Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Magnetic Exchange in {Gd^{III}-radical} Complexes: Method Assessment, Mechanism of Coupling and Magneto-structural Correlations

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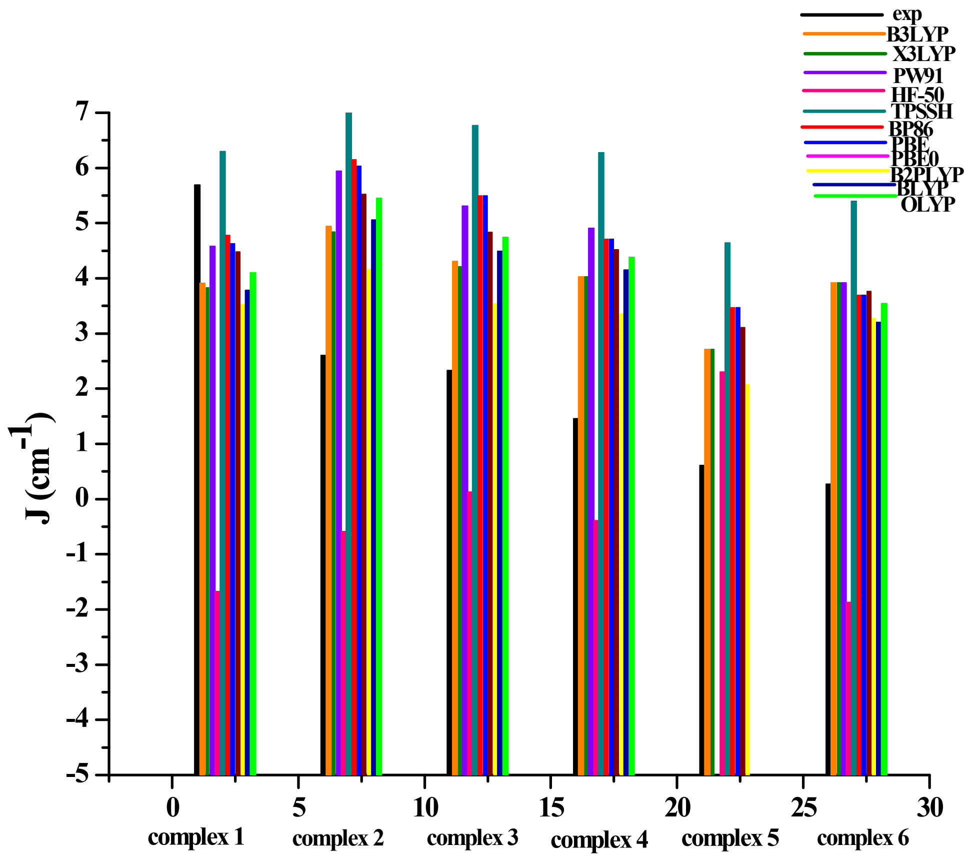

Figure S1: Graphical representation of performance of different exchange-correlations functionals for the calculations of *J* values along with experimental *J*s for complexes **1**-**6**.

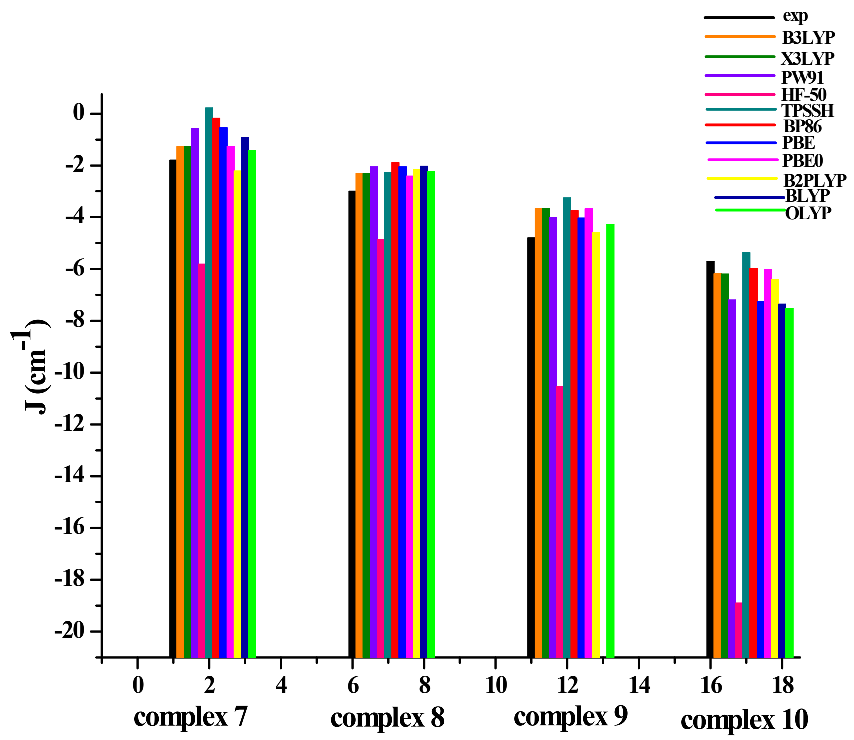

Figure S2: Graphical representation of performance of different exchange-correlations functionals for the calculations of *J* values along with experimental *J*s for complexes **7**-**10**.

Table S1: Computed overlap integrals using B3LYP functional for complex **2**:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
$4f_{z(x^2-y^2)}$	247	**0.0158**
$4f_{yz^2}$	247	0.0003
$4f_{y(3x^2-y^2)}$	247	**-0.026**
$4f_{xyz}$	247	0.0079
$4f_{z^3}$	247	-0.0071
$4f_{xyz}$	247	0.0051
$4f_{xz^2}$	247	0.0056

complex **5**:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
$4f_{xyz}$	225	**-0.010**
$4f_{y(3x^2-y^2)}$	225	**0.024**
$4f_{x(x^2-3y^2)}$	225	**-0.0138**
$4f_{z(x^2-y^2)}$	225	0.0041
$4f_{yz^2}$	225	0.0018
4fz3	225	0.0035
$4f_{xz^2}$	225	0.0028

complex 7:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
$4f_{y(3x^2-y^2)}$	107	0.008
$4f_{x(x^2-3y^2)}$	107	**0.01**
$4f_{xz^2}$	107	**0.018**
$4f_{xyz}$	107	0.0047
$4f_{yz^2}$	107	0.0069
4fz3	107	**-0.0151**
$4f_{z(x^2-y^2)}$	107	**-0.0083**

complex **9**:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
$4f_{z^3}$	194	-0.0054
$4f_{xz^2}$	194	**0.0156**
$4f_{yz^2}$	194	**0.0287**
$4f_{xyz}$	194	-0.0073
$4f_{x(x^2-3y^2)}$	194	-0.0071
$4f_{z(x^2-y^2)}$	194	**0.01474**
$4f_{y(3x^2-y^2)}$	194	**0.0174**

Table S2: Computed overlap integrals for complex **3** using

I. B3LYP functional:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
131	244	0.004
132	244	**-0.004**
133	244	**0.006**
134	244	-0.002
135	244	0.003
136	244	**-0.006**
137	244	0.00007832

II. B2PLYP functional:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
130	244	0.004
131	244	**-0.004**
132	244	**0.004**
133	244	0.006
134	244	-0.002
135	244	**0.003**
136	244	-0.006

III. X3LYP functional:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
123	244	0.029
124	244	**-0.007**
125	244	**-0.006**
126	244	-0.0005
127	244	0.00019
128	244	**-0.008**
129	244	-0.0019

IV. TPSSh functional:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
122	245	-0.02
123	245	**0.003**
124	245	**-0.001**
125	245	0.0002
126	245	0.00008
127	245	**0.005**
128	245	-0.00001

V. HF-50 functional:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
224	245	-0.025
225	245	**0.007**
226	245	**-0.007**
227	245	-0.018
229	245	0.02
230	245	**0.01**
231	245	-0.0035

VI. BP86:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
119	245	-0.001
120	245	**-0.03**
121	245	**0.01**
122	245	0.004
123	245	-0.005
124	245	**0.002**
125	245	0.002

VII: PBE

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
119	245	-0.0004
120	245	**-0.03**
121	245	**0.01**
122	245	0.005
123	245	-0.005
124	245	**-0.002**
125	245	0.002

VIII. PBE0:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
123	244	-0.01
124	244	**0.03**
125	244	**0.002**
126	244	-0.0003
127	244	-0.003
128	244	**-0.003**
129	244	0.002

IX. BLYP:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
119	245	-0.002
120	245	**0.03**
121	245	**0.01**
122	245	0.003
123	245	-0.006
124	245	**-0.003**
125	245	0.002

X.PW91:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
119	245	-0.0008
120	245	**-0.03**
121	245	**0.01**
122	245	0.004
123	245	-0.005
124	245	**0.002**
125	245	0.001

XI.OLYP:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
117	245	-0.03
118	245	**-0.01**
119	245	**0.004**
120	245	0.01
121	245	-0.004
122	245	**0.0006**
123	245	**0.0006**

XII. HF30:

type of 4f orbital on Gd(III)	π* orbital on radical	value of S
130	245	-0.0001
131	245	**0.00003**
132	245	**0.0003**
133	245	-0.00003
134	245	-0.0003
135	245	**0.0001**
136	245	-0.0001

Table S3: Computed spin density values using different functionals for complexes **1-10**:

complex **2**:

functional	Gd1	O45	N48	C58	N49	O46	<S**2>
B2PLYP	7.037	0.136	0.409	-0.359	0.310	0.543	20.1263
BP86	7.037	0.174	0.252	-0.089	0.239	0.404	20.0192
PBE0	7.042	0.159	0.309	-0.212	0.276	0.476	20.0547
PBE	7.037	0.175	0.253	-0.089	0.239	0.405	20.0197
B3LYP	7.031	0.161	0.292	-0.178	0.269	0.462	20.0432
HF50	6.999	0.158	0.292	-0.182	0.253	0.471	20.0448
TPSSh	7.055	0.164	0.292	-0.170	0.269	0.447	20.0389
X3LYP	7.031	0.160	0.296	-0.187	0.272	0.467	20.0462
PW91	7.036	0.175	0.253	-0.091	0.240	0.406	20.0198
BLYP	7.026	0.176	0.251	-0.087	0.240	0.406	20.0180
OLYP	7.016	0.179	0.254	-0.095	0.236	0.417	20.0232
HF-40	6.978	0.168	0.266	-0.132	0.234	0.436	20.0273

complex **5**:

functional	Gd1	O44	N46	C48	N47	O45	<S**2>
B2PLYP	7.036	0.149	0.410	-0.341	0.312	0.537	20.1508
BP86	7.035	0.181	0.249	-0.090	0.235	0.397	20.0198
PBE0	7.040	0.168	0.307	-0.203	0.275	0.469	20.0588
PBE	7.035	0.183	0.250	-0.091	0.235	0.397	20.0204
B3LYP	7.029	0.170	0.289	-0.172	0.267	0.456	20.0461
HF50	6.997	0.167	0.288	-0.178	0.247	0.470	20.0491
TPSSh	7.054	0.173	0.289	-0.166	0.265	0.441	20.0412
X3LYP	7.029	0.170	0.289	-0.172	0.267	0.456	20.0461
PW91	7.034	0.182	0.250	-0.092	0.235	0.399	20.0205
BLYP	7.024	0.182	0.248	-0.088	0.235	0.400	20.0187
OLYP	7.013	0.188	0.251	-0.096	0.232	0.409	20.0240
HF-40	6.979	0.176	0.260	-0.130	0.227	0.434	20.0298

complex **7**:

functional	Gd1	O2	N4	C9	N5	O3
B2PLYP	7.036	0.128	0.401	-0.305	0.241	0.577
BP86	7.044	0.141	0.261	-0.063	0.209	0.406
PBE0	7.042	0.137	0.313	-0.168	0.230	0.492
PBE	7.043	0.142	0.263	-0.063	0.210	0.406
B3LYP	7.03	0.140	0.300	-0.140	0.230	0.480
HF50	7.005	0.136	0.3000	-0.141	0.203	0.488
TPSSh	7.059	0.135	0.299	-0.133	0.228	0.458
X3LYP	7.034	0.136	0.296	-0.141	0.227	0.476
PW91	7.043	0.141	0.262	-0.065	0.210	0.409
BLYP	7.033	0.141	0.260	-0.063	0.210	0.41
OLYP	7.021	0.148	0.262	-0.066	0.206	0.421
HF-40	6.993	0.139	0.275	-0.093	0.190	0.447

complex **9**:

functional	Gd1	O44	N46	C51	N45	<S**2>
B2PLYP	7.029	0.466	0.526	-0.242	0.151	20.0500
BP86	7.031	0.414	0.419	-0.089	0.072	20.0144
PBE0	7.036	0.447	0.474	-0.149	0.091	20.0239
PBE	7.033	0.415	0.419	-0.089	0.071	20.0149
B3LYP	7.025	0.440	0.462	-0.128	0.082	20.0195
HF50	6.988	0.465	0.416	-0.103	0.080	20.0121
TPSSh	7.047	0.431	0.468	-0.136	0.084	20.0214
X3LYP	7.025	0.440	0.462	-0.128	0.082	20.0195
PW91	7.030	0.415	0.421	-0.090	0.072	20.0148
BLYP	7.020	0.415	0.418	-0.085	0.071	20.0130
OLYP	7.010	0.426	0.423	-0.094	0.075	20.0174
HF-40	6.970	0.448	0.383	-0.073	0.075	20.0076

complex **3**:

functional	Gd1	O46	N44	C54	N68	<S**2>
B2PLYP	7.034	0.121	0.390	-0.322	0.332	20.1285
BP86	7.037	0.140	0.225	-0.071	0.244	20.0194
PBE0	7.039	0.139	0.290	-0.189	0.301	20.0538
PBE	7.036	0.153	0.235	-0.085	0.264	20.0198
B3LYP	7.029	0.140	0.272	-0.160	0.294	20.0425
HF50	6.996	0.140	0.275	-0.163	0.268	20.0449
TPSSh	7.052	0.143	0.274	-0.155	0.294	20.0386
X3LYP	7.028	0.139	0.277	-0.167	0.297	20.0454
PW91	7.034	0.153	0.235	-0.086	0.264	20.0199
BLYP	7.025	0.153	0.233	-0.083	0.264	20.0181
OLYP	7.015	0.157	0.236	-0.089	0.261	20.0233
HF-40	6.979	0.149	0.250	-0.120	0.248	20.0277

complex **1**:

functional	Gd1	O60	N55	C26	N54	<S**2>
B2PLYP	7.032	0.153	0.398	-0.329	0.319	20.1286
BP86	7.031	0.180	0.251	-0.085	0.242	20.0191
PBE0	7.035	0.169	0.305	-0.195	0.282	20.0550
PBE	7.031	0.390	0.252	-0.086	0.242	20.0197
B3LYP	7.024	0.170	0.288	-0.165	0.274	20.0433
HF50	6.991	0.167	0.288	-0.171	0.255	20.0458
TPSSh	7.049	0.173	0.289	-0.158	0.273	20.0387
X3LYP	7.024	0.169	0.292	-0.172	0.277	20.0463
PW91	7.029	0.180	0.252	-0.086	0.242	20.0197
BLYP	7.019	0.393	0.249	-0.083	0.242	20.0179
OLYP	7.008	0.403	0.252	-0.089	0.238	20.0231
HF-40	6.971	0.174	0.261	-0.125	0.234	20.0276

complex **6**:

functional	Gd1	O68	N65	C11	N66	O69	<S**2>
B2PLYP	7.027	0.151	0.272	-0.155	0.291	0.462	20.0407
BP86	7.014	0.161	0.232	-0.068	0.246	0.400	20.0181
PBE0	7.037	0.149	0.289	-0.183	0.298	0.475	20.0513
PBE	7.034	0.159	0.232	-0.070	0.247	0.398	20.0195
B3LYP	7.020	0.146	0.265	-0.149	0.253	0.410	20.0105
HF50	6.993	0.149	0.274	-0.161	0.267	0.471	20.0428
TPSSh	7.05	0.154	0.274	-0.151	0.290	0.447	20.0371
X3LYP	7.027	0.150	0.276	-0.162	0.293	0.467	20.0434
PW91	7.032	0.166	0.238	-0.084	0.260	0.407	20.0194
BLYP	7.022	0.165	0.236	-0.080	0.259	0.407	20.0177
OLYP	7.011	0.171	0.239	-0.086	0.255	0.417	20.0228
HF-40	6.975	0.160	0.250	-0.119	0.246	0.436	20.0265

complex **4**:

functional	Gd1	O11	N19	C21	N20	O12	<S**2>
B2PLYP	7.033	0.132	0.401	-0.346	0.343	0.540	20.1404
BP86	7.035	0.143	0.222	-0.076	0.250	0.418	20.0191
PBE0	7.037	0.148	0.294	-0.202	0.308	0.477	20.0564
PBE	7.035	0.144	0.223	-0.0775	0.251	0.417	20.0197
B3LYP	7.027	0.149	0.275	-0.171	0.301	0.464	20.0444
X3LYP	7.027	0.149	0.275	-0.171	0.301	0.464	20.0444
PW91	7.032	0.160	0.236	-0.094	0.270	0.409	20.0202
BLYP	7.023	0.160	0.233	-0.091	0.270	0.409	20.0185
OLYP	7.013	0.165	0.237	-0.097	0.266	0.419	20.0237
HF-40	6.977	0.159	0.251	-0.128	0.254	0.439	20.0292

complex **8**:

functional	Gd1	N27	C30	N28	O20	<S**2>
B2PLYP	7.028	0.423	-0.272	0.338	0.593	20.0779
BP86	7.026	0.316	-0.081	0.292	0.469	20.0172
PBE0	7.032	0.345	-0.159	0.319	0.535	20.0352
PBE	7.026	0.317	-0.081	0.293	0.469	20.0177
B3LYP	7.022	0.325	-0.134	0.316	0.523	20.0284
HF50	6.988	0.306	-0.111	0.279	0.538	20.0233
TPSSh	7.044	0.345	-0.142	0.317	0.510	20.0292
X3LYP	7.022	0.327	-0.140	0.318	0.527	20.0298
PW91	7.025	0.317	-0.083	0.294	0.472	20.0177
BLYP	7.016	0.309	-0.078	0.295	0.472	20.0158
OLYP	7.003	0.323	-0.010	0.293	0.484	20.0207
HF-40	6.969	0.291	-0.073	0.261	0.506	20.0148

complex **10**:

functional	Gd1	O3	C54	C55	O2	<S**2>
B2PLYP	7.050	0.206	0.158	0.206	0.237	21.0378
BP86	7.058	0.186	0.147	0.168	0.205	21.0135
PBE0	7.063	0.197	0.153	0.184	0.222	21.0237
PBE	7.062	0.184	0.146	0.167	0.206	21.0144
B3LYP	7.049	0.195	0.148	0.178	0.220	21.0189
HF50	7.005	0.208	0.119	0.154	0.244	21.0157
TPSSh	7.074	0.190	0.150	0.183	0.214	21.0208
X3LYP	7.049	0.195	0.148	0.178	0.220	21.0189
PW91	7.060	0.184	0.147	0.170	0.206	21.0144
BLYP	7.046	0.186	0.142	0.166	0.208	21.0106
OLYP	7.035	0.191	0.144	0.170	0.213	21.0173
HF-40	6.992	0.202	0.111	0.144	0.236	21.0093

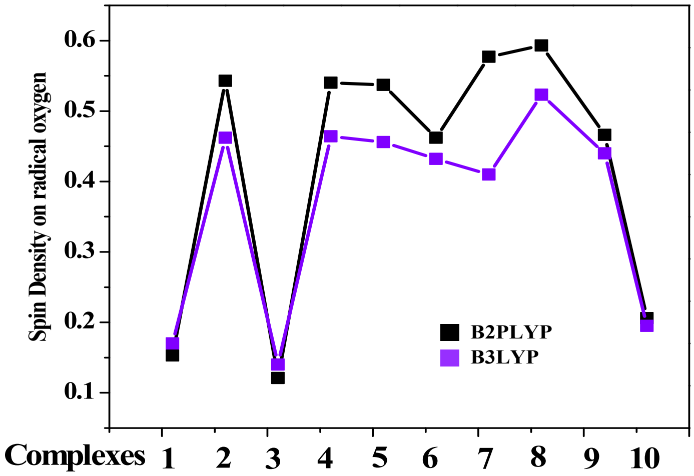

Figure S3. Graphical representation of computed spin density at the radical centres for complexes **1**-**10** by B2PLYP and B3LYP functionals.

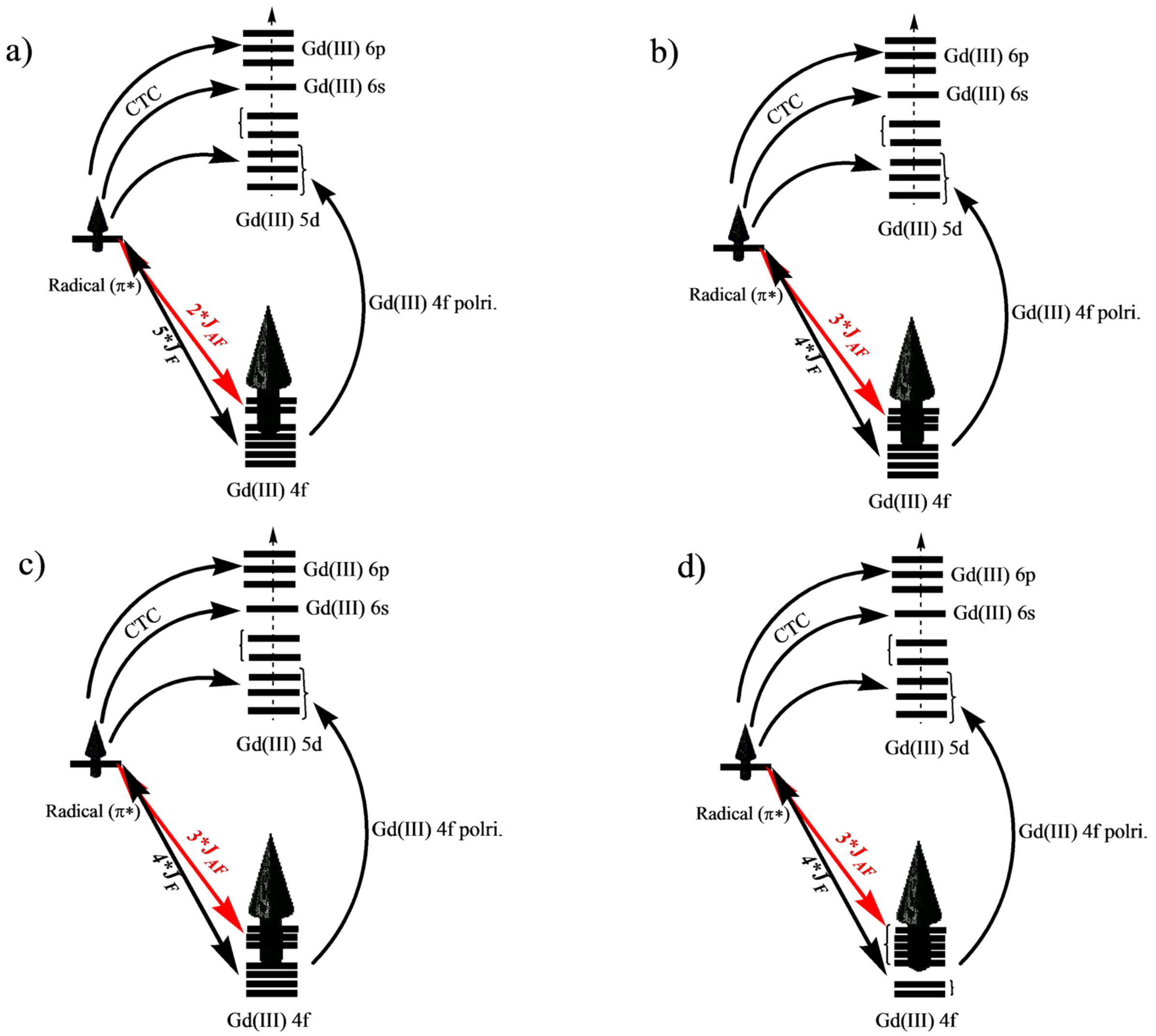

Figure S4: Schematic diagram explaining mechanism of coupling in complexes a) **2** b) **5** c) **7** d) **9**.

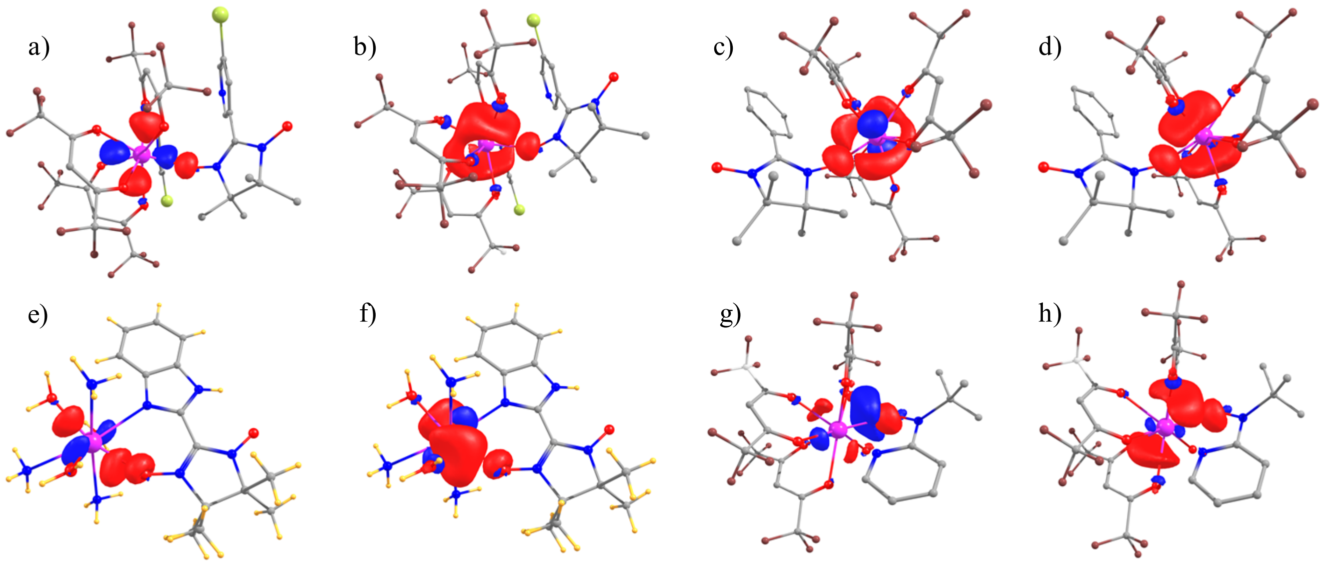

Figure S4. Second order perturbation theory donor-acceptor NBO analysis for the HS state in complex (a) **2** between Gd(d) and radical(s-p hybrid) (b) **2** between Gd(s-d hybrid) and radical (s-p hybrid) (c) **5** between Gd(s-d hybrid) and radical (s-p hybrid) (d) **5** between Gd(s-d hybrid) and radical (s-p hybrid) (e) **7** between Gd(d) and radical(s-p hybrid) (f) **7** between Gd(s-d hybrid) and radical(s-p hybrid) g) **9** between Gd(p-d hybrid) and radical(s-p hybrid) h) **9** between Gd(s-d hybrid) and radical(s-p hybrid).

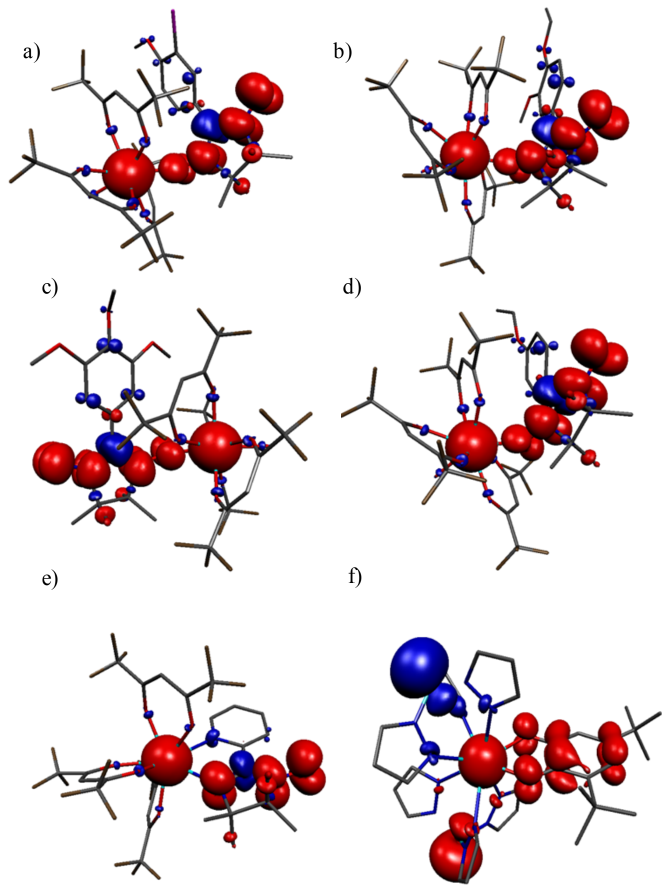

Figure S5. Spin density plots for complexes (a) **1** (b) **3** (c) **4** (d) **6** (e) **8** and (f) **10** in their High spin state.

Table S3: Second order perturbation theory NBO analysis on complex **2**,**5**,**7**,**9**:

Complex **2**:

Donor nbo	Acceptor nbo	CT interaction(Kcal/mol)
Gd(s=92.81 %,p=1.03 %,d=6.15%)	O(s=70.77 %,p=29.23 %)	96.53
O(s=36.89%,p=63.11%)	Gd(p=36.02%,d=63.69%)	4.05
O(s=43.74%,p=56.26%)	Gd(d=99.34%)	12.41
O(s=43.74%,p=56.26%)	Gd(d=99.13%)	6.95
O(s=43.74%,p=56.26%)	Gd(s=92.81%,d=6.15%)	12.22
O(s=43.74%,p=56.26%)	Gd(p=61.59%,d=36.21%)	11.46
O(s=43.74%,p=56.26%)	Gd(p=95.2%,d=4.73%)	4.15
O(s=43.74%,p=56.26%)	Gd(s=36.76%,f=58.33%)	5.07
O(s=43.74%,p=56.26%)	Gd(s=94.69%,f=2.67%)	5.38

Complex **5**:

Donor nbo	Acceptor nbo	CT interaction(Kcal/mol)
Gd(s=71.31 %,p=1.93 %,d=26.69%)	O(s=76.26 %,p=23.74 %)	55.51
Gd(s=36.89%,p=63.11%)	O(s=17.29%,p=82.71%)	51.65
Gd(s=15.33%,d=75.46%,p=9.02%)	O(s=76.26 %,p=23.74 %)	5.53
O(s=51.70%,p=48.30%)	Gd(d=96.33%,s=2.91%)	10.08
O(s=51.70%,p=48.30%)	Gd(d=94.88%,p=2.47%)	6.04
O(s=51.70%,p=48.30%)	Gd(s=71.31%,d=26.69%)	14.71
O(s=51.70%,p=48.30%)	Gd(s=15.33%,d=75.46%)	19.27
O(s=51.70%,p=48.30%)	Gd(p=70.18%,d=29.24%)	6.53
O(s=51.70%,p=48.30%)	Gd(s=27.45%,f=54.37%)	4.56
O(s=51.70%,p=48.30%)	Gd(s=20.24%,f=41.53%)	4.64
O(s=51.70%,p=48.30%)	Gd(s=80.17%,p=15%)	6.26

Complex **7**:

Donor nbo	Acceptor nbo	CT interaction(Kcal/mol)
Gd(s=64.57 %, d=35.12 %)	O(p=99.25 %)	54.31
Gd(s=64.57 %, d=35.12 %)	O(s=75.92%,p=24.08%)	32.52
Gd(s=64.57 %, d=35.12 %)	O(s=14.90%,p=85.10%)	25.97
O(s=48.22%,p=51.78%)	Gd(d=97.07%)	6.17
O(s=48.22%,p=51.78%)	Gd(s=64.57 %, d=35.12 %)	6.08
O(s=48.22%,p=51.78%)	Gd(d=97.28%)	25.30
O(s=48.22%,p=51.78%)	Gd(s=33.89%,d=64.36%)	19.86
O(s=48.22%,p=51.78%)	Gd(p=96.41%,d=33.6%)	8.67

Complex **9**:

Donor nbo	Acceptor nbo	CT interaction(Kcal/mol)
Gd(s=72.91 %, d=26.62 %)	O(s=93.77%,p=6.23%)	44.52
Gd(s=72.91 %, d=26.62 %)	O(p=95.34%,s=4.66%)	72.81
O(s=33.25%,p=66.75%)	Gd(p=59.71%,d=40.21%)	8.41
O(s=41%,p=59%)	Gd(s=72.91 %, d=26.62 %)	9.66
O(s=41%,p=59%)	Gd(p=59.71%,d=40.21%)	24.41

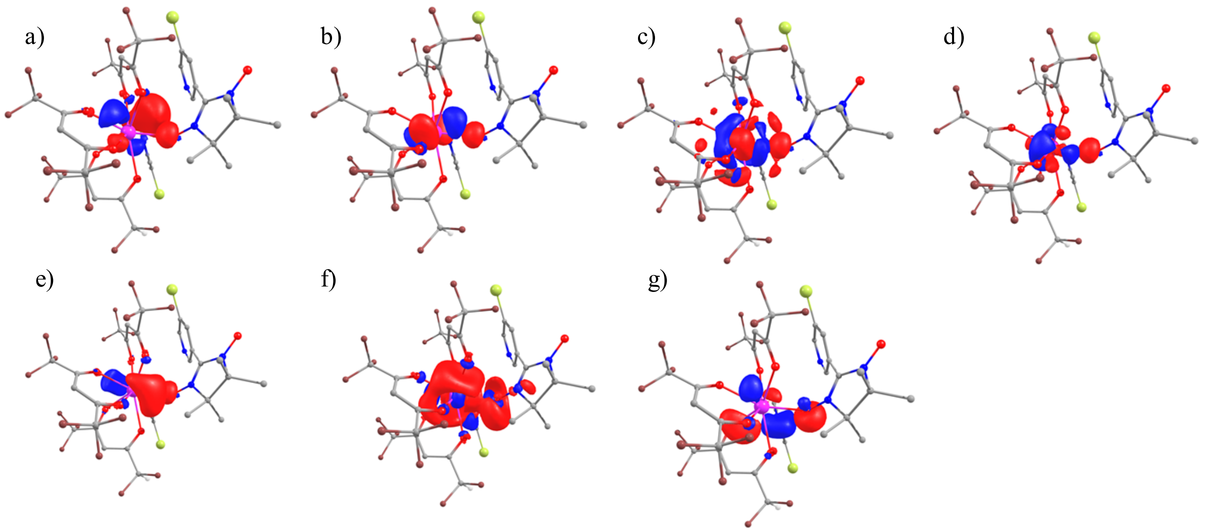

Figure S6: Second order perturbation theory donor-acceptor NBO analysis for the HS state in complex (a) **2** between Gd(p-d hybrid) and radical(s-p hybrid) (b) **2** between Gd(d) and radical (s-p hybrid) (c) **2** between Gd(s-f hybrid) and radical (s-p hybrid) (d) **2** between Gd(s-f hybrid) and radical (s-p hybrid) (e) **2** between Gd(p-d hybrid) and radical(s-p hybrid) (f) **2** between Gd(s-p-d hybrid) and radical(s-p hybrid){noteworthy in this case CT occurs from Gd to radical} (g) 2 between Gd(p-d hybrid) and radical(s-p hybrid)

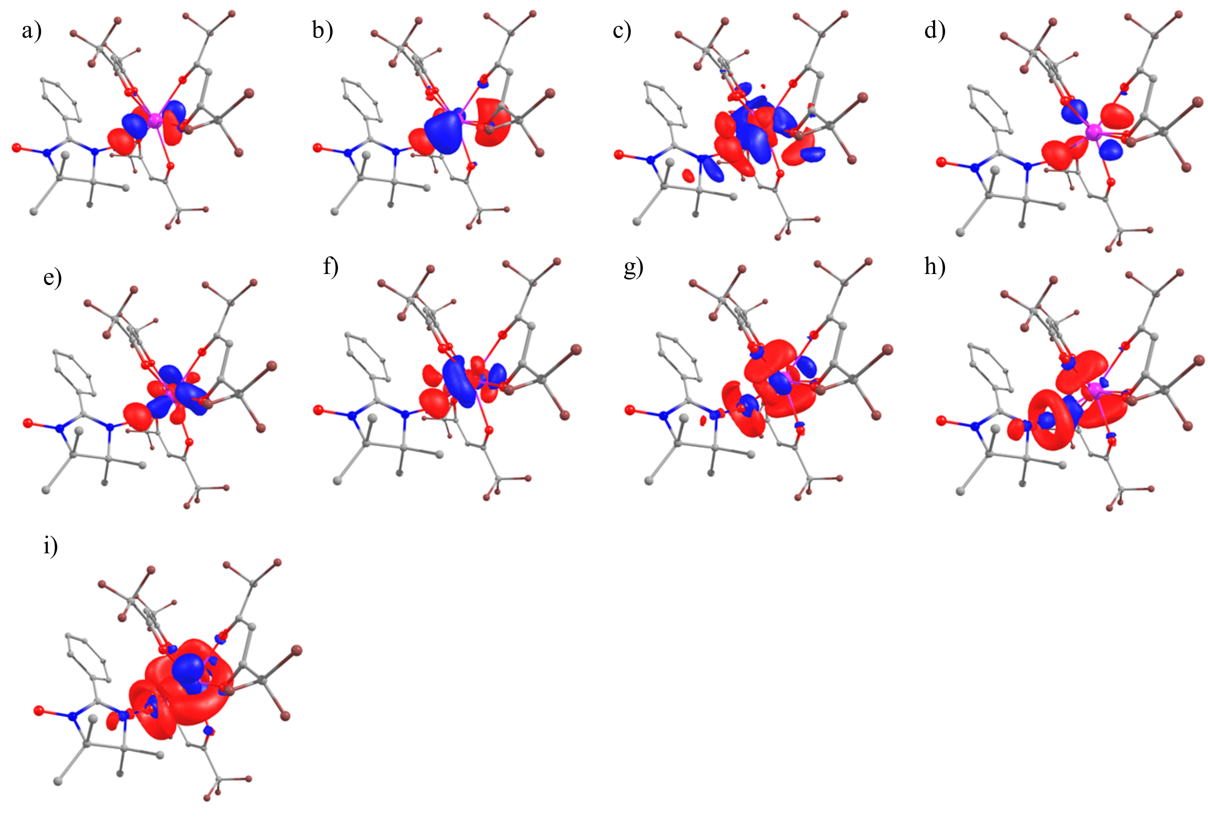

Figure S7: Second order perturbation theory donor-acceptor NBO analysis for the HS state in complex (a) **5** between Gd(s-d hybrid) and radical(s-p hybrid) (b) **5** between Gd(p-d hybrid) and radical (s-p hybrid) (c) **5** between Gd(s-p hybrid) and radical (s-p hybrid) (d) **5** between Gd(p-d hybrid) and radical (s-p hybrid) (e) **5** between Gd(s-f hybrid) and radical(s-p hybrid) (f)**5** between Gd(s-f hybrid) and radical(s-p hybrid) (g) **5** between Gd(s-p-d hybrid) and radical(s-p hybrid) {noteworthy in this case CT occurs from Gd to radical} (h) 5 between Gd(s-p hybrid) and radical(s-p hybrid) {noteworthy in this case CT occurs from Gd to radical} (i) **5** between Gd(s-p-d hybrid) and radical(s-p hybrid)

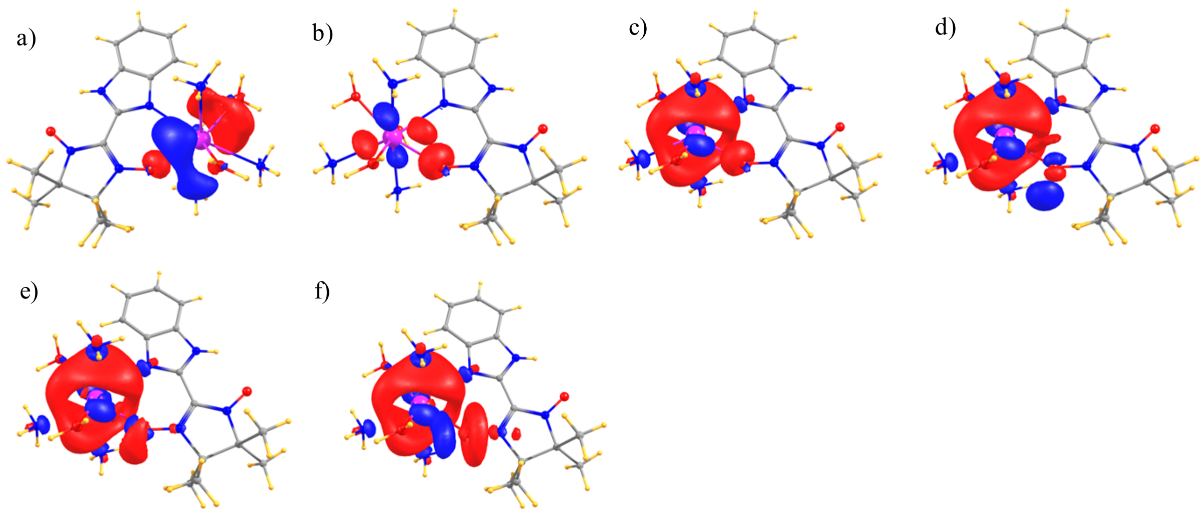

Figure S8: Second order perturbation theory donor-acceptor NBO analysis for the HS state in complex (a) **7** between Gd(p-d hybrid) and radical(s-p hybrid) (b) **7** between Gd(d) and radical (s-p hybrid) (c) **7** between Gd(s-d hybrid) and radical (s-p hybrid) (d) **7** between Gd(s-d hybrid) and radical (p) {noteworthy in this case CT occurs from Gd to radical} (e) 7 between Gd(s-d hybrid) and radical(s-p hybrid) {noteworthy in this case CT occurs from Gd to radical} (f)7 between Gd(s-d hybrid) and radical(s-p hybrid) {noteworthy in this case CT occurs from Gd to radical}

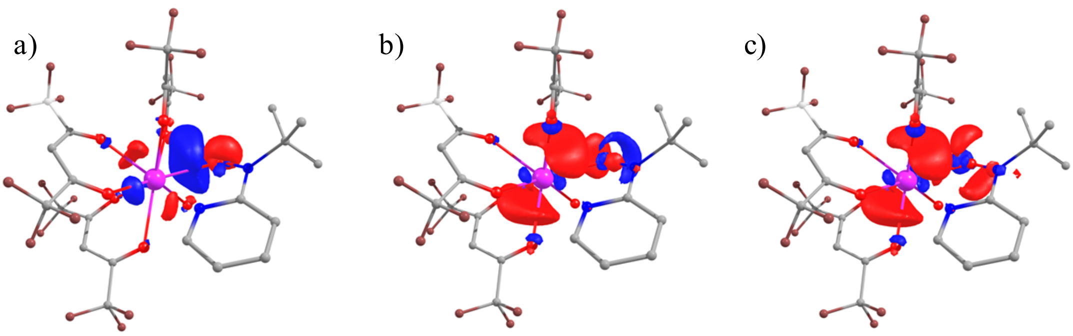

Figure S9: Second order perturbation theory donor-acceptor NBO analysis for the HS state in complex (a) **9** between Gd(p-d hybrid) and radical(s-p hybrid) (b) **9** between Gd(s-d hybrid) and radical (s-p hybrid) {noteworthy in this case CT occurs from Gd to radical} (c) 9 between Gd(s-d hybrid) and radical (s-p hybrid) {noteworthy in this case CT occurs from Gd to radical}

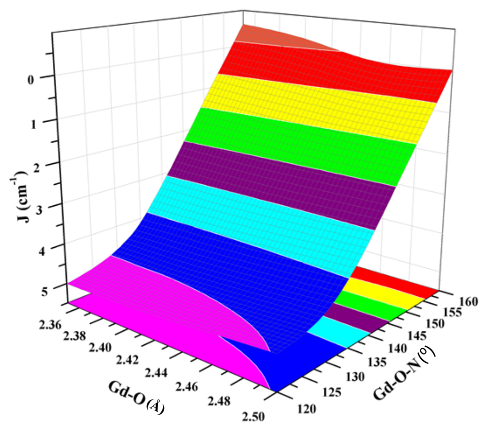

Figure S10. Magneto-structural correlation developed by varying Gd-O distance (Å) and Gd-O-N angle (°) simultaneously on complex **3**