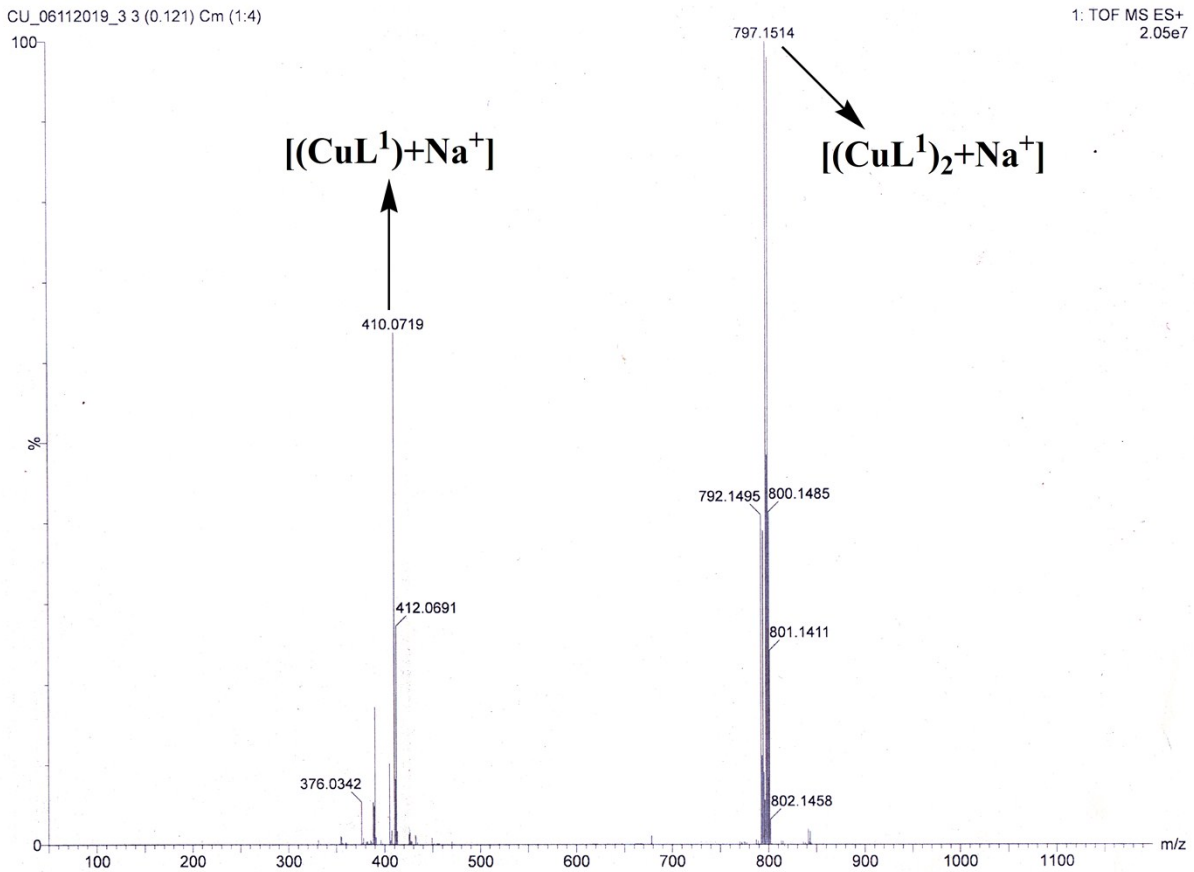

Fig. S1 ESI-MS spectrum of complex **1** (CuL^1).

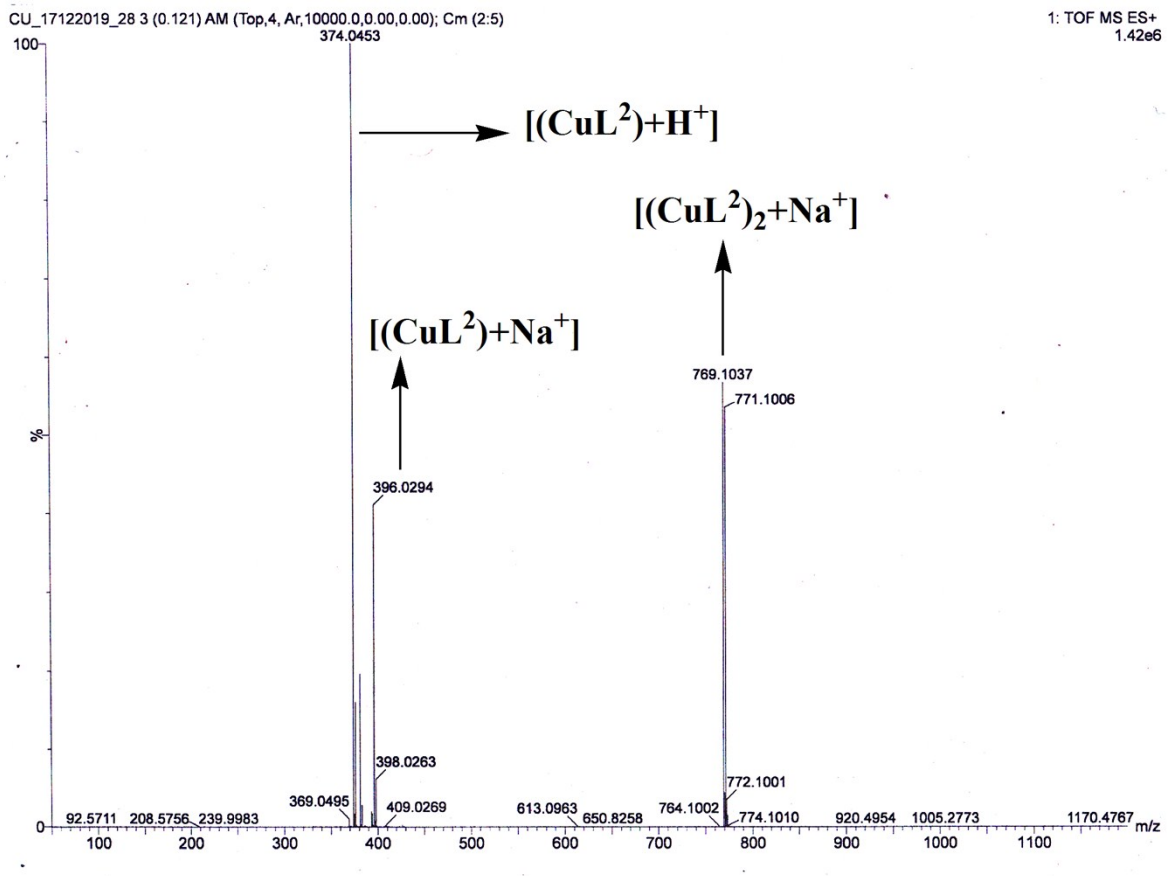

Fig. S2 ESI-MS spectrum of complex **2** (CuL^2).

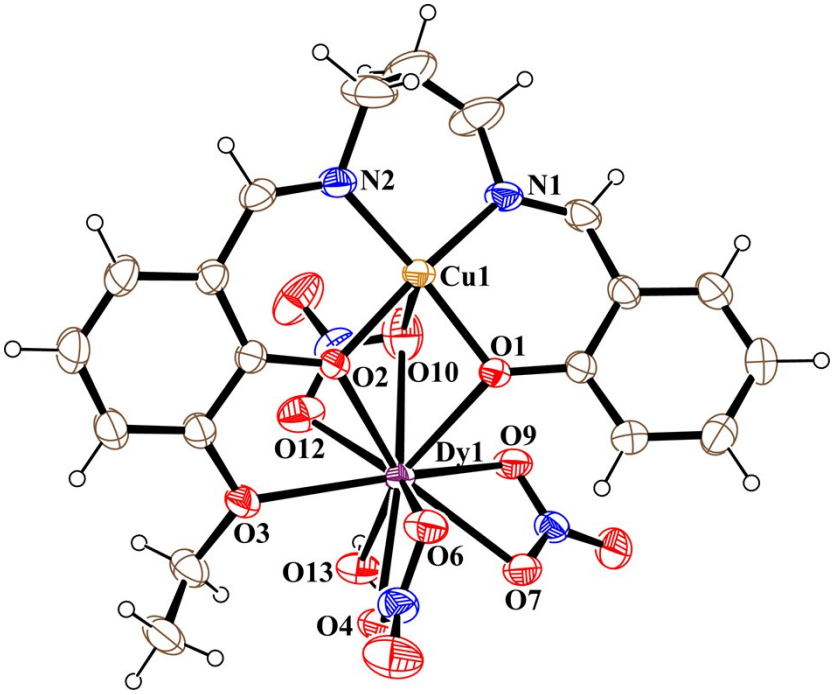

Fig. S3 ORTEP view of complex **4** with 30% ellipsoid probability. Solvent molecule, disordered atoms have been omitted for clarity.

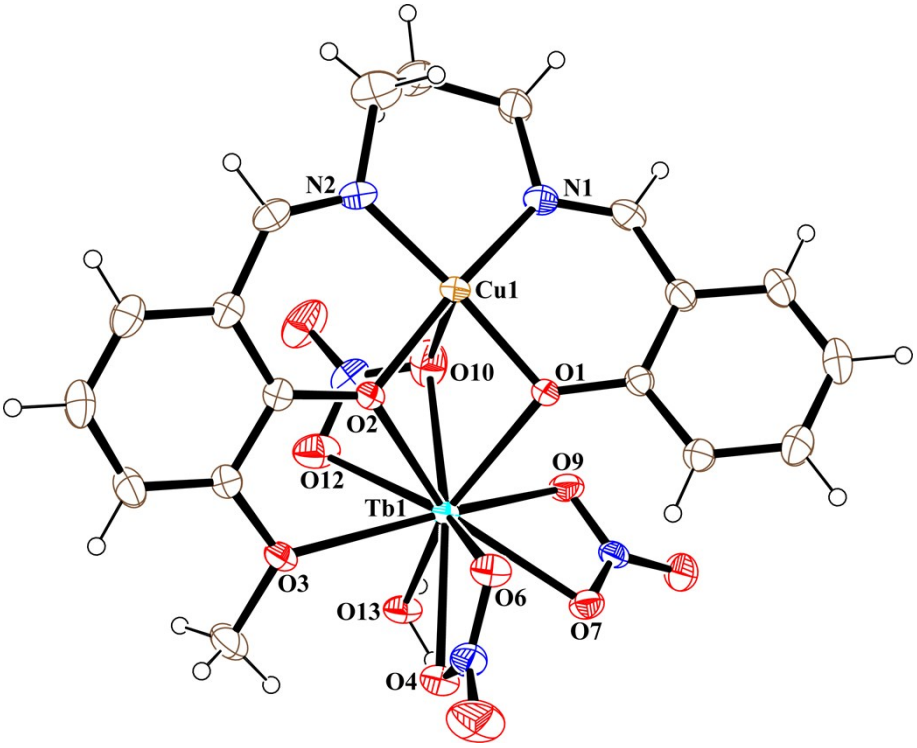

Fig. S4 ORTEP view of complex **5** with 30% ellipsoid probability. Solvent molecule, disordered atoms have been omitted for clarity.

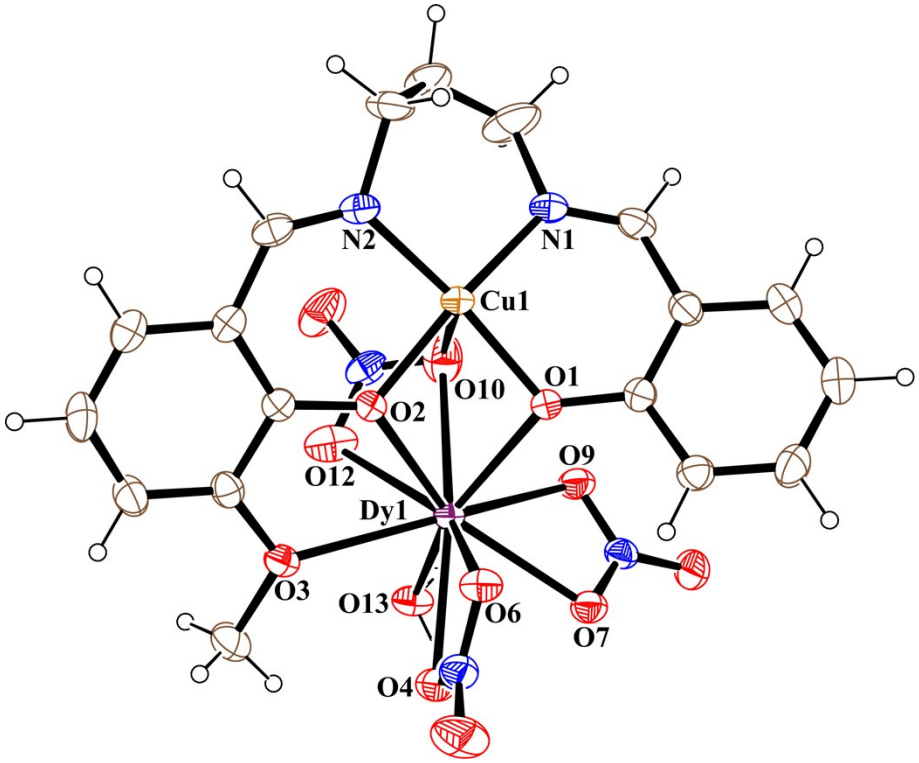

Fig. S5 ORTEP view of complex **6** with 30% ellipsoid probability. Solvent molecule, disordered atoms have been omitted for clarity.

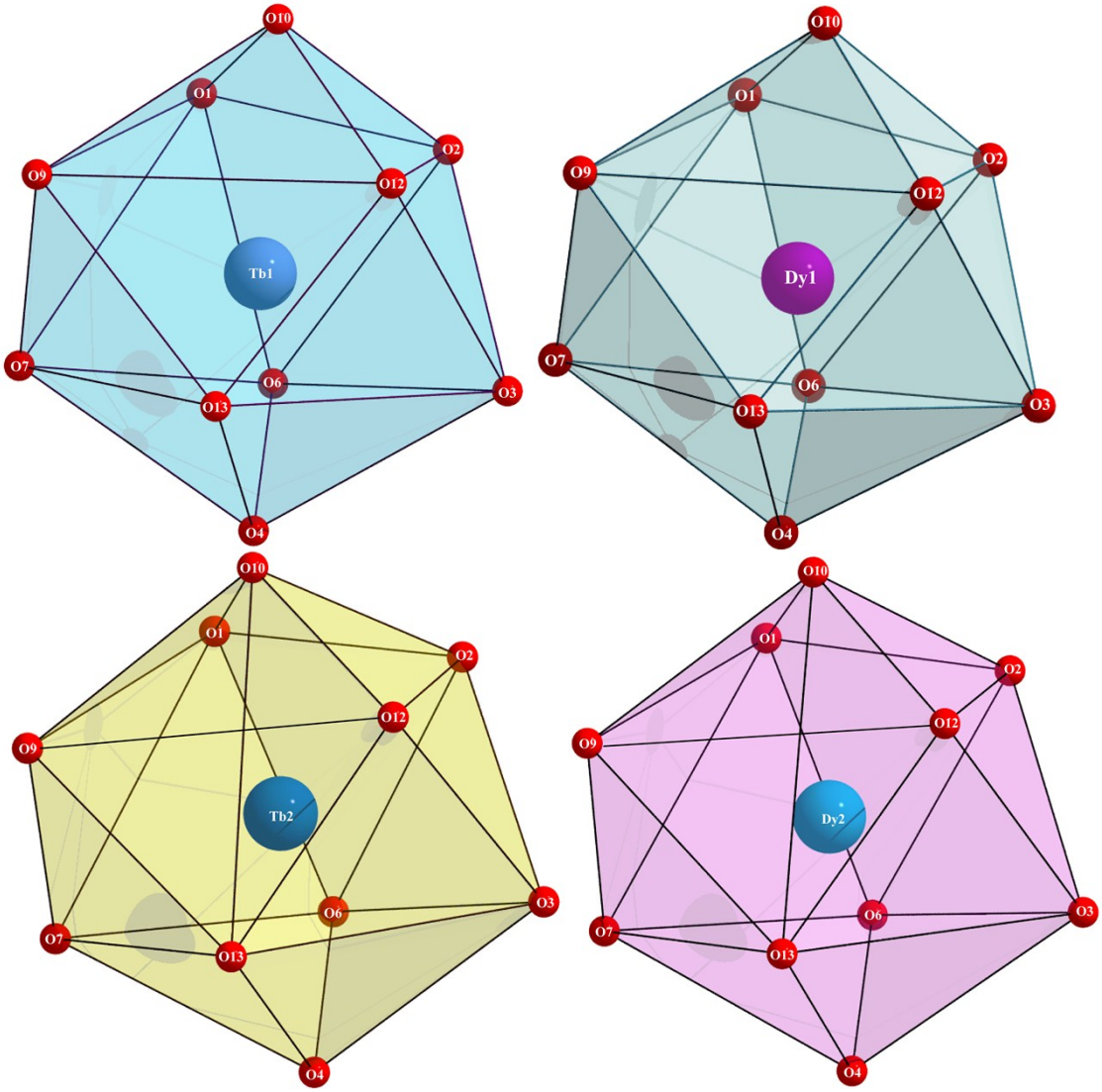

Fig. S6 Coordination polyhedra around the lanthanide centre for complexes **3**–**6**.

Table S1 Selected bond lengths (Å), bond angles (º) and torsion angles (º) of complex **3**.

	3 (M = Tb1)
M(1)–O(1)	2.398(3)
M(1)–O(2)	2.338(3)
M(1)–O(3A)	2.604(11)
M(1)–O(4)	2.527(3)
M(1)–O(6)	2.419(3)
M(1)–O(7)	2.489(3)
M(1)–O(9)	2.483(3)
M(1)–O(10)	2.665(4)

M(1)–O(12)	2.488(4)
M(1)–O(13)	2.389(4)
M(1)–O(3B)	2.700(3)
Cu(1)–O(1)	1.934(3)
Cu(1)–O(2)	1.931(3)
Cu(1)–O(10)	2.632(4)
Cu(1)–N(1)	1.943(4)
Cu(1)–N(2)	1.944(4)
O(1)–M(1)–O(2)	64.09(9)
O(1)–M(1)–O(3A)	124.3(3)
O(1)–M(1)–O(4)	123.25(11)
O(1)–M(1)–O(6)	74.77(11)
O(1)–M(1)–O(7)	88.11(10)
O(1)–M(1)–O(9)	74.82(10)
O(1)–M(1)–O(10)	67.75(12)
O(1)–M(1)–O(12)	112.70(13)
O(1)–M(1)–O(13)	152.19(12)
O(1)–M(1)–O(3B)	119.0(7)
O(2)–M(1)–O(3A)	62.9(3)
O(2)–M(1)–O(4)	115.32(11)
O(2)–M(1)–O(6)	80.46(10)
O(2)–M(1)–O(7)	148.66(10)
O(2)–M(1)–O(9)	126.77(10)
O(2)–M(1)–O(10)	69.16(11)
O(2)–M(1)–O(12)	75.00(11)
O(2)–M(1)–O(13)	136.21(11)
O(2)–M(1)–O(3B)	61.2(7)
O(3A)–M(1)–O(4)	68.7(3)
O(3A)–M(1)–O(6)	81.1(3)
O(3A)–M(1)–O(7)	134.7(3)

O(3A)–M(1)–O(9)	156.2(3)
O(3A)–M(1)–O(10)	106.9(3)
O(3A)–M(1)–O(12)	67.9(3)
O(3A)–M(1)–O(13)	82.4(3)
O(4)–M(1)–O(6)	51.39(11)
O(4)–M(1)–O(7)	66.88(11)
O(4)–M(1)–O(9)	115.06(11)
O(4)–M(1)–O(10)	168.94(13)
O(4)–M(1)–O(12)	121.87(13)
O(4)–M(1)–O(13)	70.38(12)
O(3B)–M(1)–O(4)	64.0(6)
O(6)–M(1)–O(7)	78.32(9)
O(6)–M(1)–O(9)	120.42(10)
O(6)–M(1)–O(10)	139.15(12)
O(6)–M(1)–O(12)	146.72(11)
O(6)–M(1)–O(13)	121.58(13)
O(3B)–M(1)–O(6)	71.8(7)
O(7)–M(1)–O(9)	50.79(10)
O(7)–M(1)–O(10)	115.11(11)
O(7)–M(1)–O(12)	132.51(11)
O(7)–M(1)–O(13)	75.02(12)
O(3B)–M(1)–O(7)	130.9(6)
O(9)–M(1)–O(10)	64.70(11)
O(9)–M(1)–O(12)	92.45(12)
O(9)–M(1)–O(13)	77.39(13)
O(3B)–M(1)–O(9)	164.8(7)
O(10)–M(1)–O(12)	48.18(15)
O(10)–M(1)–O(13)	99.27(12)
O(3B)–M(1)–O(10)	113.0(6)
O(12)–M(1)–O(13)	67.30(13)

O(3B)–M(1)–O(12)	76.8(7)
O(3B)–M(1)–O(13)	88.5(7)
O(1)–Cu(1)–O(2)	81.14(11)
O(1)–Cu(1)–O(10)	74.89(12)
O(1)–Cu(1)–N(1)	93.80(13)
O(1)–Cu(1)–N(2)	165.29(14)
O(2)–Cu(1)–O(10)	75.63(12)
O(2)–Cu(1)–N(1)	163.55(14)
O(2)–Cu(1)–N(2)	92.96(14)
O(10)–Cu(1)–N(1)	87.95(15)
O(10)–Cu(1)–N(2)	116.86(15)
N(1)–Cu(1)–N(2)	95.39(15)
M(1)–O(1)–Cu(1)	100.17(11)
M(1)–O(2)–Cu(1)	102.40(11)
M(1)–O(4)–N(3)	94.0(3)
M(1)–O(6)–N(3)	98.7(2)
M(1)–O(7)–N(4)	96.3(2)
M(1)–O(9)–N(4)	97.2(2)
M(1)–O(10)–Cu(1)	78.08(11)
M(1)–O(10)–N(5)	93.8(3)
Cu(1)–O(10)–N(5)	118.6(3)
M(1)–O(12)–N(5)	101.9(3)
Cu(1)–O(1)–O(2)–Ln(1)	147.1(1)

Table S2 Selected bond lengths (Å), bond angles (º) and torsion angles (º) of complexes **4**–**6**.

	4 (M = Dy1)	**5 (M = Tb2)**	**6 (M = Dy2)**
M(1)–O(1)	2.389(4)	2.385(2)	2.357(3)
M(1)–O(2)	2.325(3)	2.340(2)	2.315(3)
M(1)–O(3)	2.616(4)	2.618(2)	2.593(4)

M(1)–O(4)	2.520(4)	2.534(3)	2.508(3)
M(1)–O(6)	2.414(4)	2.419(2)	2.387(3)
M(1)–O(7)	2.479(4)	2.489(2)	2.461(3)
M(1)–O(9)	2.469(4)	2.509(2)	2.485(4)
M(1)–O(10)	2.694(6)	2.620(3)	2.615(5)
M(1)–O(12)	2.467(5)	2.519(3)	2.482(4)
M(1)–O(13)	2.389(4)	2.376(2)	2.351(4)
Cu(1)–O(1)	1.946(3)	1.941(2)	1.933(3)
Cu(1)–O(2)	1.930(3)	1.930(2)	1.919(3)
Cu(1)–O(10)	2.613(5)	2.668(3)	2.616(4)
Cu(1)–N(1)	1.948(4)	1.944(3)	1.934(4)
Cu(1)–N(2)	1.951(4)	1.952(3)	1.945(3)
O(1)–M(1)–O(2)	64.34(11)	64.01(7)	64.28(11)
O(1)–M(1)–O(3)	123.72(10)	122.72(7)	123.20(10)
O(1)–M(1)–O(4)	123.30(13)	123.20(7)	123.40(11)
O(1)–M(1)–O(6)	74.91(13)	74.98(7)	75.11(11)
O(1)–M(1)–O(7)	87.78(13)	87.64(7)	87.41(11)
O(1)–M(1)–O(9)	74.76(12)	73.65(7)	73.58(10)
O(1)–M(1)–O(10)	67.62(14)	69.35(9)	68.72(12)
O(1)–M(1)–O(12)	112.38(15)	113.15(9)	112.72(13)
O(1)–M(1)–O(13)	152.02(12)	150.83(8)	150.74(11)
O(2)–M(1)–O(3)	62.82(12)	62.69(7)	62.84(11)
O(2)–M(1)–O(4)	115.79(11)	115.94(8)	115.93(11)
O(2)–M(1)–O(6)	80.51(12)	80.88(7)	80.74(11)
O(2)–M(1)–O(7)	148.68(13)	147.77(8)	147.83(12)
O(2)–M(1)–O(9)	126.56(13)	126.51(7)	126.35(11)
O(2)–M(1)–O(10)	68.65(13)	69.54(7)	69.25(11)
O(2)–M(1)–O(12)	74.88(14)	72.53(8)	72.66(12)
O(2)–M(1)–O(13)	135.82(13)	135.89(8)	135.64(12)
O(3)–M(1)–O(4)	67.53(13)	66.90(7)	66.75(11)

O(3)–M(1)–O(6)	78.74(14)	77.47(7)	77.48(11)
O(3)–M(1)–O(7)	133.72(13)	132.53(7)	132.56(11)
O(3)–M(1)–O(9)	157.74(13)	161.08(7)	160.44(11)
O(3)–M(1)–O(10)	108.38(15)	108.84(8)	109.05(12)
O(3)–M(1)–O(12)	70.53(15)	68.26(8)	68.90(12)
O(3)–M(1)–O(13)	83.38(13)	85.43(8)	85.02(12)
O(4)–M(1)–O(6)	51.54(14)	51.25(8)	51.44(12)
O(4)–M(1)–O(7)	66.71(14)	65.86(7)	66.05(11)
O(4)–M(1)–O(9)	114.98(13)	114.04(7)	114.46(11)
O(4)–M(1)–O(10)	169.02(16)	167.35(9)	167.78(13)
O(4)–M(1)–O(12)	122.39(17)	120.62(9)	121.09(13)
O(4)–M(1)–O(13)	70.43(14)	72.14(8)	72.03(11)
O(6)–M(1)–O(7)	78.51(13)	76.95(7)	77.22(12)
O(6)–M(1)–O(9)	121.00(14)	118.64(7)	119.36(11)
O(6)–M(1)–O(10)	138.89(16)	140.87(9)	140.24(12)
O(6)–M(1)–O(12)	146.93(15)	143.44(8)	143.90(12)
O(6)–M(1)–O(13)	121.84(14)	123.19(7)	123.30(11)
O(7)–M(1)–O(9)	51.04(13)	50.60(7)	50.98(11)
O(7)–M(1)–O(10)	115.28(15)	116.27(8)	116.10(12)
O(7)–M(1)–O(12)	132.32(15)	136.66(8)	136.23(12)
O(7)–M(1)–O(13)	75.42(15)	76.29(8)	76.48(12)
O(9)–M(1)–O(10)	64.70(15)	65.84(8)	65.38(11)
O(9)–M(1)–O(12)	91.61(16)	97.48(8)	96.22(12)
O(9)–M(1)–O(13)	77.29(15)	77.36(8)	77.31(12)
O(10)–M(1)–O(12)	47.69(18)	48.54(10)	48.33(14)
O(10)–M(1)–O(13)	99.27(15)	95.93(8)	96.45(12)
O(12)–M(1)–O(13)	67.13(16)	67.43(8)	67.36(12)
O(1)–Cu(1)–O(2)	80.77(13)	80.66(9)	80.39(13)
O(1)–Cu(1)–O(10)	75.47(16)	74.67(9)	74.76(14)
O(1)–Cu(1)–N(1)	93.94(15)	93.13(11)	93.23(15)

O(1)–Cu(1)–N(2)	165.07(14)	167.16(10)	166.92(13)
O(2)–Cu(1)–O(10)	75.95(15)	74.30(9)	74.90(13)
O(2)–Cu(1)–N(1)	163.71(15)	164.18(10)	164.68(14)
O(2)–Cu(1)–N(2)	93.17(16)	92.76(12)	92.76(15)
O(10)–Cu(1)–N(1)	87.82(18)	90.06(11)	90.02(15)
O(10)–Cu(1)–N(2)	116.48(18)	114.32(11)	114.40(16)
N(1)–Cu(1)–N(2)	95.39(18)	95.92(13)	96.00(17)
M(1)–O(1)–Cu(1)	100.00(14)	100.44(9)	100.39(14)
M(1)–O(2)–Cu(1)	102.72(12)	102.36(9)	102.33(12)
M(1)–O(4)–N(3)	93.9(3)	93.77(18)	93.9(3)
M(1)–O(6)–N(3)	98.4(3)	98.89(18)	99.2(3)
M(1)–O(7)–N(4)	96.1(3)	97.10(17)	97.1(2)
M(1)–O(9)–N(4)	97.5(3)	96.74(16)	96.5(3)
M(1)–O(10)–Cu(1)	77.78(15)	78.24(8)	78.44(12)
M(1)–O(10)–N(5)	93.2(4)	95.3(2)	94.8(3)
Cu(1)–O(10)–N(5)	119.5(4)	114.8(19)	116.2(3)
M(1)–O(12)–N(5)	102.9(4)	99.4(2)	100.5(4)
Cu(1)–O(1)–O(2)–Ln(1)	147.2(1)	146.8(1)	146.7(1)

Table S3 SHAPE analysis for lanthanide centres in complexes **3**–**6**.

Geometry	Symmetry	Geometry (in words)	Complex **3**	Complex **4**	Complex **5**	Complex **6**
DP-10	D_{10h}	Decagon	34.101	33.874	33.718	33.741
EPY-10	C_{9v}	Enneagonal pyramid	23.093	23.253	22.861	22.898
OBPY-10	D_{8h}	Octagonal bipyramid	15.670	15.618	15.515	15.521
PPR-10	D_{5h}	Pentagonal prism	10.172	10.351	10.377	10.489
PAPR-10	D_{5d}	Pentagonal	9.180	9.254	9.246	9.321

		antiprism				
JBCCU-10	D_{4h}	Bicapped cube J15	8.501	8.261	9.191	9.017
JBCSAPR-10	D_{4d}	Bicapped square antiprism J17	4.252	4.015	4.746	4.543
JMBIC-10	C_{2v}	Metabidiminished icosahedron J62	5.926	5.961	5.969	5.977
JATDI-10	C_{3v}	Augmented tridiminished icosahedron J64	17.018	17.020	17.075	17.080
JSPC-10	C_{2v}	Sphenocorona J87	**3.066**	**3.118**	**2.888**	**2.844**
SDD-10	D_2	Staggered Dodecahedron (2:6:2)	4.840	5.004	4.753	4.804
TD-10	C_{2v}	Tetradecahedron (2:6:2)	5.065	4.926	4.966	4.979
HD-10	D_{4h}	Hexadecahedron (2:6:2) or (1:4:4:1)	6.571	6.481	7.137	7.046

Table S4 Geometrical features of hydrogen bonding interactions (distances (Å) and angles (°)) of Complexes **3**–**6**.

Complex	**D−H···A**	**D−H**	**H···A**	**D···A**	**∠D−H···A**
3	O13–H13A···O11	0.85	1.88	2.710(5)	167
	O13–H13B···O7	0.82	2.10	2.848(5)	151
4	O13–H13A···O4	0.85	2.56	3.353(12)	156
	O13–H13B···O11	0.89	1.82	2.705(7)	173
5	O13–H13A···O7	0.87	2.07	2.769(3)	137
	O13–H13B···O11	0.87	1.88	2.726(4)	163
6	O13–H13A···O7	0.87	2.04	2.760(5)	139
	O13–H13B···O11	0.87	1.88	2.710(6)	158

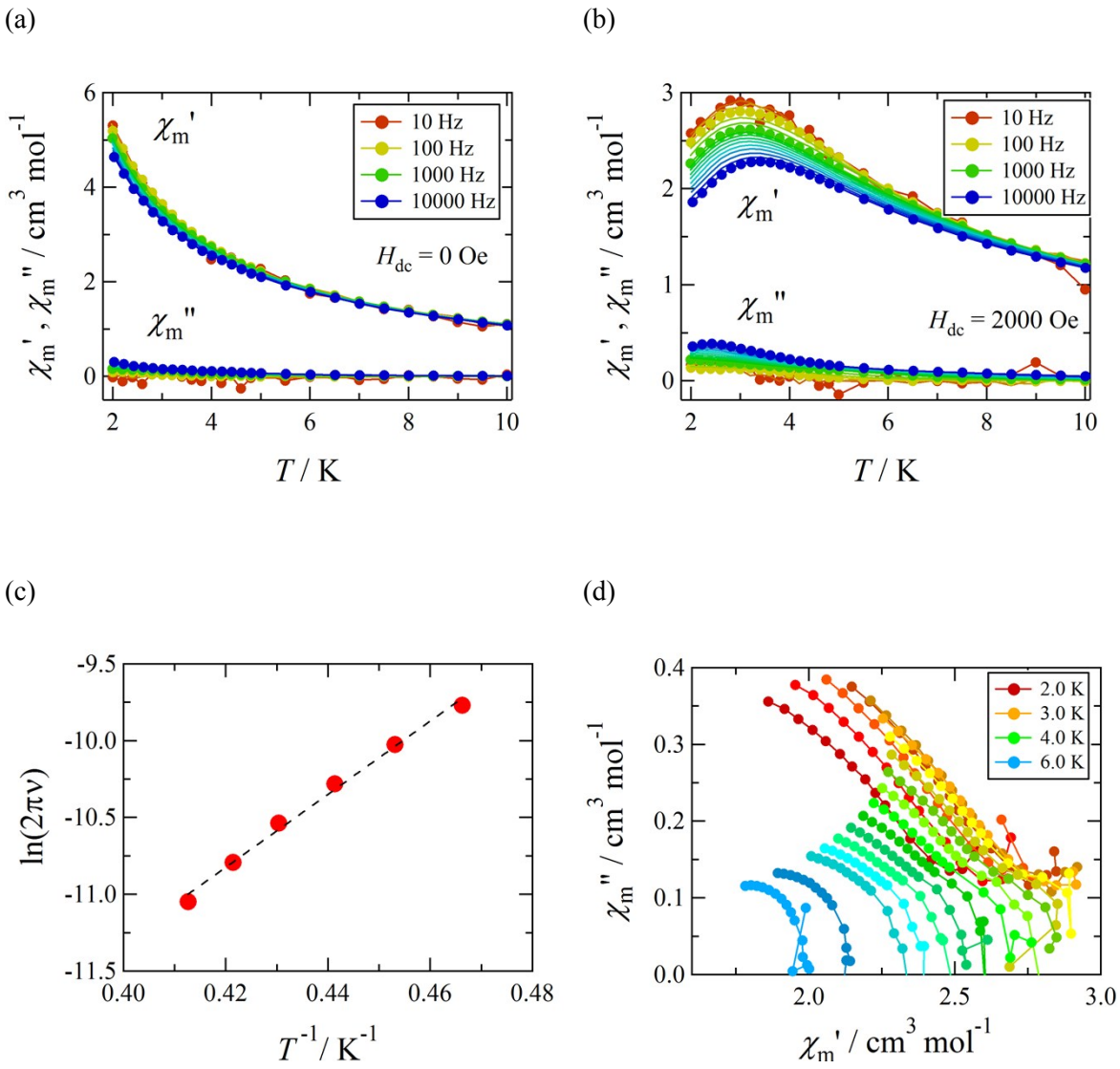

Fig. S7 AC magnetic susceptibility results in dc applied fields of 0 Oe (a) and 2000 Oe for **5** (b) Arrhenius plot (c) and Cole-Cole plot (d) from the 2000 Oe applied data for **5**.

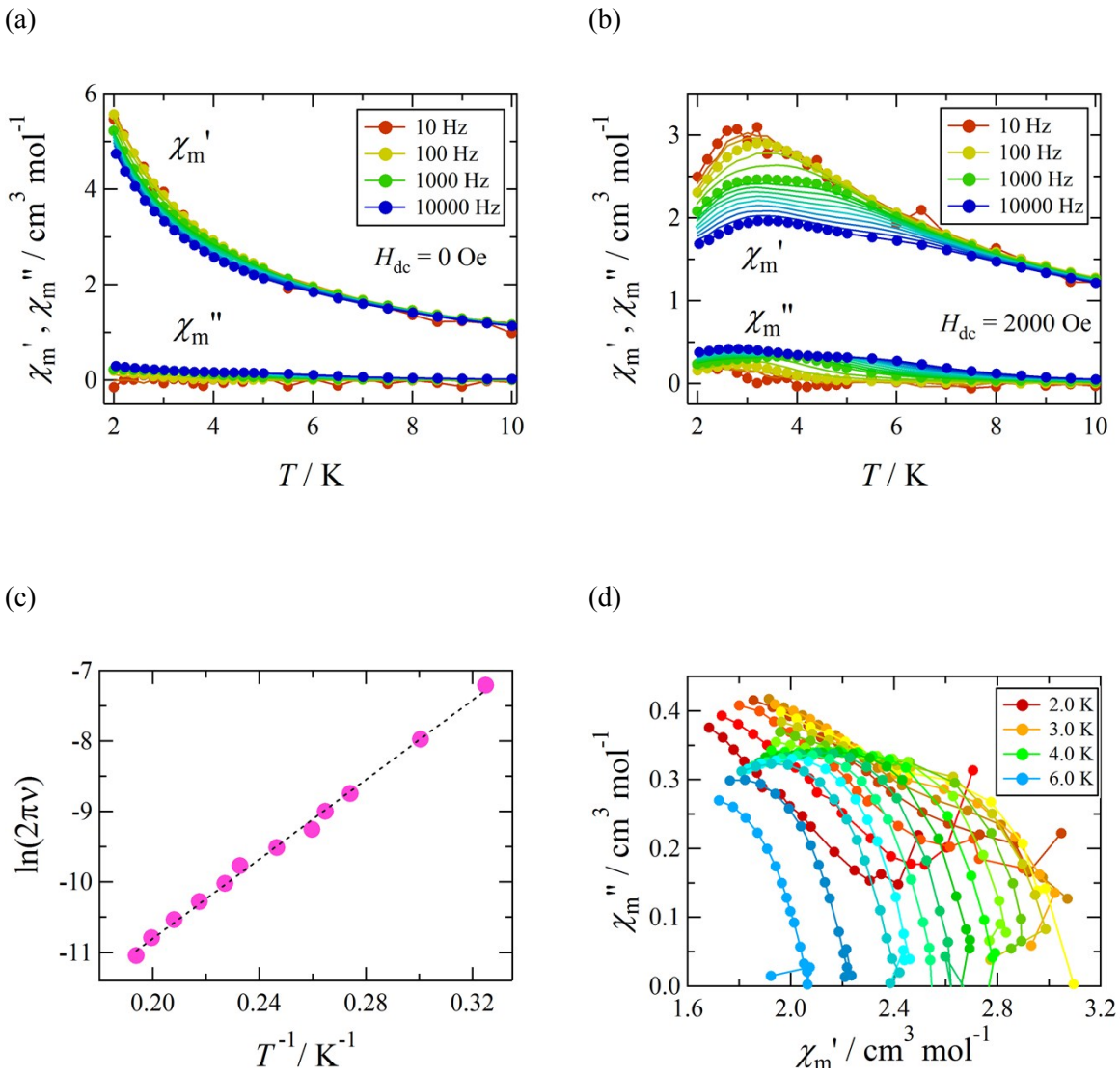

Fig. S8 AC magnetic susceptibility results in dc applied fields of 0 Oe (a) and 2000 Oe for **6** (b) Arrhenius plot (c) and Cole-Cole plot (d) from the 2000 Oe applied data for **6**.