New J. Chem.

Electronic Supplementary Information

Ligand-directed assembly of trinuclear and one-dimensional heterotrimetallic $Cu^{II}Ln^{III}Fe^{III}$ complexes. Unusual antiferromagnetic $Cu^{II}Fe^{III}$ coupling via cyano bridges

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Table S1 Selected bond distances (Å) and bond angles (°) for complexes **1-3**[a]

Complex	**1**	**2**	**3**	
Ln1–O1	2.330(3)	2.373(3)	Dy1–O1	2.311(3)
Ln1–O2	2.591(3)	2.552(3)	Dy1–O2	2.456(3)
Ln1–O3	2.335(3)	2.317(3)	Dy1–O3	2.453(3)
Ln1–O4	2.576(3)	2.587(3)	Dy1–O4	2.290(2)
Ln1–O2W	2.387(3)	2.353(3)	Dy1–O1W	2.355(3)
Ln1–O3W	2.371(3)	2.294(3)	Dy1–O2W	2.352(3)
Ln1–O4W	2.432(4)	2.411(4)	Dy1–O6W	2.398(3)
Ln1–N8	2.473(4)	2.461(4)	Dy1–N8	2.412(3)
Ln1–O1W’	2.753(10)	2.733(13)		
Cu1–O1	1.940(3)	1.917(3)	Cu1–O1	1.970(2)
Cu1–O3	1.952(3)	1.998(3)	Cu1–O4	1.976(3)
Cu1–N1	1.952(4)	1.940(5)	Cu1–N6	1.965(3)
Cu1–N6	1.962(4)	2.006(4)	Cu1–N7	1.982(4)
Cu1–O1W	2.683(16)	2.605(13)	Cu1–O1W	2.447(3)
Cu1–O1W’	2.714(7)	2.657(9)		
Fe1–C1	1.937(4)	1.935(4)	Fe1–C7	1.923(4)
Fe1–C9	1.940(5)	1.948(5)	Fe1–C14	1.939(4)
Fe1–C14	1.947(4)	1.953(4)	Fe1–C15	1.936(4)
Fe1–C16	1.941(4)	1.950(4)	Fe1–C20	1.940(4)
Fe1–C19	1.932(5)	1.929(5)	Fe1–C21	1.951(4)
Fe1–C23	1.937(5)	1.946(5)	Fe1–C22	1.948(4)
Fe1–C≡N	174.7(4) - 177.9(3)	174.9(4) – 177.9(4)	Fe1–C≡N	171.1(5) – 179.0(4)
Ln1–N8–C1	168.9(3)	169.6(3)	Dy1–N8–C7	155.3(3)
Cu1–O1–Ln1	106.10(12)	106.90(12)	Cu1–O1–Dy1	106.42(11)
Cu1–O3–Ln1	105.53(12)	106.27(12)	Cu1–O4–Dy1	106.99(11)

[a] In complexes **1** and **2**, the atoms O1W and O1W’ are crystallographically disordered, and their occupancies are refined.

Table S2 Selected bond distances (Å) and bond angles (°) for complexes **4-7**.

Complex	**4**	**5**	**6**	**7**
Ln1-O1	2.386(8)	2.379(5)	2.358(5)	2.350(3)
Ln1-O5	2.343(8)	2.338(4)	2.319(4)	2.307(3)
Ln1-O2	2.376(7)	2.364(5)	2.335(4)	2.325(3)
Ln1-O3	2.637(9)	2.624(5)	2.617(5)	2.621(3)
Ln1-O4	2.549(8)	2.530(5)	2.526(5)	2.502(3)
Ln1-O7	2.573(8)	2.551(5)	2.551(5)	2.530(3)
Ln1-O6	2.597(8)	2.590(5)	2.575(5)	2.588(3)
Ln1-OW1	2.354(8)	2.360(6)	2.327(5)	2.287(3)
Ln1-O8	2.366(8)	2.368(5)	2.348(5)	2.345(3)
Cu2-O5	2.011(8)	1.994(5)	1.999(5)	2.000(3)
Cu2-N1	2.004(10)	1.983(7)	1.988(6)	1.992(3)
Cu2-N2	1.988(10)	1.977(6)	1.969(6)	1.986(3)
Cu2-O8	1.964(8)	1.962(4)	1.964(4)	1.967(3)
Cu2-N10#1	2.167(12)	2.163(8)	2.180(7)	2.193(4)
Cu1-O1	1.992(7)	1.977(5)	1.978(5)	1.978(3)
Cu1-O2	2.001(8)	1.993(5)	1.997(5)	1.997(3)
Cu1-N3	1.981(10)	1.990(6)	1.976(6)	1.988(3)
Cu1-N8	2.158(10)	2.201(7)	2.178(6)	2.182(3)
Cu1-N9	1.983(10)	1.993(6)	1.976(6)	1.987(3)
Fe–C(cyano)	1.919(12) - 1.959(14)	1.904(11) - 1.939(10)	1.914(11) - 1.937(9)	1.921(4) - 1.947(4)
Cu–N≡C	150.4(10), 149.2(11)	151.3(7), 149.2(7)	152.8(6), 149.7(7)	150.0(3), 145.9(3)
Fe–C≡N	172.7(16) - 179.1(13)	175.9(11) - 178.8(9)	175.8(8) - 179.0(8)	175.5(4) - 178.9(5)
Cu1–O1–Ln1	106.9(3)	107.5(2)	107.2(2)	107.22(11)
Cu1–O2–Ln1	107.0(3)	107.5(2)	107.46(19)	107.54(11)
Cu2–O5–Ln1	107.0(4)	107.8(2)	107.4(2)	107.51(11)
Cu2–O8–Ln1	107.8(3)	107.8(2)	107.6(2)	107.20(12)

Table S3 Magnetic data for complexes **1-6**.

	$^{2S+1}L_J$ (Ln^{III})	Theoretical $\chi_m T$ (cm^3 K mol^{-1})	Experimental $\chi_m T$ (cm^3 K mol^{-1})	Weiss constant (K)
CuFeGd (**1**)	$^8S_{7/2}$	8.64	9.19	1.47
CuFeTb (**2**)	$^7F_6$	12.58	12.81	1.30
CuFeDy (**3**)	$^6H_{15/2}$	14.93	16.09	14.72
Cu_2FeGd (**4**)	$^8S_{7/2}$	9.01	9.96	5.55
Cu_2FeTb (**5**)	$^7F_6$	12.95	13.97	38.96
Cu_2FeDy (**6**)	$^6H_{15/2}$	15.30	16.97	53.20

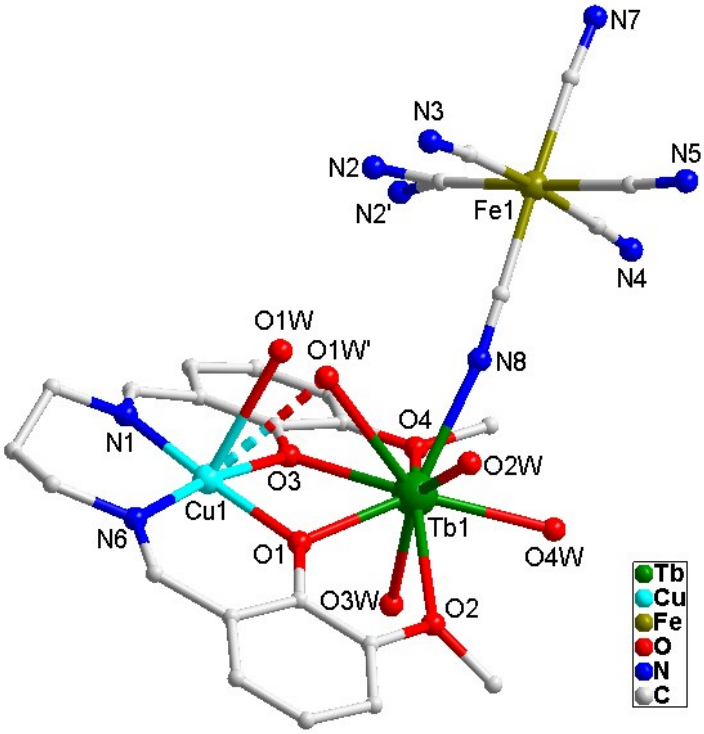

Fig. S1. Crystal structure of complex **2**. O1W and O1W' are disordered. Hydrogen and solvent have been omitted for clarity.

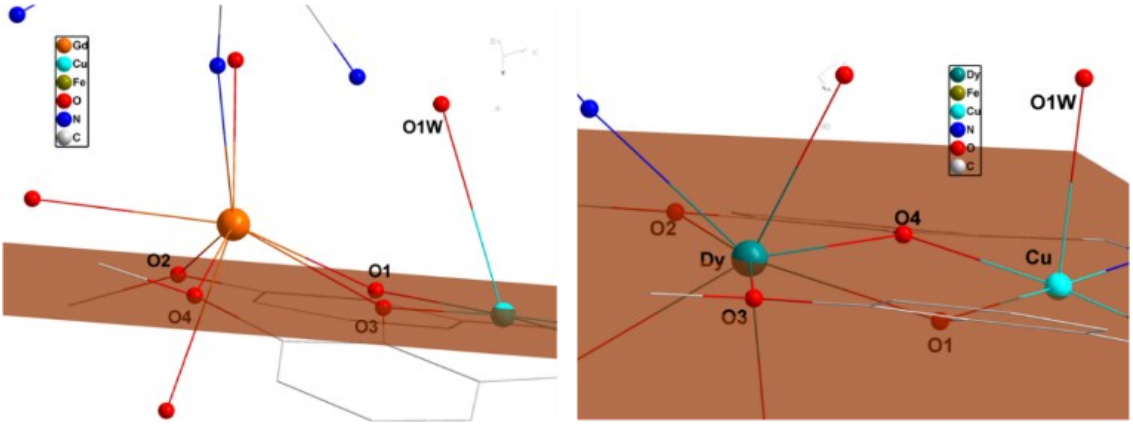

Fig. S2. The relative positions of lanthanide ion deviate from O1O2O3O4 plane in complexes **1** (left) and **3** (right).

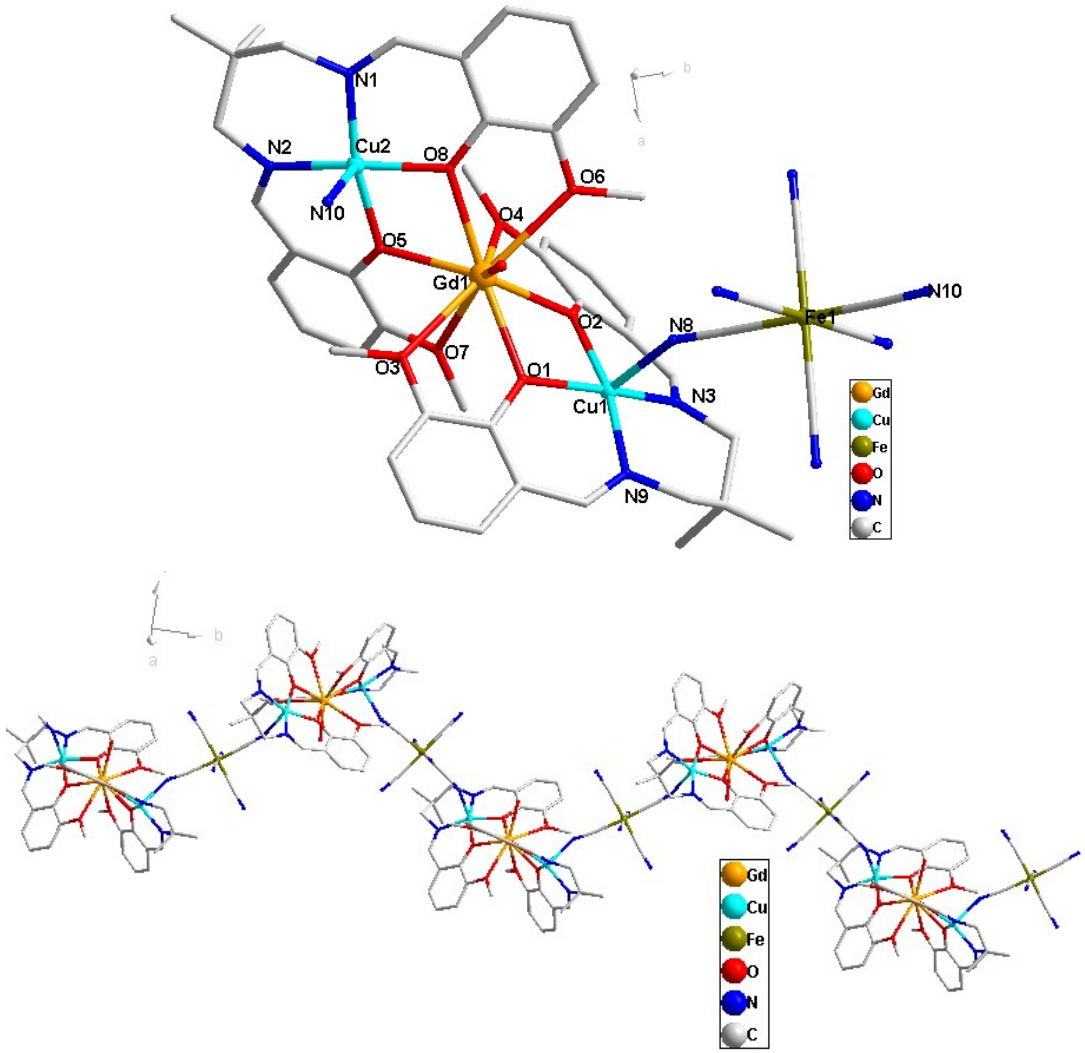

Fig. S3. Crystal structure of complex **4** (above) and the 1D zig-zag chain parallel with b axis (below). Hydrogen and solvent have been omitted for clarity.

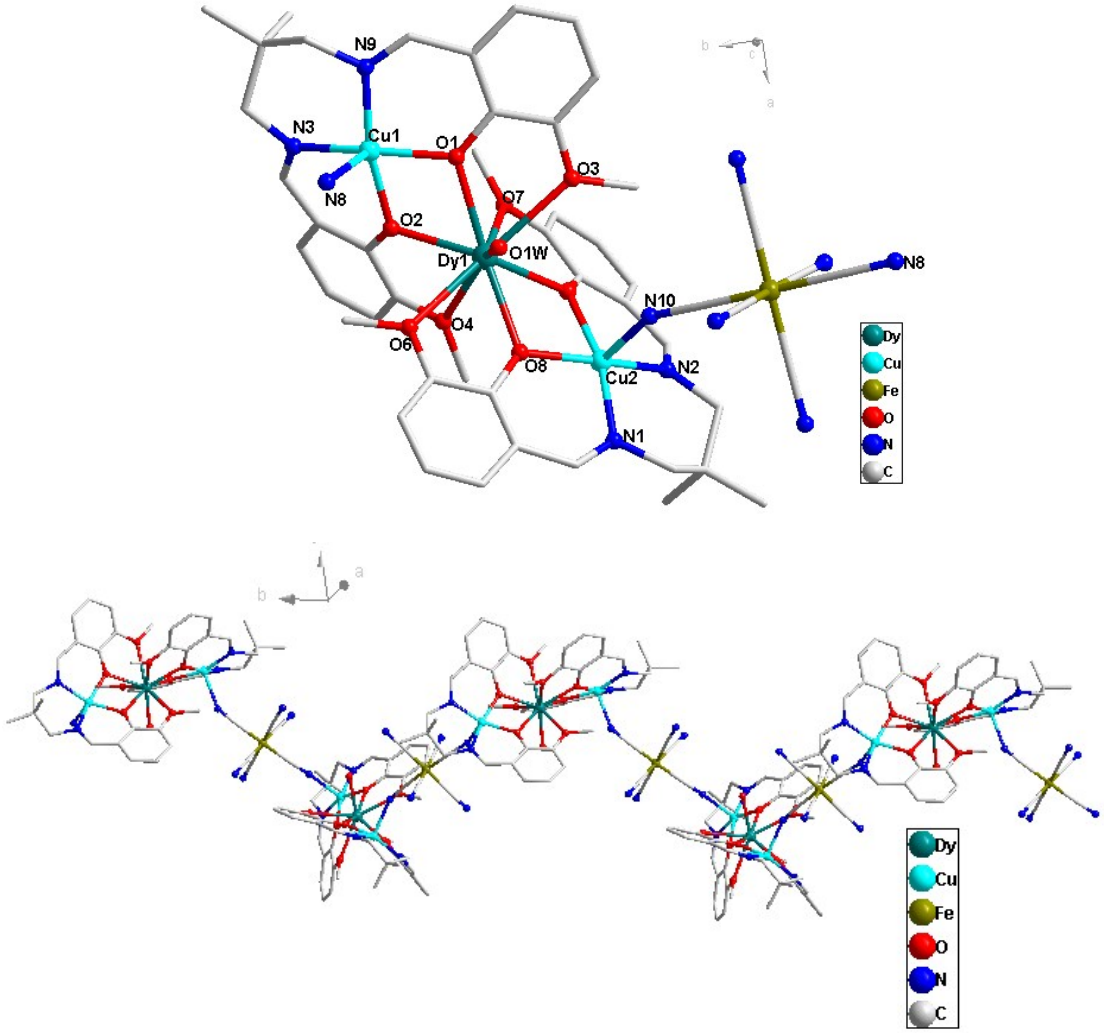

Fig. S4. Crystal structure of complex **6** (above) and the 1D zig-zag chain (below). Hydrogen and solvent have been omitted for clarity.

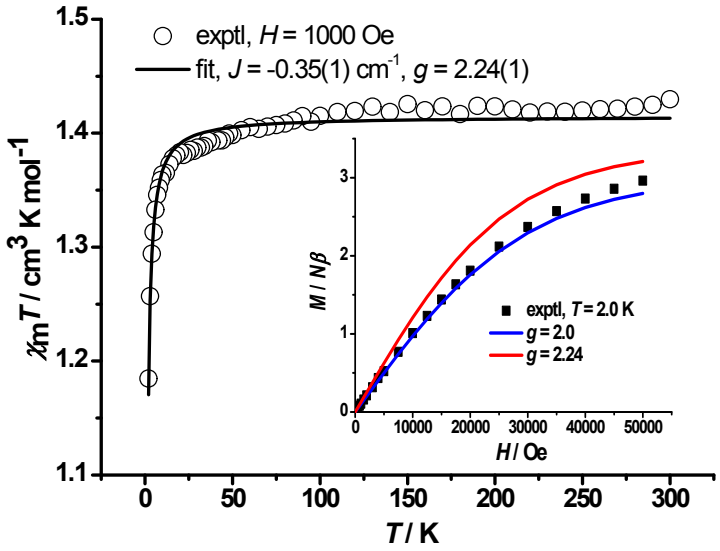

Fig. S5. Temperature dependence of $\chi_m T$ for complex **7**. The solid lines indicate the best fitting results. Inset: Field dependence of magnetization for complex **7** at 2.0 K.

Table S4 Structural and magnetic data for complexes with the CuO_2Gd bridging mode

complexes	$2J_{CuGd}/cm^{-1}$	Gd-O_2-Cu/°	Cu-O-Gd/°	Gd-Cu/Å	Ref
Complex **1**	4.78	19.74	105.82	3.421	/
Complex **4**	5.89	18.06	107.18	3.515	/
$\{[Cu(L^{\alpha\text{-}Me})]_2Gd(H_2O)(NO_3)_2\}NO_3$	3.62	38.0	97.1,97.9	3.212	20a
$[Cu(H_2L)(CH_3OH)]_2Gd(DMF)Fe(CN)_6$	15.94	3.61	107.04	3.450	20b
$[Cu(H_2L)(CH_3OH)]_2Gd(DMF)Fe(CN)_6$	9.08	10.35	108.06	3.442	20b
$Gd(hfa)_3Cu(salen)$	0.4	33.78	94.38	3.215	24d
$Cu(salabza)Gd(hfac)_3$	0.8	34.28	95.8	3.248	24e
$Cu(salen)Gd(pta)_3$	1.21	23.72	97.5	3.288	24f
$Cu(acacen)Gd(hfa)_3$	1.25	25.53	97.8	3.301	24f
$Gd(hfa)_3Cu(salen)(Meim)$	1.42	27.72	96.7	3.252	24d
$Cu(acacen)Gd(pta)_3$	1.47	29.81	96.3	3.274	24f
$Cu(prpen)Gd(hfac)_3$	1.91	30.78	97.1	3.252	24g
$CuGd(hmp)_2(NO_3)_3(H_2O)_2$	3.36	15.32	102.4	3.246	24h
$[CuGd(ems)(NO_3)\cdot 3H_2O]Cu(ems)$	3.76	17.77	99.5	3.306	24i
$L^aCu(C_3H_6O)Gd(NO_3)_3$	4.8	13.52	107.8	3.523	24j
$L^bCuGd(NO_3)_3$	4.98	14.12	103.6	3.443	24k
$L^cCu(H_2O)Gd(NCS)_3\cdot Me_2CO$	5.5	15.44	106.5	3.454	24l
$L^dCuGd(NO_3)_3\cdot Me_2CO$	5.6	9.60	109.4	3.425	24m
$L^aCu(MeOH)Gd(NO_3)_3$	6.8	10.00	107.8	3.484	24j
$L^eCuGd(NO_3)_3\cdot Me_2CO$	7.0	10.15	106.7	3.428	24n
$L^fCuGd(NO_3)_3\cdot Me_2CO$	7.3	12.7	107.1	3.475	20c
$L^1CuGd(NO_3)_3\cdot Me_2CO$	7.4	10.18	107.6	3.475	24o
$L^gCuGd(NO_3)_3$	7.6	9.22	108.0	3.499	24p
$L^hCuGd(NO_3)_3$	8.08	3.36	105.2	3.400	24q
$L^iCuGd(NO_3)_3\cdot Me_2CO$	8.63	11.11	107.0	3.454	24r
$L^iCuGd(NO_3)(N(CN)_2)_2\cdot Me_2CO$	8.50	3.27	107.67	3.481	24r
$[L^2CuCl_2Gd(H_2O)_4]Cl\cdot 2H_2O$	10.1	1.38	108.8	3.512	24s
$L^jCuGd(NO_3)_3$	10.8	7.1	106.6	3.449	24t
$L^kCuGd(NO_3)_3$	12.6	2.10	105.0	3.401	24t
$[L^m{}_2Cu_2Gd_2(NO_3)_6(H_2O)_2]$	4.5	20.44	103.0	3.395	24c
$[\{CuL^1\}Gd(H_2O)_3\{Co(CN)_6\}]$	7.24	10.19	106.52	3.508	6b
$[(bipy)W(CN)_6Cu(L^1)Gd(NO_3)_2]_3$	8.67	12.89	107.06	3.466	12c
$[\{CuL\}_2Gd(TCNQ)_2]\cdot TCNQ$	7.7	17.13	107.24	3.477	24u
$[GdCu_3L^n(hfac)_3]^-$	0.86	39.08	96.09	3.393	24v
$L^1CuGd(hfac)_2(ac)$	2.6	24.47	104.49	3.437	24a
$Gd_6Cu_3(OH)(pdm)_3(O_2C^tBu)_9(CO_3)_4$	0.8	24.34	102.78	3.491	24x
$[CuLn(L^p)(NO_3)_2(H_2O)_3MeOH]NO_3$	7.89	2.52	107.94	3.539	24y
$[Cu(valaepy)_2Gd(O_2NO)_3(H_2O)]$	4.94	2.52	108.67	3.506	24b
$GdCuL^qCl_3(CH_3OH)_2$	11.2	15.39	/	3.409	24w
$[Gd_2Cu_4L^r{}_4Cl_2(OH)](PF_6)_3$	9.8	23.36	106.30	3.479	24w

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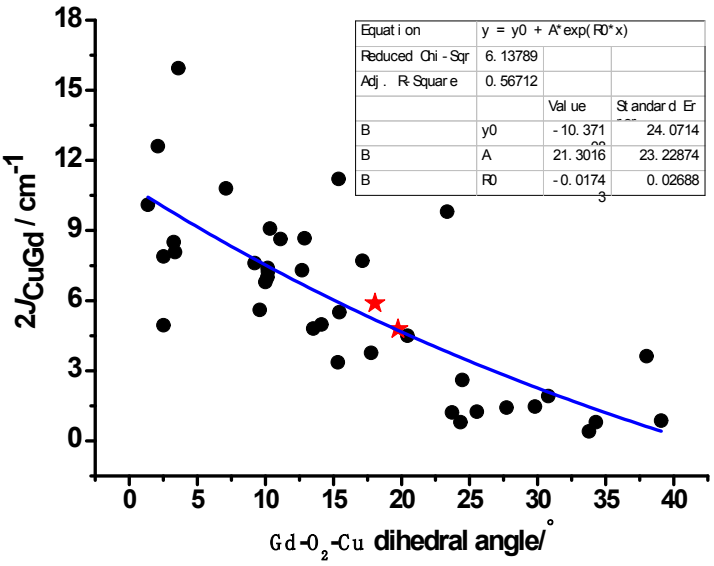

Fig. S6. Magneto-structural correlationship for bis-phenoxo-bridged Cu(II)-Gd(III) complexes. The solid line represents the exponential fit to the experimental data. The pentagrams correspond to complexes **1** and **4**.

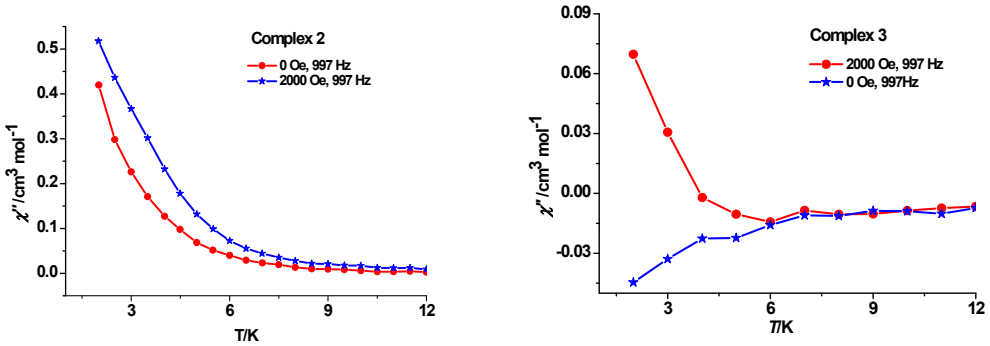

Fig. S7. Temperature dependence of the out-of-phase (χ''_m) parameters for complexes **2** (left) and **3** (right) at 997 Hz.

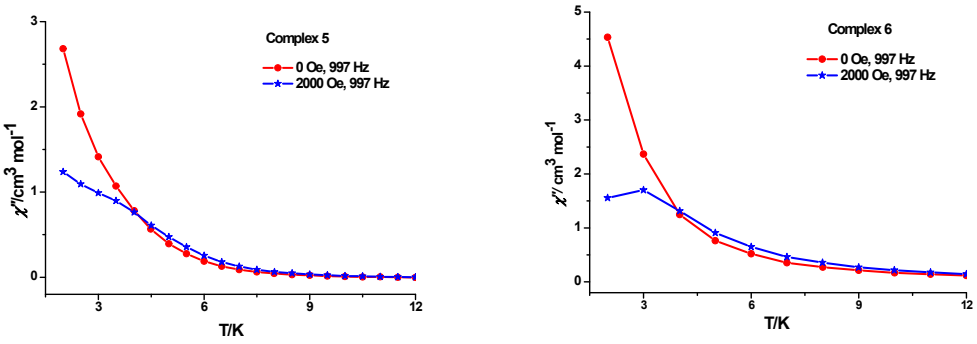

Fig. S8. Temperature dependence of the out-of-phase (χ''_m) parameters for complexes **5** (left) and **6** (right) at 997 Hz.

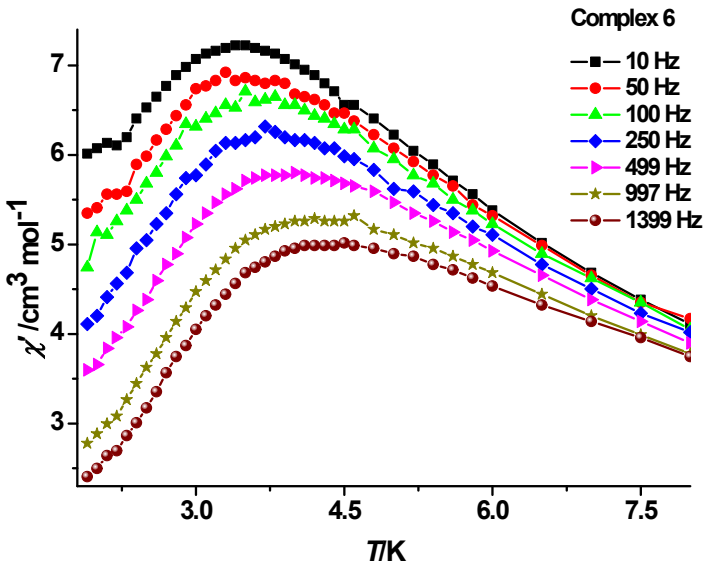

Fig. S9. Temperature dependence of the out-of-phase (χ'_m) parameters for complex **6**.

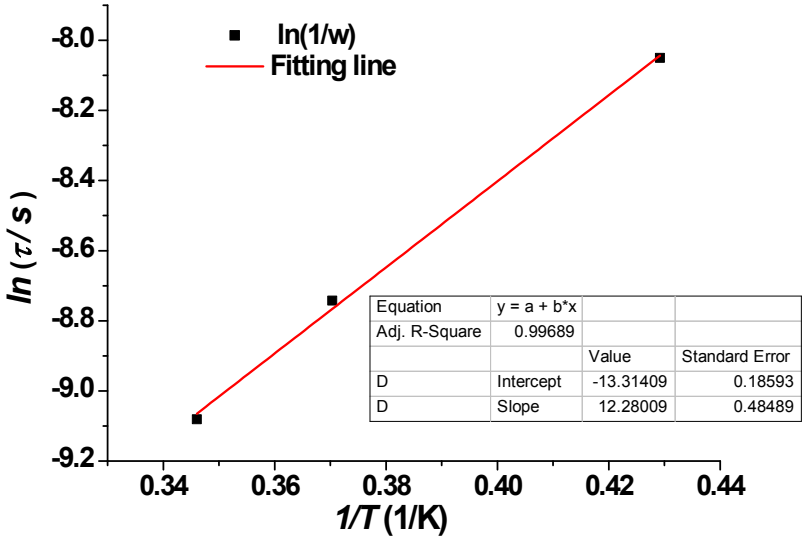

Fig. S10. The ln(τ) vs. T^{-1} plots based on the Arrhenius relationship for complex **6**.