Electronic Supplementary Information

Metallocyclic $Ni_4Ln_2M_2$ single-molecule magnets

Mei-Jiao Liu,[a] Kong-Qiu Hu,[a] Cai-Ming Liu,[b] Ai-Li Cui[a] and Hui-Zhong Kou[a,*]
[a] Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.
Email: kouhz@mail.tsinghua.edu.cn
[b] Beijing National Laboratory for Molecular Sciences, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

Table S1. Selected bond distances (Å) and bond angles (°) for complexes **1**and **3-9**.

Complex	**1 (Ln = Dy, M = Cr)**	**3 (Ln = Dy, M = Co)**	**4 (Ln = Tb, M = Cr)**	**5 (Ln = Tb, M = Fe)**	**6 (Ln = Gd, M = Cr)**	**7 (Ln = Gd, M = Fe)**
Ln1-O1	2.329(5)	2.330(3)	2.337(4)	2.338(5)	2.349(6)	2.362(7)
Ln1-O2	2.379(5)	2.388(3)	2.391(4)	2.409(5)	2.400(6)	2.415(4)
Ln1-O3	2.516(4)	2.521(3)	2.525(4)	2.531(5)	2.532(5)	2.527(6)
Ln1-O4	2.498(5)	2.500(3)	2.511 (5)	2.509(5)	2.520(5)	2.509(6)
Ln1-O5	2.316(3)	2.341(3)	2.343(4)	2.356(5)	2.349(5)	2.357(4)
Ln1-O6	2.384(5)	2.401(3)	2.399(4)	2.421(5)	2.388(5)	2.398(5)
Ln1-O7	2.525(4)	2.534(3)	2.538(4)	2.542(5)	2.532(5)	2.556(5)
Ln1-O8	2.495(5)	2.504(4)	2.508(4)	2.515(5)	2.515(6)	2.505(5)
Ln1-O1W	2.309(6)	2.311(4)	2.327(5)	2.336(6)	2.359(6)	2.323(6)
Ni1-N9	2.028(7)	2.024(5)	1.992(6)	2.001(7)	2.014(8)	2.021(6)
Ni1-N10	2.027(6)	2.026(4)	2.026(6)	2.030(8)	2.031(7)	2.018(6)
Ni1-O5	2.038(4)	2.017(4)	2.032(6)	2.024(7)	2.030(7)	2.018(5)
Ni1-O6	2.012(4)	2.020(3)	2.029(4)	2.031(5)	2.018(5)	2.012(5)
Ni2-N7	2.068(7)	2.031(4)	2.011(7)	2.012(7)	2.022(8)	2.012(5)
Ni2-N8	2.007(7)	2.006(5)	2.020(5)	2.043(6)	2.008(8)	2.015(7)
Ni2-O1	2.022(5)	2.031(3)	2.014(4)	2.018(5)	2.042(6)	2.018(4)
Ni2-O2	2.012(5)	2.011(3)	1.977(6)	2.024(7)	2.015(6)	2.005(7)
Ni1-N_{cyano}	1.993(7)	1.996(4)	2.008(4)	2.014(5)	1.992(8)	1.99(1)
Ni2-N_{cyano}	2.003(8)	2.002(4)	2.054(7)	2.051(7)	2.001(8)	1.985(6)
M-C_{cyano}	2.047(7)-2.077(8)	1.888(5)-1.909(6)	2.047(6)-2.072(7)	1.937(8)-1.967(9)	2.036(8)-2.08(1)	1.923(5)-1.97(1)
C≡N-Ni	164.6(8)-163.9(7)	162.7(4)-163.1(4)	165.2(6)-166.8(5)	162.4(6)-164.1(6)	166.4(7)-166.8(7)	159.8(7)-164.3(7)
M-C≡N	172.5(8)-177.6(9)	175.5(4)-179.5(5)	174.0(6)-178.2(8)	175.0(7)-179.6(8)	169.7(7)-177.7(9)	175.5(7)-179.3(8)

Continuing

Complex	**8** **(Ln = Y, M = Cr)**	**9** **(Ln = Y, M = Fe)**
Ln1-O1	2.308(3)	2.321(3)
Ln1-O2	2.372(3)	2.382(3)
Ln1-O3	2.484(3)	2.515(3)
Ln1-O4	2.509(3)	2.485(3)
Ln1-O5	2.366(3)	2.367(3)
Ln1-O6	2.310(3)	2.315(4)
Ln1-O7	2.516(3)	2.538(3)
Ln1-O8	2.480(3)	2.471(3)
Ln1-O1W	2.304(4)	2.292(3)
Ni1-N7	2.005(4)	2.006(4)
Ni1-N8	2.031(4)	2.017(4)
Ni1-O1	2.034(3)	2.024(3)
Ni1-O2	2.009(3)	2.002(4)
Ni2-N9	2.019(4)	2.022(5)
Ni2-N10	2.012(4)	2.016(4)
Ni2-O5	2.014(3)	2.012(4)
Ni2-O6	2.021(3)	2.010(3)
Ni1-N_{cyano}	1.993(5)	1.995(5)
Ni2-N_{cyano}	1.985(5)	1.976(5)
M-C_{cyano}	2.031(5)-2.070(6)	1.920(6)-1.959(7)
C≡N-Ni	165.8(4)-165.8(4)	159.7(5)-163.4(5)
M-C≡N	172.1(4)-178.0(5)	176.1(5)-179.2(5)

Table S2. Selected bond distances (Å) and bond angles (°) for complex **2**.

Dy1-O9	2.330(5)	Dy2-O1	2.346(6)
Dy1-O10	2.525(5)	Dy2-O2	2.379(6)
Dy1-O11	2.362(6)	Dy2-O3	2.506(5)
Dy1-O12	2.392(6)	Dy2-O4	2.539(6)
Dy1-O13	2.347(6)	Dy2-O5	2.338(5)
Dy1-O14	2.553(6)	Dy2-O6	2.357(6)
Dy1-O15	2.545(5)	Dy2-O7	2.523(5)
Dy1-O16	2.525(6)	Dy2-O8	2.500(5)
Dy1-O1W	2.295(5)	Dy2-O2W	2.296(5)
Ni1-O9	2.015(6)	Ni3-O5	2.013(6)
Ni1-O11	2.000(5)	Ni3-O6	2.013(5)
Ni1-N19	2.012(7)	Ni3-N10	1.995(7)
Ni1-N20	1.989(6)	Ni3-N15	2.033(7)
Ni1-N19	1.987(9)	Ni3-N16	1.989(8)
Ni2-O12	2.004(6)	Ni4-O1	2.006(6)
Ni2-O13	2.032(5)	Ni4-O2	2.009(6)
Ni2-N6	1.982(8)	Ni4-N13	2.023(8)
Ni2-N17	2.029(9)	Ni4-N14	2.034(8)
Ni2-N18	2.006(8)	Ni4-N12	2.002(8)
Cr1-C	2.020(8)-2.084(9)	Cr2-C	2.015(8)-2.07(1)
C≡N-Ni1	163.9(7)	C≡N-Ni3	161.4(7)
C≡N-Ni2	164.6(8)	C≡N-Ni4	162.9(8)
C≡N-Cr1	172.5(8)-177.6(9)	C≡N-Cr2	173.0(8)-178.1(9)

Table S3. Magnetic data for complexes **1-9**.

	$^{2S+1}L_J$ (Ln^{III})	Theoretical $\chi_m T$ /cm^3 K mol^{-1}	Experimental $\chi_m T$ /cm^3 K mol^{-1}	Weiss constant/K	Magnetization (theoretical)/$N\beta$
$Ni_4Cr_2Dy_2$ (**1**)	$^6H_{15/2}$	36.09	38.50	12.3	30.3 (34)
$Ni_4Cr_2Dy_2$ (**2**)	$^6H_{15/2}$	36.09	41.75	40.5	30.7 (34)
$Ni_4Co_2Dy_2$ (**3**)	$^6H_{15/2}$	32.34	37.6	40.8	25.0 (28)
$Ni_4Cr_2Tb_2$ (**4**)	$^7F_6$	31.39	30.58	29.5	22.0 (32)
$Ni_4Fe_2Tb_2$ (**5**)	$^7F_6$	28.39	28.47	27.9	23.4 (28)
$Ni_4Cr_2Gd_2$ (**6**)	$^8S_{7/2}$	23.51	25.93	24.8	27.6 (28)
$Ni_4Fe_2Gd_2$ (**7**)	$^8S_{7/2}$	20.51	21.84	21.0	24.7 (24)
$Ni_4Cr_2Y_2$ (**8**)	/	7.75	9.15	8.6	13.2 (14)
$Ni_4Fe_2Y_2$ (**9**)	/	4.75	6.03	6.0	6.8 (10)

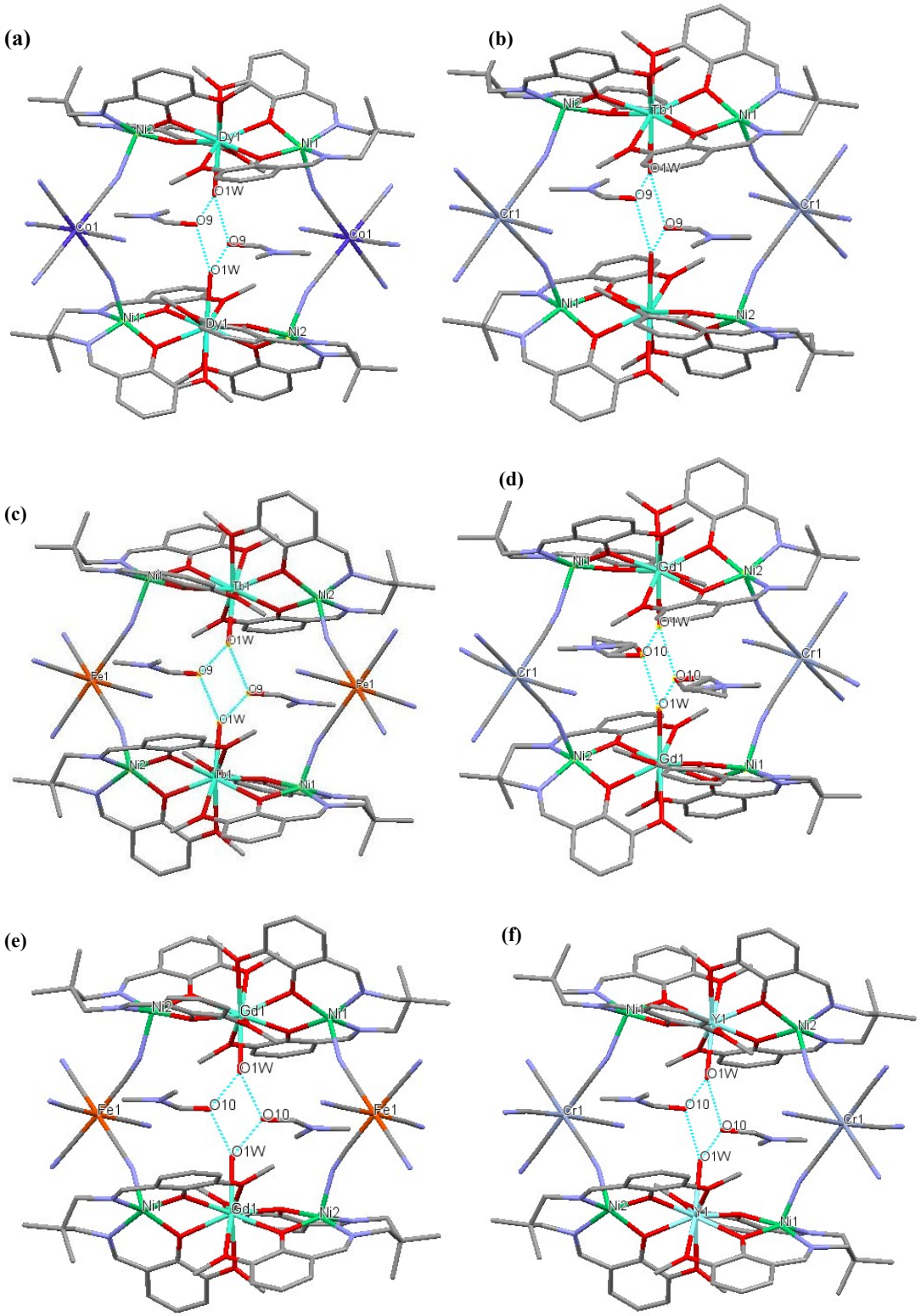
Table S4. Cole-Cole plots fitting parameters for complexes **1-5**.

	T / K	α		τ		χ		β
		α_1	α_2	τ_1	τ_2	χ_T	χ_S	β
1	2	5.8×10^{-2}	-	1.91	-	13.0	0.47	-
	3	5.7×10^{-2}	0.23	6.7×10^{-3}	9.3×10^{-2}	24.85	0.37	0.85
	3.5	4.4×10^{-2}	0.24	1.0×10^{-3}	2.4×10^{-3}	23.33	3.62×10^{-14}	0.74
2	2	0.18	-	2.42	-	104.53	2.58	-
3	3	8.4×10^{-2}	0.24	2.2×10^{-2}	4.7×10^{-3}	22.5	0.70	0.54
	4	6.5×10^{-2}	0.12	4.3×10^{-3}	1.04×10^{-3}	17.7	1.50	0.49
4	2	0.55	0.34	0.11	1.78×10^{-2}	32.41	6.99	0.38
	2.2	0.38	1.39	9.16×10^{-3}	0.47	25.70	12.24	1.44
	2.4	0.38	1.35	2.93×10^{-3}	0.24	23.83	12.34	1.59
	2.6	0.37	0.62	1.77×10^{-2}	9.94×10^{-3}	28.05	4.42	0.58
	2.8	0.39	0.42	8.99×10^{-4}	2.21×10^{-2}	25.96	4.63	0.79
5	2	0.21	0.25	3.82×10^{-3}	5.46×10^{-2}	46.09	5.95	0.68
	2.5	0.26	0.18	3.40×10^{-4}	5.88×10^{-3}	42.27	0.11	0.75

Table S5. Magnetic data for 3d-3d'-4f heterotrimetallic complexes with cyanide bridges.

Complexes	SMM/SCM (Yes or No)	U_{eff} (K)	External dc field (kOe)	Ref
NiDyM system (M = Fe, Cr)				
$[(CN)_7W(CN)Ni(dmf)(valdmpn)Dy(dmf)_4]\cdot H_2O$	N	/		8b
$[\{Ru(acac)_2(\mu\text{-}CN)_2\}\{Ni(\mu\text{-}L)Dy((CH_3OH)(NO_3)_2\}_2][Ru(acac)_2(CN)_2]$	N	/	0	4d
$\{[Ni(valpn)Dy(ONO_2)_2(H_2O)(\mu\text{-}NC)_3Fe(bipy)(CN)]\cdot 2H_2O\cdot 2CH_3CN\}_n$	N	/	/	11
$[\{LMe_2Ni(H_2O)Dy(H_2O)_{4.5}\}_2\{W(CN)_8\}_2]\cdot 15H_2O$	SMM	/	0	21a
$[Ni_4Dy_2Cr_2]$-**1**	SMM	38.9	0	This work
$[Ni_4Dy_2Cr_2]$-**2**	SMM	37.2	0	This work
$[Ni_4Dy_2Co_2]$-**3**	SMM	24.4	0	This work
$\{[Ni(Me_2valpn)]_2Dy(H_2O)Fe(CN)_6\}_2\cdot 14H_2O\cdot 4DMF$	SMM	25.0	0	10
$[\{L^{Me2}NiDy(H_2O)NiL^{Me2}\}W(CN)_8]_2\cdot 10MeCN\cdot H_2O$	SMM	26.4	0	12
$[Ni(valpn)(H_2O)Dy(H_2O)_3Fe(CN)_6]_2\cdot 8H_2O$	SMM	17.9	2	10
$\{[Cu(Me_2valpn)]_2Dy(H_2O)Fe(CN)_6\cdot 5.5H_2O\cdot 6.5CH_3CN\}_n$	SMM	12.3	2	13
$[\{(CuL)_2Dy\}\{Mo(CN)_8]\cdot CH_3CN\cdot H_2O$	SMM	19.1	0	7a
$\{[Zn(Me_2valpn)]_2Dy(H_2O)Co(CN)_6\}_2\cdot 15H_2O\cdot 2DMF\cdot 5CH_3CN$	SIM	85.9	0	4c
$\{[Zn(Me_2valpn)]_2Dy(H_2O)Cr(CN)_6\}_2\cdot 7H_2O\cdot 4DMF$	SIM	100.9	0	4c
$\{[Ni(valpn)Dy(NO_3)(H_2O)(\mu\text{-}NC)_4W(bipy)(CN)_2]\cdot 3.9H_2O\cdot 2CH_3CN\}_n$	SCM	22.8	2.5	4e
$\{[Ni(L)Dy(NO_3)_2(H_2O)Fe(Tp^*)(CN)_3]\cdot 2CH_3CN\cdot CH_3OH\}_n$	SCM	58.2	0	7c
NiTbM system				
$[\{L^{Me2}NiTb(H_2O)NiL^{Me2}\}Co(CN)_6]_2\cdot 2Me_2CO_2\cdot H_2O$	N	/	/	12
$[(CN)_7W(CN)Ni(dmf)(valdmpn)Tb(dmf)_4]\cdot H_2O$	N	/		8b
$[\{LMe_2Ni(H_2O)Tb(H_2O)_{4.5}\}_2\{W(CN)_8\}_2]\cdot 15H_2O$	SMM	/	3	21a
$[\{L^{Me2}Ni(DMF)Tb(DMF)_4\}\{W(CN)_8\}]\cdot 3H_2O$	SMM	/	0	21b
$[\{L^{Me2}Ni(H_2O)Tb(DMF)_{2.5}(H_2O)_{1.5}\}\{W(CN)_8\}]\ H_2O\cdot 0.5DMF$	SMM	15.3	0	21b
$[Ni_4Tb_2Cr_2]$-**4**	SMM	21.9	0	This work
$[\{L^{Me2}NiTb(H_2O)NiL^{Me2}\}W(CN)_8]_2\cdot 10MeCN\cdot 2H_2O$	SMM	23.0	0	12
$[Ni_4Tb_2Fe_2]$-**5**	SMM	29.6	0	This work
$\{[Ni(valpn)Tb(ONO_2)_2(H_2O)(\mu\text{-}NC)_3Fe(bipy)(CN)]\cdot 2H_2O\cdot 2CH_3CN\}_n$	SCM	29.1	0	11
$\{[Ni(L)Tb(NO_3)_2(H_2O)Fe(Tp^*)(CN)_3]\cdot 2CH_3CN\cdot CH_3OH\}_n$	SCM	55.6	0	7c

Cu(II)Tb(III)M(III/V) system				
$[(CN)_5(bipy)W(CN)Cu(3\text{-}MeOsalpn)Tb(O_2NO)_2(H_2O)]\cdot 3MeCN$	N	/	/	21c
$[Cu(valpn)(H_2O)Tb(H_2O)_3Fe(CN)_6]\cdot 2H_2O$	N	/	0/2	13
$\{[Cu(Me_2valpn)]_2Tb(H_2O)Fe(CN)_6\cdot 4.5H_2O\cdot 1.5CH_3CN\}_n$	N	/	0/2	13
$[Cu(valpn)(H_2O)Tb(H_2O)_3Fe(CN)_6]\cdot 1.75H_2O$	SMM	/	0/2	13
$[\{LCuTb(H_2O)_3\}\{Fe(CN)_6\}]\cdot 4H_2O$	SMM	/	3	7b
$[L_2CuTb(H_2O)_5(\mu\text{-}NC)Mo(CN)_7]$	SMM	/	0	8a
$[Cu(H_2L)(CH_3OH)]_2Tb(H_2O)_{0.57}(DMF)_{0.43}Fe(CN)\cdot 65.5H_2O$	SMM	13	2	4a
$[(Mo(CN)_8)_2(CuLTb)_4)](Mo(CN)_8)$	SMM	19.25	0	9
$[\{W(CN)_8\}Cu(valen)Tb(H_2O)_4]_n\cdot nCH_3CN\cdot nH_2O$	SCM	53.9	0	7d
$\{[Cu_3Tb(L^{Pr})W(CN)_8(DMF)_3(H_2O)_3]\cdot (DMF)_{1.5}\cdot (H_2O)_{0.5}\}_n$	SCM	20	0.8	21d


(a)
Ni2
Dy1
Ni1
O1W
O9
Co1
O9
Co1
O1W
Ni1
Dy1
Ni2
(b)
Ni2
Tb1
Ni1
O1W
O9
Cr1
Cr1
O9
Ni1
Ni2
(c)
Ni1
Tb1
Ni2
O1W
O9
Fe1
O9
Fe1
O1W
Ni2
Tb1
Ni1
(d)
Ni1
Gd1
Ni2
O1W
O10
Cr1
Cr1
O10
O1W
Ni2
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Ni1
Gd1
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Ni1

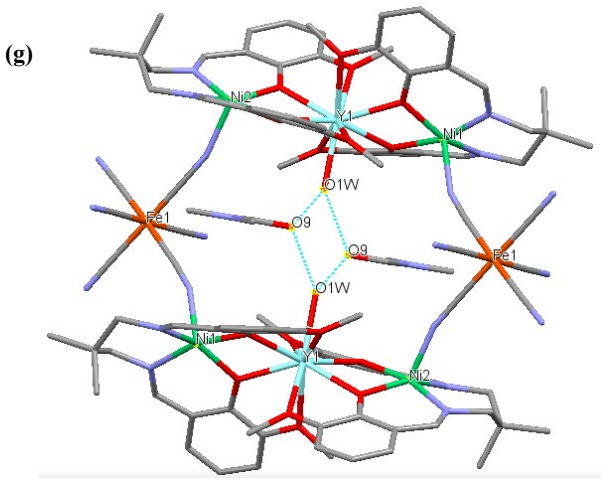

Fig. S1. Main molecular structure of complexes **3** (a), **4** (b), **5** (c), **6** (d),**7** (e), **8** (f) and **9** (g). Hydrogen and most solvents have been omitted for clarity.

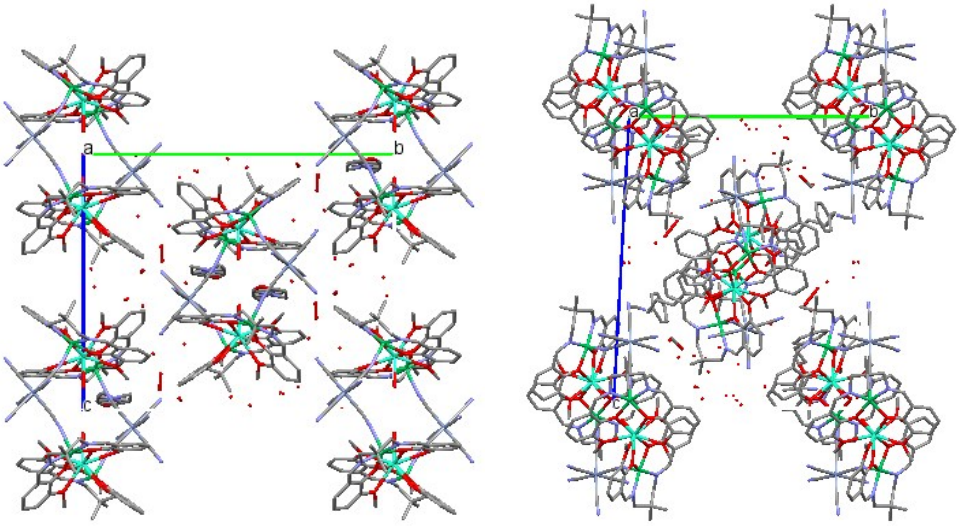

Fig. S2. Cell packing diagram for complexes **1** (left) and **2** (right).

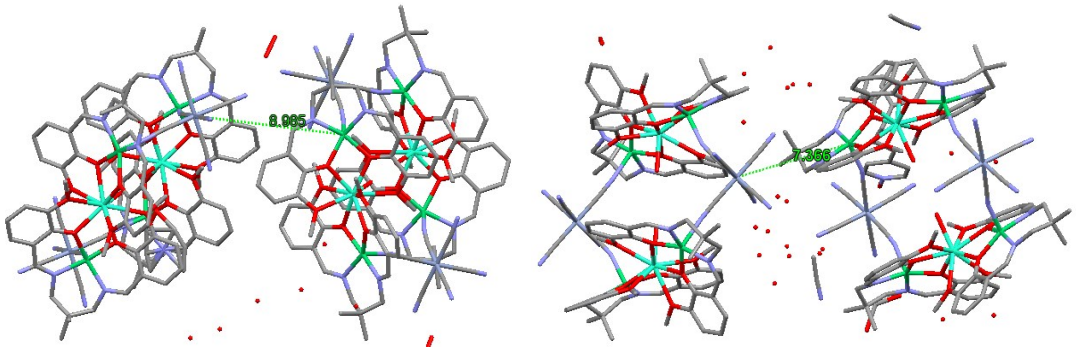

Fig. S3. The nearest intermolecular distance of sketches for complexes **1** (left) and **2** (right).

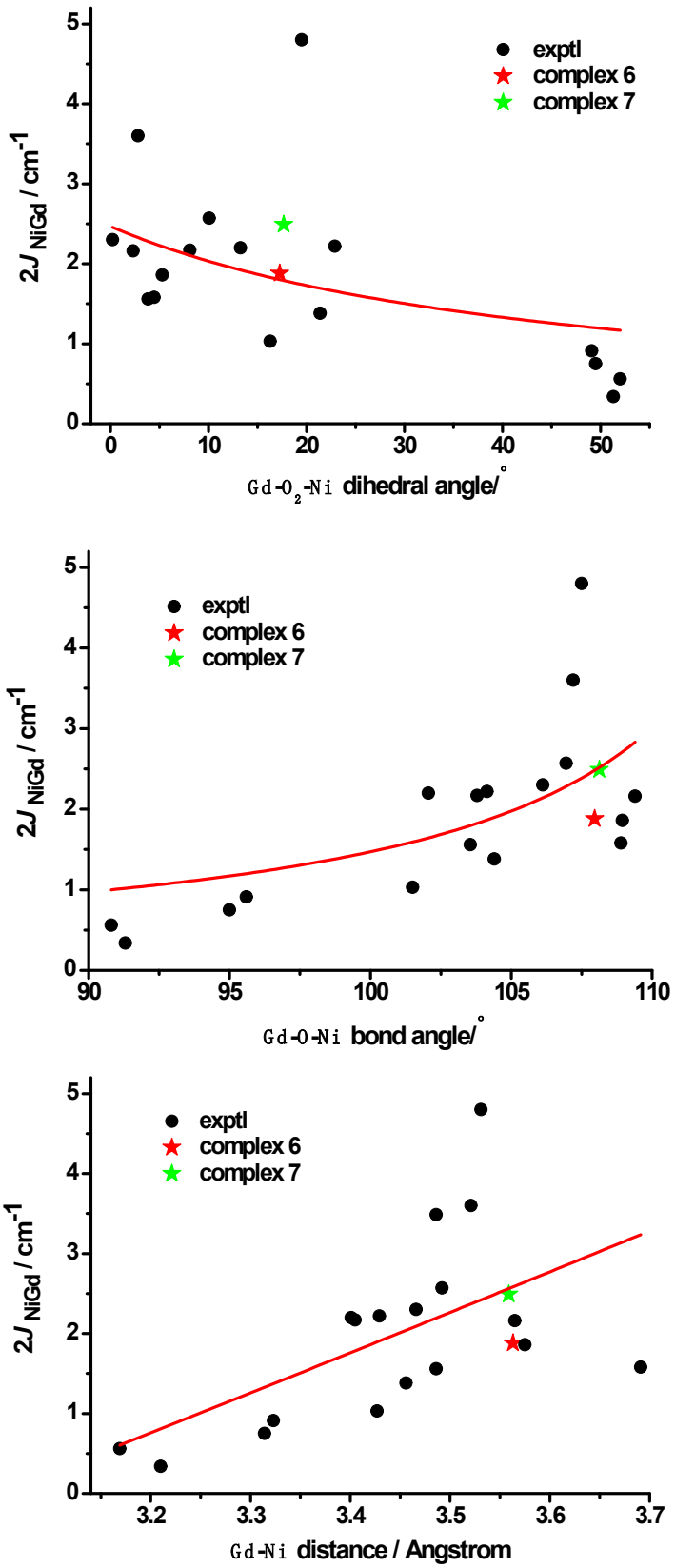

Fig. S4. Magneto-structural correlation for bis-phenoxo-bridged Ni(II)-Gd(III) complexes. The pentagrams correspond to complexes **6** and **7**. The lines are guides for eyes.

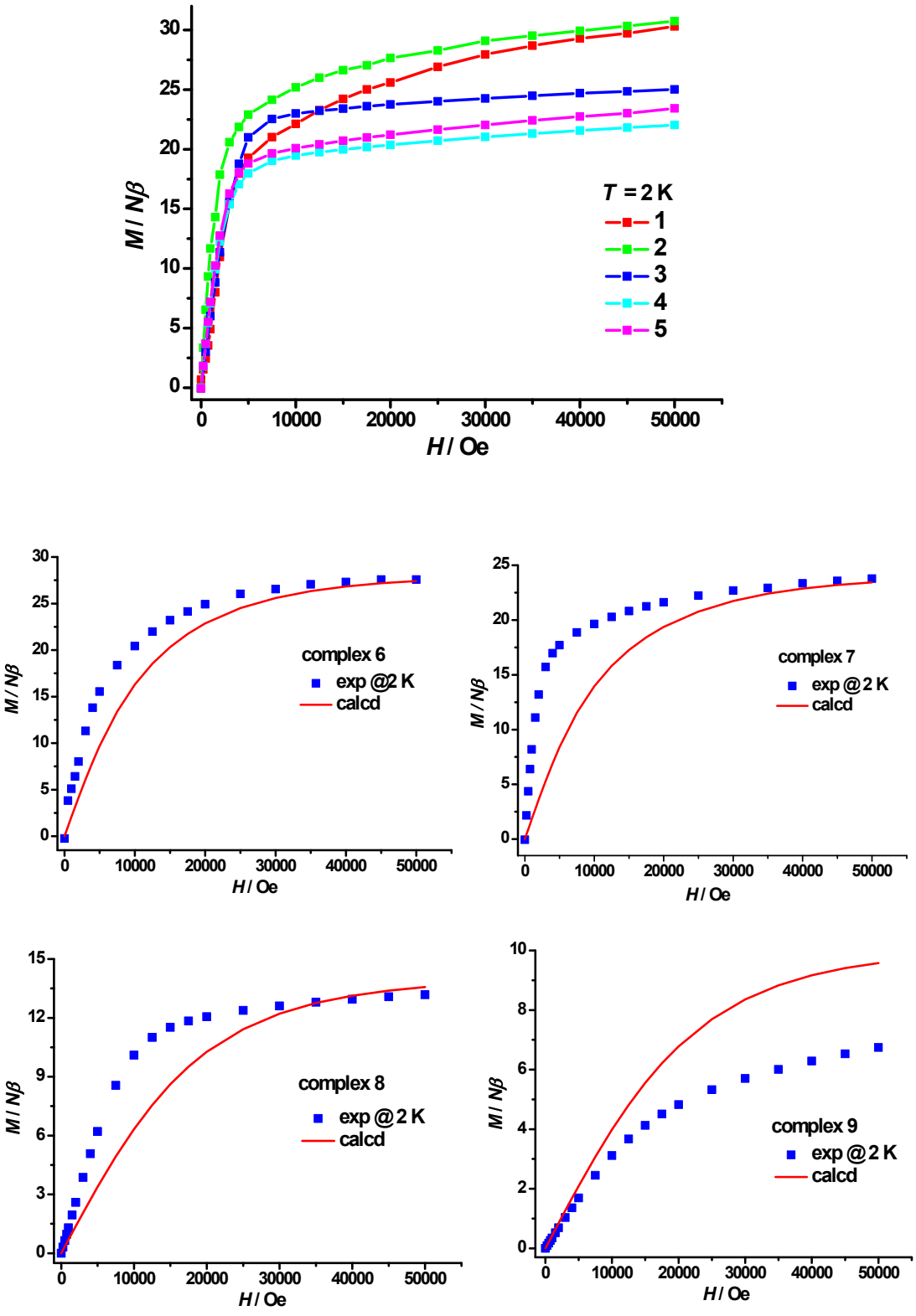

Fig. S5. Magnetization curve for complexes **1-9** at 2 K. The solid lines for complexes **6-9** represent the calculated data based on the Brillouin function for non-coupling spins with $g = 2.0$.

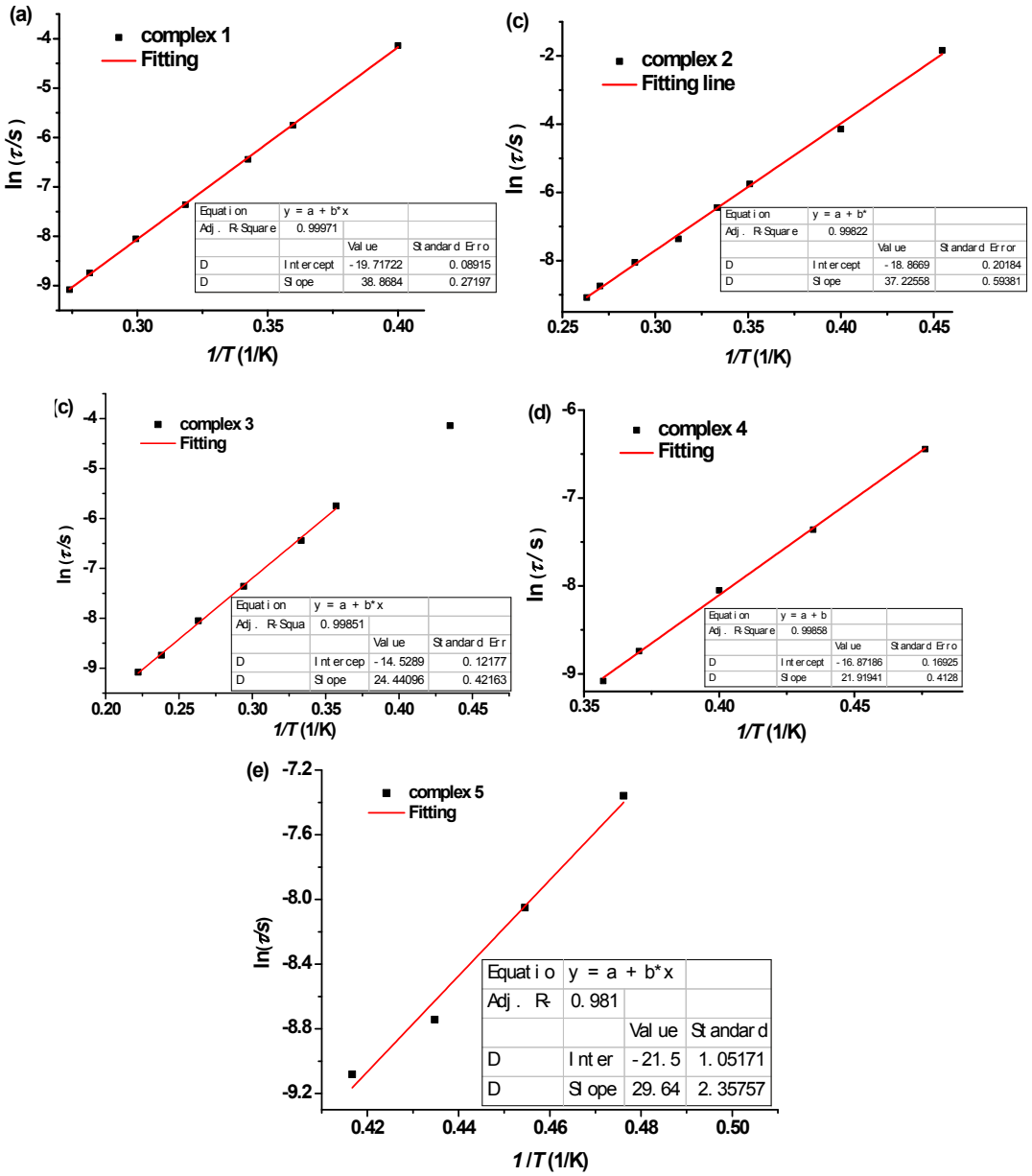

Fig. S6. The ln(τ) vs. T^{-1} plots based on the Arrhenius relationship for complexes **1-5**.

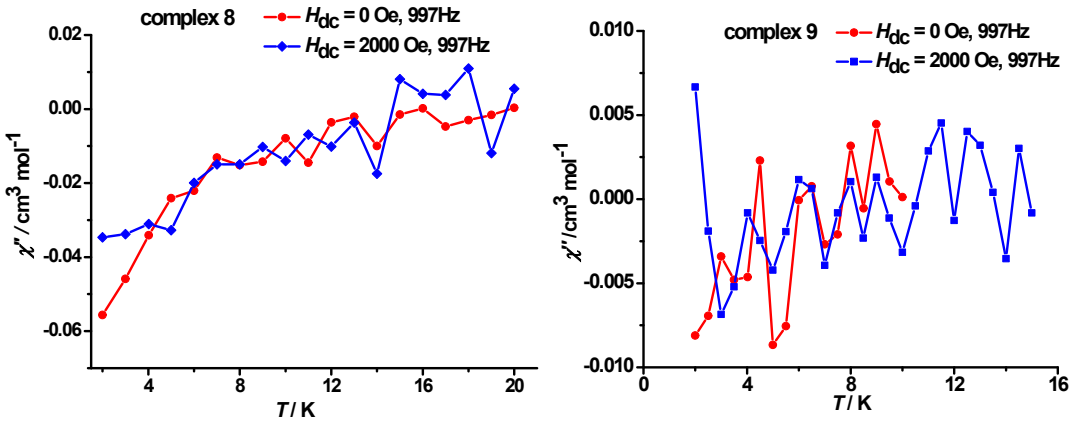

Fig. S7. Temperature dependence of the out-of-phase (χ'') components of the ac magnetic susceptibility for **8** (left) and **9** (right) with an oscillation field of 2.5 Oe.

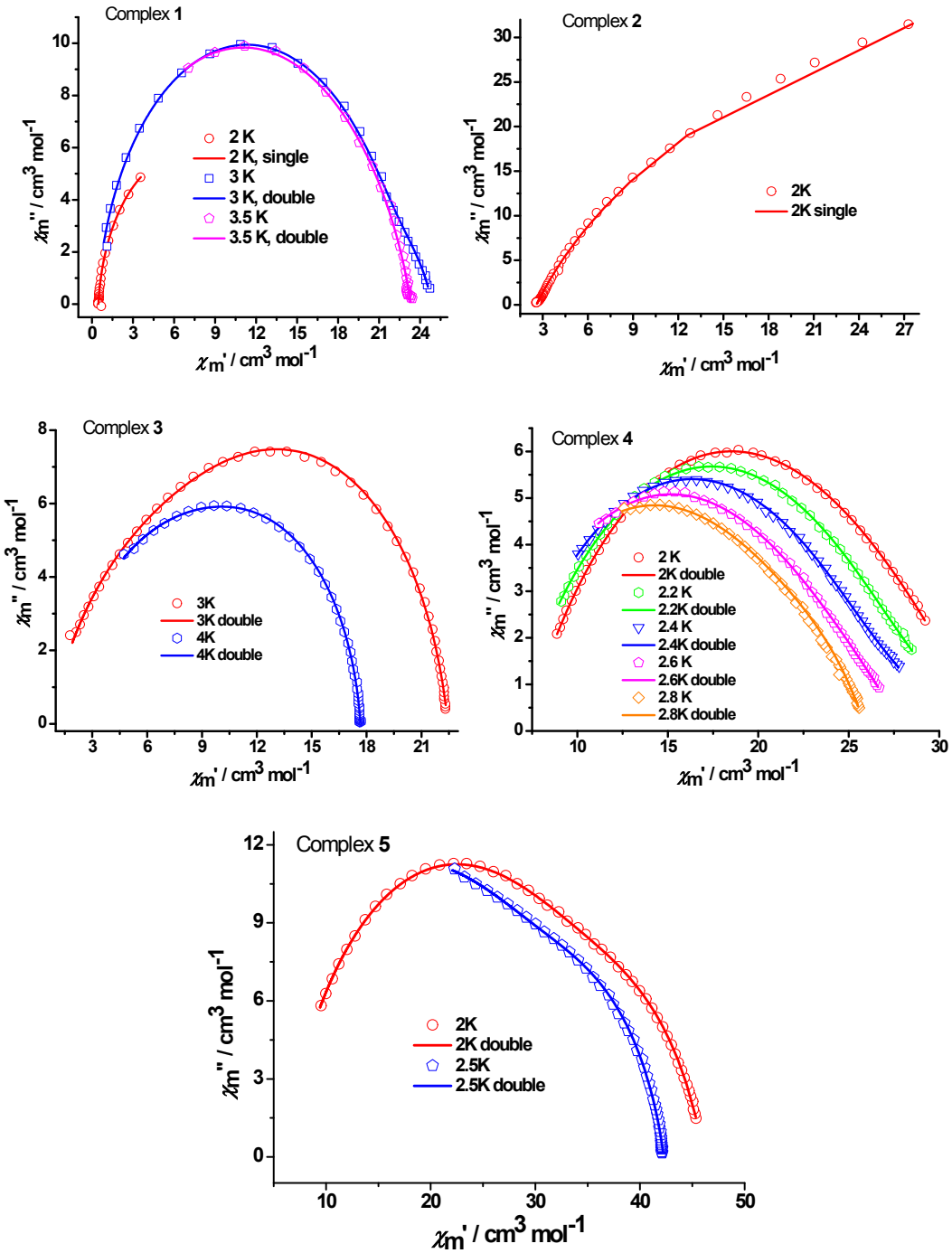

Fig. S8. Cole-Cole plots of complexes **1-5**. The solid lines represent the fitting results using the parameters listed in Table S4.