Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supporting Information

Decisive Interaction Which Determines Ferro/Antiferromagnetic coupling in {3d-4f} pair: A case study on dinuclear {V-Gd} complexes

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We performed the DFT and CASSCF calculations on the complexes. The energies, spin densities and the *J* values are given in the table for the all the complexes **1**, **2** and **3**.

Table S1. DFT and CASSCF computed *J* values for parent complex 1, 2, 3 ad their model complexes.

Complex	J_{cal} (cm^{-1})			J_{exp} (cm^{-1})
	level I	*level II* DKH	*CASSCF* f^7+d^1	
1	2.2	-1.1	1.08	1.5
2	-0.7	-6.27	0.63	-2.6
Exchange	J_1	J_2		
3	0.94	-0.01	-	0.46

Table S2: DFT computed energies for dinuclear complex 1 and 2 and their model complexes.

Complexes	**Spin states**	**Energies**	***J* (cm^{-1})**	**Spin value <S**2>**	
				HS	**BS**
Complex-1	HS	-3234.602642	2.01697	20.023	13.0229
	BS	-3234.602605			
Complex-2	HS	-3390.6798	-0.707	20.0268	13.0268
	BS	-3390.679812			
Model of Complex 1					
1A	HS	-3239.161573	2.36649	20.0228	13.0227
	BS	-3239.16153			
2A Model Complex of Complex 2 with square pyramidal geometry					
	HS	-3197.55213587	-0.062	20.0278	13.0278
	BS	-3197.55213699			

Table S3. DFT computed energies for tetranuclear complex **3**

Complex	**Spin states**	**Energies**		**Spin value <S**2>**
Complex-3			***J*(cm^{-1})**	
	HS	-8320.05306815		72.0439
	BS1	-8320.05303417	0.94	44.0439
	BS2	-8320.05306866	-0.01	8.044

Figure S1. Pictorial representation of complex 1 and complex 2 with the labelling on alll the atoms to follow table S4.

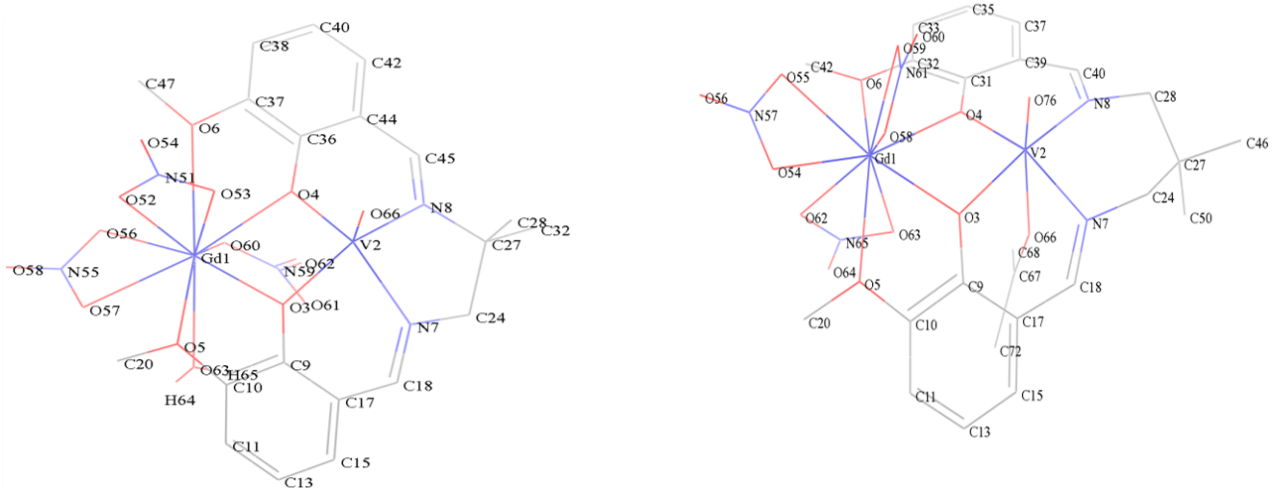


Table S4. DFT calculated spin densities on metals as well as their coordinating atoms of **1** and **2.**

Complex 1

1	Gd	7.027100
2	V	1.150492
3	O	0.002295
4	O	-0.001012
5	O	-0.000772
6	O	-0.001356
7	N	-0.015197
8	N	-0.012296
51	N	0.002196
52	O	-0.005480
53	O	-0.004272
54	O	-0.000707
55	N	0.001507
56	O	-0.003771
57	O	-0.002555
58	O	-0.000226
59	N	0.000613
61	O	-0.000655
62	O	-0.000110
63	O	-0.000748
64	H	-0.000054
65	H	0.000046
66	O	-0.150471

Complex 2

1	Gd	7.029698
2	V	1.175478
3	O	-0.002576
4	O	-0.002617
5	O	-0.001076
6	O	-0.001066
7	N	-0.027028
8	N	-0.026958
54	O	-0.003412
55	O	-0.003541
56	O	-0.000272
57	N	0.001490
58	O	-0.004900
59	O	-0.004828
60	O	-0.000638
61	N	0.001718
62	O	-0.004225
63	O	-0.004035
64	O	-0.000394
65	N	0.002386
66	O	-0.002630
67	C	0.000705
68	C	-0.000141
72	C	-0.000239
76	O	-0.174317

Figure S2. The eigenvalues of the seven f- orbitals of complex **1** and **2** computed at CASSCF level of theory.

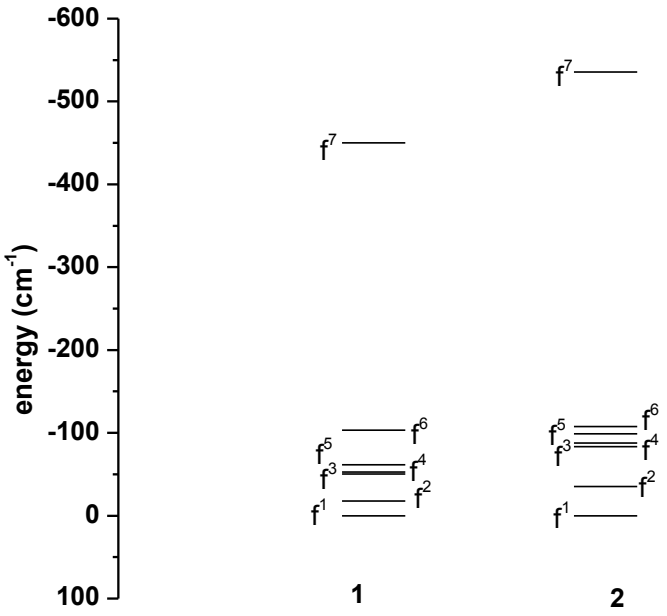


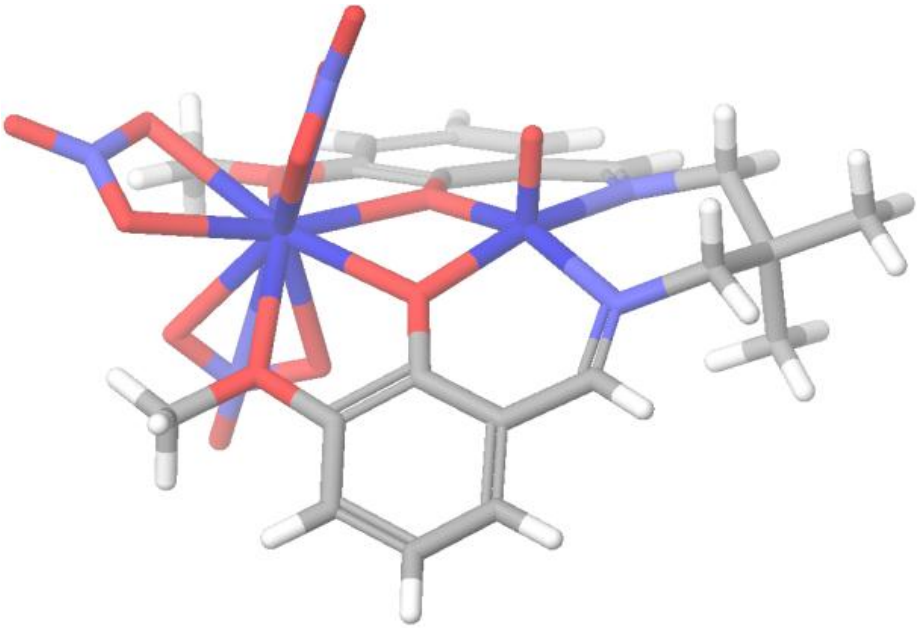
Table S5: Calculated overlap integrals for complex **1** and complex **2**

Overlap integrals values are given for complex 1 and 2. The computed overlaps are given in the table as alpha for V(IV) and beta for Gd(III). The Gd-f orbital numbers given are the MO number generated from the DFT calculations

Complex **1**	J = 2.2 cm^{-1}
Gd-f orbital	V-orbital (176)
220	0.0084
221	-0.0062
222	-0.0005
223 f_{xyz}	0.0105
224	0.0014
225	0.0024
226	0.0007

Complex **2**	J =-0.7 cm^{-1}
Gd-f orbital	V-orbital (192)
241 f_{xyz}	0.0118
242	0.0082
243	0.0114
246	-0.0020
248	0.0091
249	-0.0027
245	-0.0014

Figure S3. square pyramidal model of complex **2**



Complex 2A

Fitting

Bond Distance: Exponential function y=y0 + A*exp(R0*x)

Where y0=-0.17158, A=56707.58781, R0=-4.62901

Out of plane shift: Exponential function y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))

where A_1= 2.83956, A_2=22.32277, x0=2.33158, dx=2.56009

Dihedral Angle: Exponential function y=y0 + A*exp(R0*x)

Where y0=3.1014, A=-0.5907 R0=-0.05326

Bond Angle: Exponential function y=y0 + A*exp(R0*x)

Where y0= 9.22915, A = -3803.58059 R0 = -0.05869

Table S6. Calculated overlap integrals for different bond angles.

Bond-Angle-99	J = -2.12 cm^{-1}
Gd-f orbital	V orbital (180)
228	-0.0050
229	0.0064
230	-0.0038
232	0.0182
234	0.0211
235	-0.0087
236 f_{xyz}	-0.0216

Bond-Angle-103	J = -0.26 cm^{-1}
Gd-f orbital	V-orbital (180)
228	-0.016
229	-0.007
230	-0.006
232	0.008
233	0.002
234 f_{xyz}	-0.018
236	-0.000

Bond-Angle-112	J = 4.93 cm^{-1}
Gd-f orbital	V-orbital (180)
228	0.003
229	-0.003
230	-0.006
232	-0.002
233	-0.002
234 f_{xyz}	-0.018
236	0.000

Bond-Angle-117	J =5.19 cm^{-1}
Gd-f orbital	V-orbital (181)
228	0.001
229	0.012
230	-0.001
231	-0.001
232 f_{xyz}	0.005
233	-0.002
235	-0.002

Bond-Angle-122	J =6.12 cm^{-1}
Gd-f orbital	V-orbital (181)
228	0.00219
229	-0.009
230	-0.005
232	0.005
233 f_{xyz}	-0.007
234	0.006
235	0.006

Figure S4. Thermal variation of χT for complex 3. Same as above but simulation upto 2K.

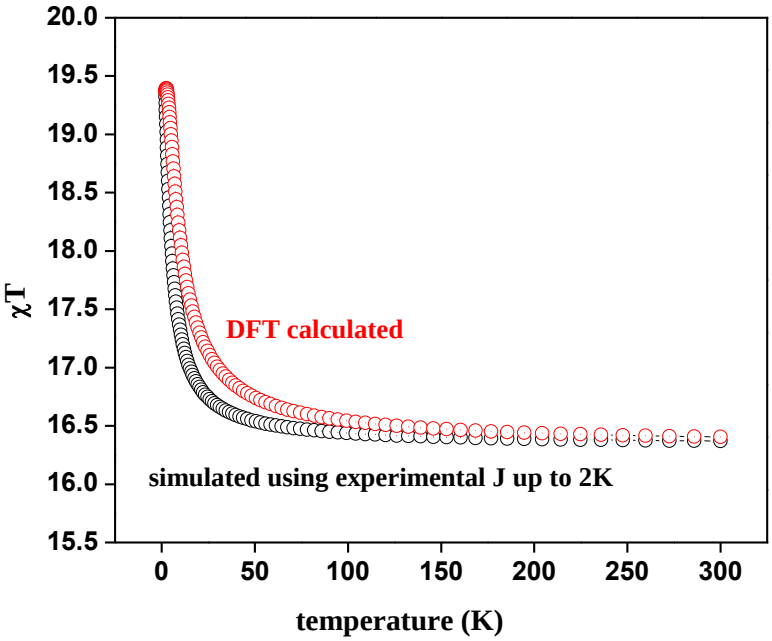


Figure S5. Spin density along with labels for the core structure of the tetrameric complex **3**.