Supplementary Material

Density Functional Studies on Dinuclear {$Ni^{II}Gd^{III}$} and Trinuclear {$Ni^{II}Gd^{III}Ni^{II}$} Complexes: Magnetic Exchange and Magneto-Structural Maps

Saurabh Kumar Singh, Neeraj KumarTibrewal and Gopalan Rajaraman*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076. India
Fax: (+91)22-2576-7152; Tel: (+91)-22-2576-7183; E-mail: rajaraman@chem.iitb.ac.in

We performed DFT calculations on complexes. The energies, spin density and J values are given in table for dimer and trimer as well as their model complexes (calculated at theoretical *level I*).

Table S1: DFT computed energies of high spin (HS) and broken symmetry (BS) state, $<S^2>$ values and the computed *J* values for dinuclear complexes **1** and **2** along with their model complexes.

	TOTAL ENERGY		**$<S^2>$ VALUES**		***J* values**
	HS	BS			
Complex 1	-2499.4324	-2499.43231	24.7644	10.7643	2.142073
Models with one bridge absent					
1a	-2424.4966	-2424.49663	24.7667	10.7668	-0.71274
Model with no bridge					
1b	-2349.4066	-2349.40682	24.7717	10.7772	-4.91349
Complex 2	-3711.6362	-3711.63618	24.7653	10.7653	0.364054
Models with one bridge absent					
Model 2b	-3636.7725	-3636.77262	24.7669	10.7676	-2.29378
Model 2c	-3636.782	-3636.7821	24.7671	10.7677	-1.56869
Model 2a	-3636.7707	-3636.7708	24.7668	10.7676	-2.25839
Models with two bridge absent					
2aa	-3561.7424	-3561.74247	24.7724	10.7739	-1.26664
2bb	-3561.7032	-3561.70318	24.773	10.7737	0.785719
2cc	-3561.7622	-3561.76218	24.7716	10.7729	-0.68394

Table S2: DFT computed energies and J values for Complex **3** and **4**.

Complex 3

Spin Configurations	Energy	J value(cm^{-1})
HS	-3128.135079610000	
		J_1 = 2.16
BS 1	-3128.135002600000	
		J_2 = 2.05
BS 2	-3128.135002600000	
		J_3 = - 0.15
BS 3	-3128.134925670000	

Complex 4

Spin Configurations	Energy	J value(cm^{-1})
HS	-3926.428739510000	
		J_1 = 0.59
BS1	-3926.428720780000	
		J_2 = 0.56
BS2	-3926.428720720000	
		J_3 = -0.12
BS3	-3926.428699850000	

Overlap integral analysis: The overlap integral analysis reported for complex **1** and complex **2** as well as for all model complexes, which confirms the antiferromagnetic contribution in particular complexes. The suitability of DFT orbitals for qualitative analysis has been found to be valid at many occasions and had provided many useful insights.[1-3] According the Kahn-Brait model,[3] the *J* has been related to the overlap between nonorthogonal localized magnetic orbitals. At many occasions empty-magnetic orbitals are shown to be superior to represent Kahn-Brait model and had been successfully employed for qualitative interpretation.[2] Therefore, we have decided to use these orbitals for our orbital analysis.

Complex1 and their model

Table S3: Overlap integral values are given for complex **1** and their model complexes. The computed orbital numbers are given in the table with alpha for Ni^{II} and beta for Gd^{III}.

Complex **1**	*J* value=2.142072	
Gd	Ni 178	Ni 179
f orbitals	dz^2	dx^2-y^2
206	-0.002	-0.005
209	0.003	0.001
210	0.000	0.003
211	-0.005	-0.004
212	0.005	0.006
213	-0.003	-0.008
214	-0.003	0.007

Complex **1a**	*J* value= - 0.71274	
Gd	Ni 172	Ni 173
f orbitals	dx^2-y^2	dz^2
187	-0.015	0.005
188	-0.014	0.009
189	0.003	-0.001
193	0.005	-0.004
194	0.005	-0.007
196	0.014	-0.007
197	-0.005	0.002

Complex **1b**	*J* value = - 4.91349	
Gd	Ni 168	Ni 170
f orbitals	dx^2-y^2	dz^2
179	-0.028	0.009
181	0.019	0.015
182	-0.006	-0.060
183	-0.002	0.012
184	0.001	0.008
186	0.004	0.032
187	0.007	-0.007

Complex 2 and their model complexes:

Table S4: Overlap integral values are given for complex 2 and their model complexes. The computed orbital numbers are given in the table with alpha for Ni^{II} and beta for Gd^{III}.

Complex **2**	*J*value=.364	
GD	Ni 253	Ni 254
f orbitals	dz^2	dx^2-y^2
287	-0.002	-0.001
289	0.000	0.002
291	0.002	-0.004
293	-0.012	0.001
294	0.003	-0.001
295	-0.006	0.001
305	0.002	-0.022

Complex **2a**	J value = -2.25839	
Gd	Ni 244	Ni 250
f orbitals	dz^2	dx^2-y^2
267	0.010	-0.006
268	-0.025	0.004
271	0.017	-0.001
273	-0.006	0.010
276	0.012	-0.005
280	0.007	0.003
278	-0.001	0.007

Complex **2b**	J value= -2.29378	
Gd	Ni 244	Ni 246
f orbitals	dz^2	dx^2-y^2
266	-0.003	0.000
269	0.012	0.003
270	-0.012	-0.004
271	-0.024	-0.004
276	-0.002	0.006
279	0.010	-0.012
280	-0.010	-0.009

Complex **2c**	Jvalue= -1.56869	
GD	Ni 244	Ni 247
f orbitals	dz^2	dx^2-y^2
269	0.008	0.007
272	-0.015	0.003
273	-0.014	0.001
276	0.004	0.002
277	-0.001	0.009
279	0.001	0.008
281	-0.011	0.002

Complex **2aa** J value= -1.26

Gd		Ni 240	Ni 241
f orbitals		dx^2-y^2	dz^2
	258	0.009	0.010
	260	-0.027	0.025
	261	-0.010	0.007
	262	-0.025	0.034
	263	-0.006	-0.015
	264	0.012	0.001
	265	-0.004	-0.014

Complex **2bb** J value = -0.68

Gd		Ni 240	Ni 241
f orbitals		dx^2-y^2	dz^2
	258	0.017	-0.015
	259	-0.027	-0.004
	261	0.019	-0.010
	262	-0.025	0.019
	263	0.027	0.011
	264	0.000	-0.017
	268	0.007	0.006

Complex **2cc** J value = 0.78

Gd		Ni242	Ni241
f orbitals		dx^2-y^2	dz^2
	259	-0.001	-0.001
	261	0.007	0.010
	263	-0.034	-0.019
	264	-0.008	-0.006
	265	0.007	-0.006
	266	0.019	0.005
	268	-0.006	-0.031

Pictorial Representation of all model complexes of 1

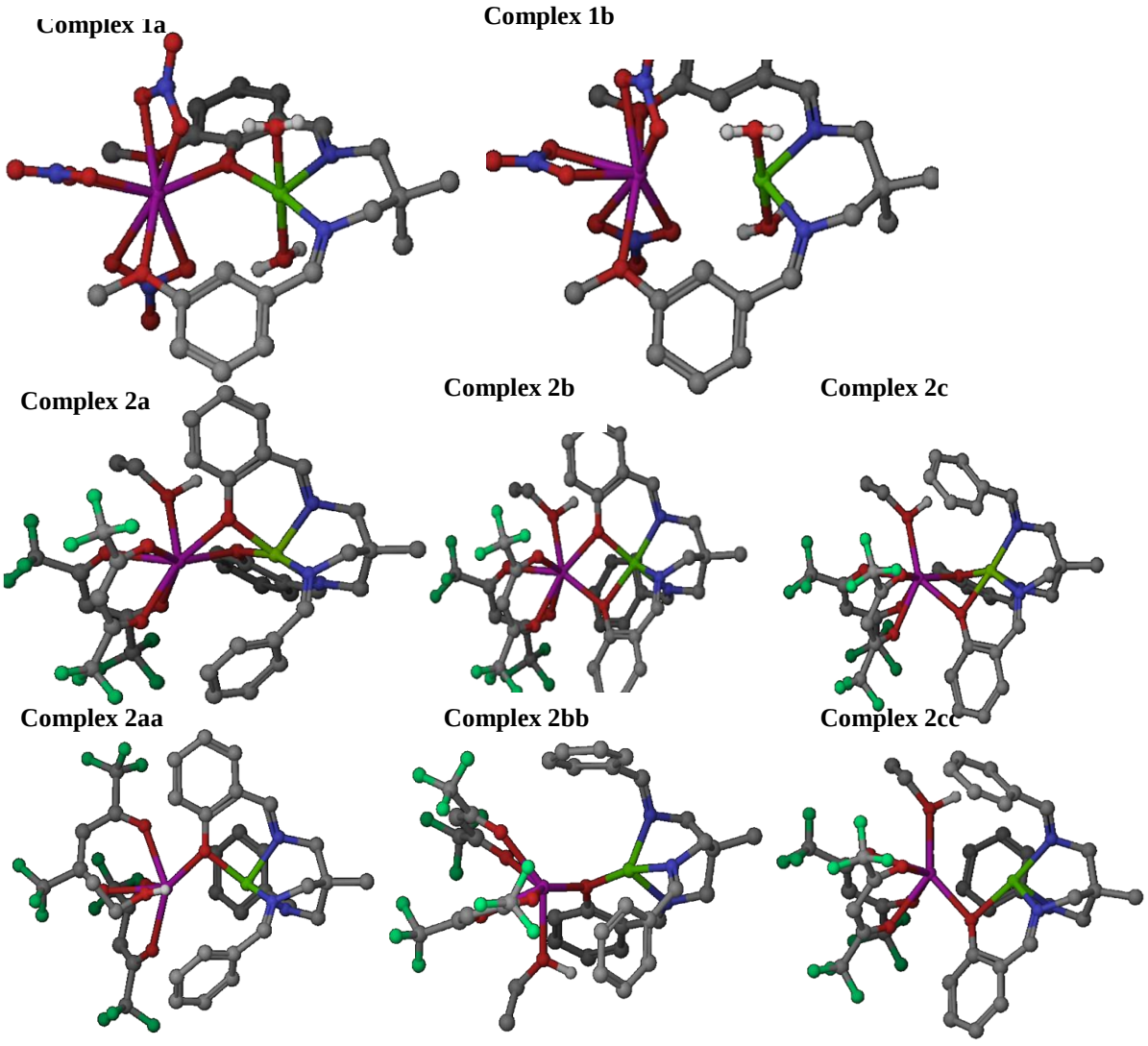

Figure-S1: The structures of the model complexes presented in Table S1.

Correlation developed for Complex 1b having no bridging groups:

For complex 1b we calculated the *J* value which is antiferromagnetic in nature. Our orbital analysis indicates a direct interaction of dz^2 orbital of Ni^{II} with the f orbitals of Gd^{III} in the absence of the bridging group (see Figure above). If direct interaction is the sole reason for the antiferromagnetic behaviour, the magnitude of the *J* should be correlated to the Ni-Gd distance. To probe this further, we have developed such correlation (see Figure S3) in the model 1b. We found that, as the bond distance between the Ni-Gd increases the antiferromagnetic interaction decreases as expected and at larger distances the interaction approaches to zero.

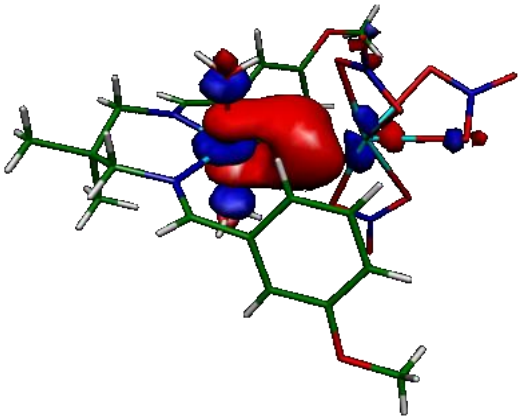

Figure-S2:- Representation of dz^2 orbital of Ni(II), showing interaction with f orbital of Gd (III). The red and blue colour represents positive and negative electron density. The isodensity surface represented a value of 0.02 e^- /$bohr^3$.

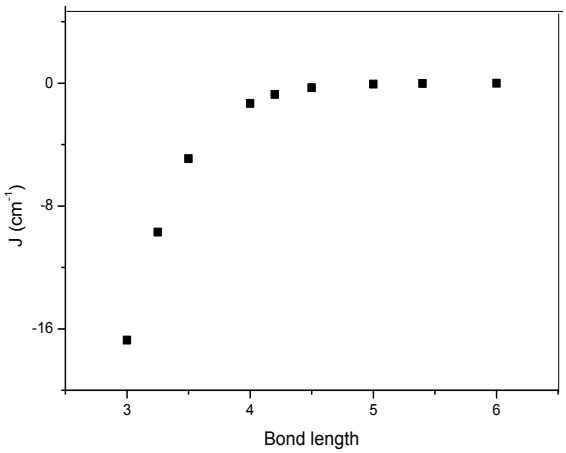

Figure-S3: This graphical plot represents the variation of *J* with increase the distance between Ni and Gd.

NBO-analysis for structure 1:

Table S5: Electron occupancies of 6s, 4f and the 5d orbitals of Gd^{III} for complex **1** and its model complexes.

	Original structure	*Model 1a*	*Model 1b*
6s	0.22	0.21	0.20
4f	7.01	7.01	7.01
5d	0.17	0.22	0.31

Magneto structural correlation for Complex 2

We developed magneto-structural correlation for complex 2 i.e. variation of J with variation of two dihedrals angles. As dihedral angle increases J value becomes antiferromagnetic. The planar framework of Ni-O-Gd-O gives ferromagnetic *J*.

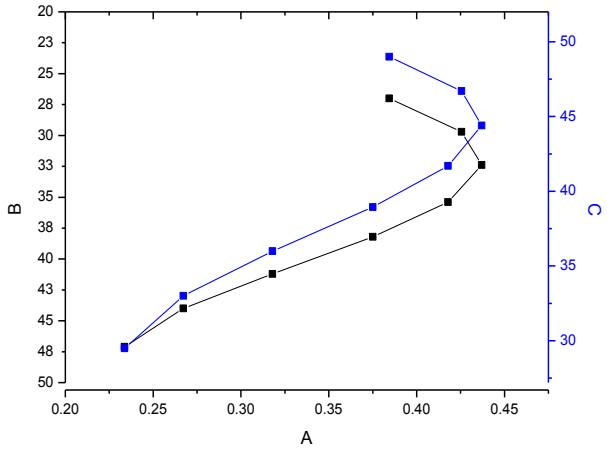

Figure-S4: Magneto-Structural correlation for complex **2** by changing two dihedral angles at a time.

Spin Density Chart for Complex 1 and their model complexes:

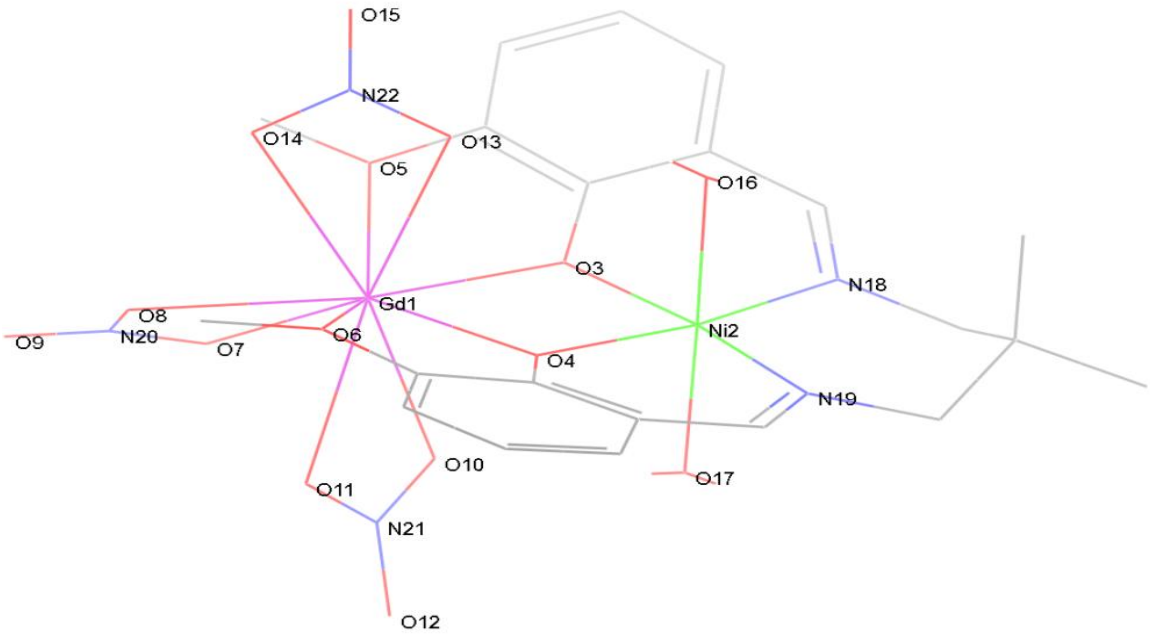

Figure-S5: Complex 1 with numbering of atoms for which the spin densities are given in following table.

Table-S6: Spin densities of core atoms for complex 1

Atom number	atom list	1 HS	1 BS	1a HS	1a BS	1b HS	1b BS
1	Gd	7.0286900000	7.028026	7.036423	7.043296	7.062645	7.090078
2	Ni	1.6635110000	-1.662209	1.646062	-1.6423	1.566535	-1.54692
3	O	0.0519970000	-0.058561	0.048112	-0.05722	-	
4	O	0.0486720000	-0.05611			-	
7	O	-0.0038730000	-0.003972	-0.00742	-0.00839	-0.01459	-0.01473
8	O	-0.0034160000	-0.003443	-0.00529	-0.00503	-0.02016	-0.02486
10	O	-0.0035080000	-0.003609	-0.00381	-0.00532	-0.00753	-0.00795
11	O	-0.0039080000	-0.004007	-0.00526	-0.00533	-0.00813	-0.00848
13	O	-0.0032630000	-0.003366	-0.00472	-0.00526	-0.00692	-0.00772
14	O	-0.0027170000	-0.002798	0.003623	-0.00397	-0.00549	-0.0054
5	O	-0.0017630000	-0.001564	-0.00259	-0.00308	0.001492	-0.00233
6	O	-0.0017720000	-0.001671	0.001451	-0.00163	0.001492	-0.01948
16	O	0.0332660000	-0.033311	0.037461	-0.03742	0.030517	-0.03046
17	O	0.0378610000	-0.037911	0.042212	-0.04221	0.041729	-0.04152
18	N	0.0889140000	-0.08869	0.158075	-0.15804	0.159589	-0.15855
19	N	0.0843180000	-0.08398	0.074313	-0.07433	0.157216	-0.15618

The spin densities on atoms (which are directly related with metals) are given in table. The numbering for atoms are given in table, are correlated with numbering in crystal structure which shown above.

Spin Density Chart for Complex 2 and their model complexes:

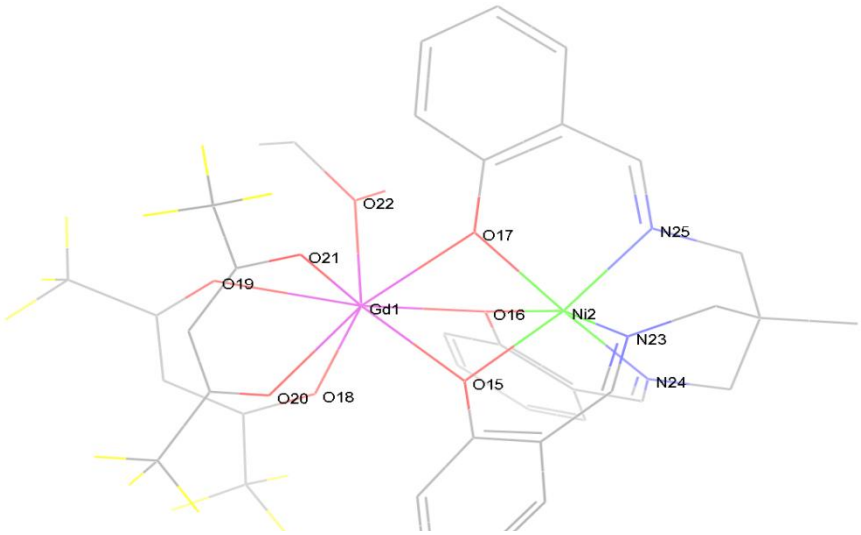

Figure-S6: Complex **2** with numbering of atoms for which the spin densities are given in following table.

Model Complexes with one bridge absent

Model complexes with two bridges absent

2a HS

2aa HS

Table-S7: Spin densities of core atoms for complex 2 along with model complexes

Complex **2**

atom number	atom list	2 HS	2 BS		2c BS	2b HS	2b BS	2c HS	2C BS		2aa BS	2bb HS	2bb BS	2cc HS	2cc BS
1	Gd	7.019519	7.022986	7.02089	7.03184	7.019702	7.035076	7.021324	7.033253	7.028186	7.048605	7.030319	7.043766	7.026595	7.046371
2	Ni	1.620215	-1.616379	1.685367	-1.68014	1.586132	-1.57971	1.583552	-1.57744	1.540087	-1.52926	1.529388	-1.52048	1.542214	-1.53153
15	O	0.043488	-0.050685	-	-	0.049823	-0.05943	0.058651	-0.06957	-	-	0.056659	-0.07062	-	-
16	O	0.045864	-0.051274	0.061417	-0.07069	-	-	0.049444	-0.05584	0.057519	-0.0701	-	-	-	-
17	O	0.044387	-0.050036	0.046682	-0.05283	0.055138	-0.06447	-	-	-	-	-	-	0.054704	-0.06735
18	O	-0.002528	-0.002433	-0.00348	-0.00358	-0.00316	-0.00334	-0.00482	-0.00512	-0.00702	-0.0078	-0.00615	-0.00658	-0.00433	-0.0064
19	O	-0.002403	-0.002438	-0.00418	-0.00446	-0.00316	-0.00333	-0.00349	-0.00384	-0.00623	-0.01001	-0.00479	-0.00592	-0.00552	-0.00771
20	O	-0.002403	-0.002493	-0.00361	-0.004	-0.00383	-0.00388	-0.00338	-0.0033	-0.00529	-0.00609	-0.0055	-0.00674	-0.00565	-0.00573
21	O	-0.002417	-0.002642	-0.00373	-0.00406	-0.00465	-0.00529	-0.0036	-0.00401	-0.00567	-0.00723	-0.00664	-0.00806	-0.00658	-0.0083
22	O	-0.001627	-0.00187	-0.00274	-0.00289	-0.00203	-0.0025	-0.00262	-0.00311	-0.00398	-0.00458	-0.00329	-0.00413	-0.00331	-0.0037
23	N	0.08715	-0.087373	0.071526	-0.07132	0.144206	-0.14445	0.096219	-0.09672	0.056404	-0.05708	0.190258	-0.19058	0.141343	-0.14097
24	N	0.08881	-0.089096	0.03023	-0.03078	0.080525	-0.08052	0.145257	-0.14542	0.193005	-0.19367	0.147043	-0.14668	0.065483	-0.06608
25	N	0.082428	-0.082598	0.067427	-0.06778	0.093882	-0.09458	0.071463	-0.07149	0.130785	0.130352	0.051936	-0.05256	0.179094	-0.17993

Bond Angle correlation in Complex **1** confirmed by overlap integral analysis:

Table-S8: Overlap integral analysis for bond angle correlation for complex **1**

Complex **1** at angle 80.15		*J* value = - 0.31
Gd	Ni 176	Ni179
f orbitals	dz2	dx2-y2
204	-0.012	0.005
205	-0.001	0.001
207	-0.008	0.002
208	-0.004	-0.007
209	0.003	0.003
211	-0.001	0.001
212	-0.001	0.005

Complex **1** at angle 119.15	*J* value = 2.58	
Gd	Ni 178	Ni179
f orbitals	dz^2	dx^2-y^2
209	0.003	0.001
210	0.000	0.003
211	-0.005	-0.004
212	0.005	0.006
213	-0.003	-0.008
214	-0.003	0.007
218	0.003	0.002

MAGPACK Simulated Plot: Since the experimental data is not available readily, we have created the experimental data from the spin Hamiltonian parameter (J_1= 4.8 cm^{-1}, J_2= 0.05 cm^{-1}, D= 0.03 cm^{-1} and g= 2.03) reported by the authors for the complex **3**. Since these parameters yield excellent fit to the experimental points, we have simulated the experimental points based on these data (black squares) and the simulated curve using DFT *J* values (J_1= 2.16 cm^{-1}, J_2= 2.05 cm^{-1}, J_3=-0.15 cm-1, D= 18.0 cm^{-1} and g= 2.03) as shown below. An excellent fit between two sets is evident.

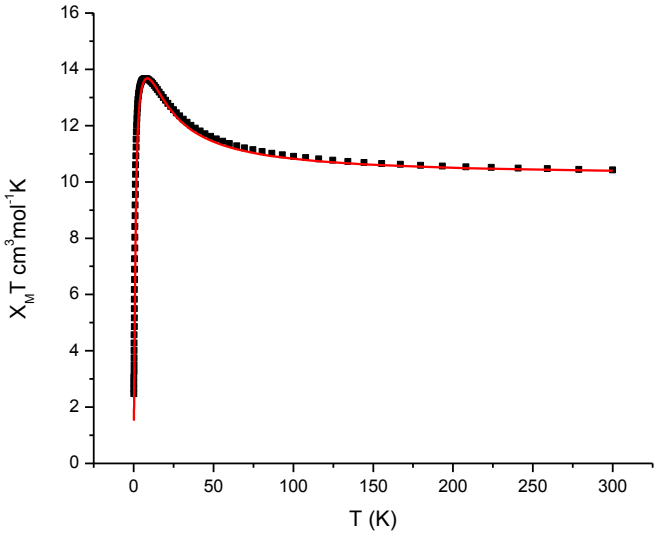

Figure-S7: Thermal variation of $X_M T$ for complex **3** experimental and DFT calculated curves.

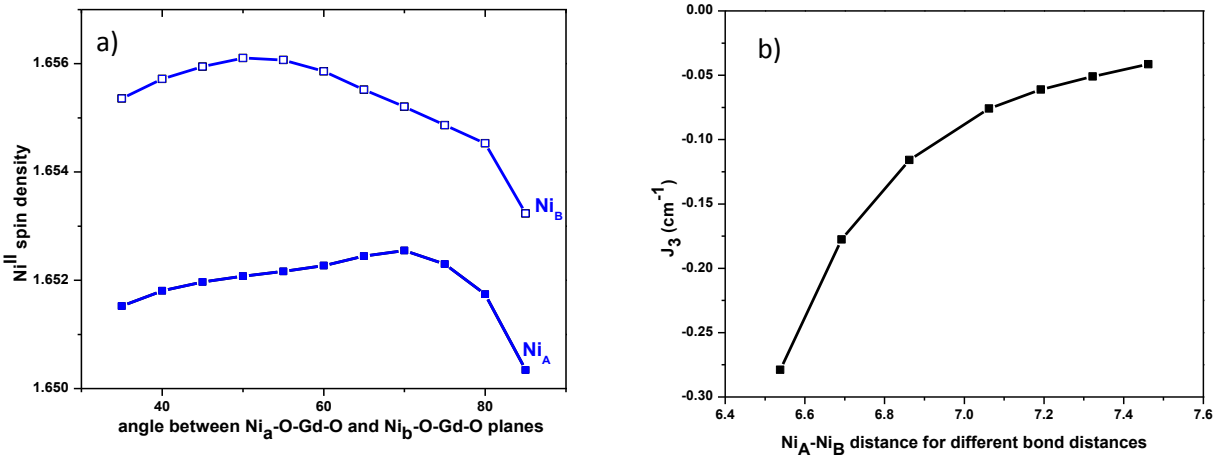

Figure-S8. a) variation spin-densities of Ni^{II} along the twist angle correlation b) dependence of J_3 on Ni_A-Ni_B distance for bond length correlation.

Some Ni-Gd Complexes like complex 1 and 2.

Table S9: Different Ni-Gd complexes along with J value as well as structural parameters, which has been taken as experimental points (red colour) in magneto-structural correlation for Complex **1**.

	Bond Length Ni-O-Gd		Bond Angle	Bond length Gd-O			Bond Angle Gd-O-Ni			
IYERAF[5]	J value=+0.19									
	Ni1-O1	2.113	87.34	Gd-O1	2.459			Ni-O-Gd-O	35.29	Ni-O-Gd-O	45.69
	Ni1-O2	2.09	93.11	Gd-O2	2.268			Ni-O-Gd-O	43.31	Ni-O-Gd-O	34.26
	Ni1-O3	2.075	90.61	Gd-O3	2.371			Ni-O-Gd-O	32.96	Ni-O-Gd-O	32.42
	Ni2-O4	2.081	90.82	Gd-O4	2.363						
	Ni2-O5	2.146	87.21	Gd-O5	2.441						
	Ni2-O6	2.068	93.28	Gd-O6	2.288						
IYEREJ[5]	J value=+0.32									
	Ni1-O1	2.077	91.98	Gd1-O1	2.378			Ni-O-Gd-O	37.96	Ni-O-Gd-O	37.95
	Ni1-O2	2.073	92.34	Gd1-O2	2.368			Ni-O-Gd-O	36.61	Ni-O-Gd-O	36.61
	Ni1-O3	2.059	92.3	Gd1-O3	2.382			Ni-O-Gd-O	36.19	Ni-O-Gd-O	36.18
	Ni2-O1	2.077	91.99	Gd1-O4	2.535	Gd1-O4-GD2	116.61				
	Ni2-O2	2.073	92.36	Gd1-O5	2.562	Gd1-O5-GD2	116.63				
	Ni2-O3	2.059	92.3	Gd2-O1	2.378						
				Gd2-O2	2.369						
				Gd2-O3	2.383						
				Gd2-O5	2.534						
UDEZAF[6]	J value=+0.79		Ni-O-GD							
	Ni1-O2	1.988	106.87	GD1-O2	2.454	GD1-O2-Ni1	108.38	Ni-O-Gd-O	3.69		
	Ni1-O3	2.009	109.39	GD1-O3	2.502	GD1-O3-Ni1	109.32	Ni-O-Gd-O	3.69		
	Ni2-O2	1.989	106.87	GD1-O2	2.454	GD1-O2-Ni2	108.38				
	Ni2-O3	2.01	109.39	GD1-O3	2.501	GD1-O3-Ni2	109.32				
UDUYIB[7]	J value=+0.56									
	Ni1-O1	2.117	92.25	Gd1-O1	2.33	GD1-O1-Ni1	92.25	Ni-O-Gd-O	41.22		
	Ni1-O2	2.208	90.17	Gd1-O2	2.323	GD1-O2-Ni1	90.17	Ni-O-Gd-O	38.55		
	Ni1-O3	2.069	94.33	Gd1-O3	2.303	GD1-O3-Ni1	94.33	Ni-O-Gd-O	32.22		
UDEYUY[6]	J=+0.79 for Ni-Gd									
	Ni1-O7	2.03	108.17	Gd1-O7	2.511	Gd1-O7-Ni1	108.17	Ni-O-Gd-O	2.15		
	Ni1-O2	2.017	108.16	Gd1-O2	2.523	Gd1-O2-Ni1	108.16	Ni-O-Gd-O	1.68		
	Ni2-O6	2.011	109.16	Gd1-O6	2.485	Gd1-O6-Ni2	109.16				
	Ni2-O3	2.018	107.27	Gd1-O3	2.53	Gd1-O3-Ni2	107.27				
LOJMUT[8]	J value=+0.34									
	Ni1-O1	2.099	91.5	Gd1-O1	2.311		2.311	Ni-O-Gd-O	38.49		
	Ni1-O2	2.081	89.41	Gd1-O2	2.402		2.402	Ni-O-Gd-O	34.59		
	Ni1-O3	2.065	90.86	Gd1-O3	2.364		2.364	Ni-O-Gd-O	38.63		
XOFSER[9]	Jvalue=+0.54									
	Ni1-O1	2.067	94.71	Gd1-O1	2.2426			Ni-O-Gd-O	36.32	Ni-O-Gd-O	36.32
	Ni1-O3	2.042	95.55	Gd1-O3	2.242			Ni-O-Gd-O	35.86	Ni-O-Gd-O	35.85
	Ni1-O5	2.067	94.86	Gd1-O5	2.2422			Ni-O-Gd-O	36.73	Ni-O-Gd-O	36.75
	Ni1-O1'	2.067	94.71	Gd1-O1'	2.2426						

Ni1-O3'	2.042	95.55	Gd1-O3'	2.242
Ni1-O5'	2.067	94.84	Gd1-O5'	2.2422

References:

1. E. Ruiz, S. Alvarez, A. Rodríguez-Fortea, P. Alemany, Y. Pouillon, C. Massobrio, In *Magnetism: Molecules to Materials* (Eds. J.S. Miller, M. Drillon), Wiley-VCH, Weinheim, Vol. 2, p 227, 2001**.**
2. C. Desplanches, E. Ruiz, A. Rodríguez-Fortea, S. Alvarez, *J. Am. Chem. Soc.* 2002, **124**, 5197**.**
3. O. Kahn, B.J. Briat, *Chem*. *Soc*., *Faraday Trans*. *2* 1976, **72**, 268−281.
4. C. Blanchet-Boiteux, J. M. Mouesca, *Theor. Chem. Acc.* 2000, **104**, 257.
5. T. Yamaguchi, Y. Sunatsuki, M. Kojima, H. Akashi, M. Tsuchimoto, N. Re, S. Osa, N. Matsumoto, *Chem. Comm*., 2004, 1048.
6. T. Shiga, N. Ito, A. Hidaka, H. Okawa, S. Kitagawa, M. Ohba, *Inorg. Chem*., 2007, **46,** 3492.
7. Q. –Y. Chen, Q. -H. Luo, L. -M. Zheng, Z. –L. Wang, J. –T. Chen, *Inorg. Chem*., 2002, **41,** 605.
8. T. Yamaguchi, Y. Sunatsuki, H. Ishida, M. Kojima, H. Akashi, N. Re, N. Matsumoto, A. Pochaba, J. Mrozinski, *Inorg. Chem*., 2008, **47**, 5736.
9. V. Chandrasekhar, B. M. Pandian, R. Boomishankar, A. Steiner, J. J. Vittal, A. Houri, R. Clerac, *Inorg. Chem*., 2008, **47,** 4918.