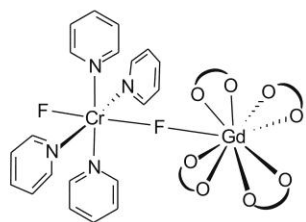# Electronic Supporting Information
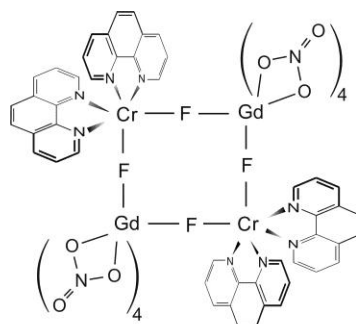
Angular dependence of the exchange interaction in fluoride-bridged Gd^{III}-Cr^{III} complexes

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Molecular connectivities

1: *trans*-[CrF$_2$(py)$_4$]Gd(hfac)$_4$

2: *cyclo*-{*cis*-[CrF$_2$(phen)$_2$]Gd(NO$_3$)$_4$}$_2$
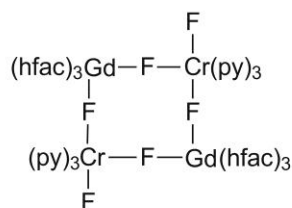
3: *cyclo*-{*mer*-[CrF$_3$(py)$_3$]Gd(hfac)$_3$}$_2$
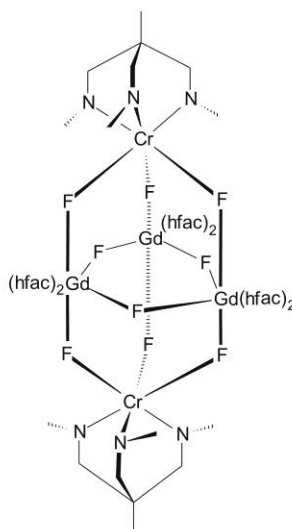
4: {*fac*-[CrF$_3$(Me$_3$tame)]}$_2$Gd$_3$(hfac)$_6$}$_2$

Scheme S1. Molecular connectivities for complexes **1-4**.

Electronic Supporting Information

Synthesis

[Gd(hfac)$_3$(H$_2$O)$_2$] and *trans*-[CrF$_2$(py)$_4$]NO$_3$ were synthesized as described in the literature.[i,ii] **1** was synthesized similarly to the isostructural Dy compound.[iii] To a solution of *trans*-[CrF$_2$(py)$_4$]NO$_3$ (1.2 g, 2.6 mmol) in chloroform (25 ml) was added a solution of one equivalent [Gd(hfac)$_3$(H$_2$O)$_2$] (2.1 g, 2.6 mmol) in chloroform (40 ml). Red-violet, block-shaped crystals of [Gd(hfac)$_4$–CrF$_2$(py)$_4$]·0.35CHCl$_3$ (**1**) were filtered off after 1 day and washed with successive aliquots of chloroform. The samples were stored in closed vials in a freezer to suppress solvent loss. Yield: 1.7 g; 46% (based on Cr), Anal. calc. (found) for (C$_{40}$H$_{24}$CrGdF$_{26}$N$_4$O$_8$)·0.35(CHCl$_3$): C: 33.8 % (33.43 %), H: 1.71 % (1.45 %), N: 3.91 % (4.01 %).

Crystallography

Single-crystal X-ray diffraction data were collected at 122 K using a Nonius Kappa CCD area-detector diffractometer with Mo Ka radiation ($\lambda = 0.71073$ Å) equipped with an Oxford Cryostreams low-temperature device. The structures were solved using direct methods (SHELXS97) and refined using the SHELXL97 software package. (G. M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112-122.) All non-hydrogen atoms were refined anisotropically except for those of the co-crystallized CHCl$_3$, whereas hydrogen atoms were fixed. CCDC-921006 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Database via www.ccdc.cam.uk/data_request/cif.
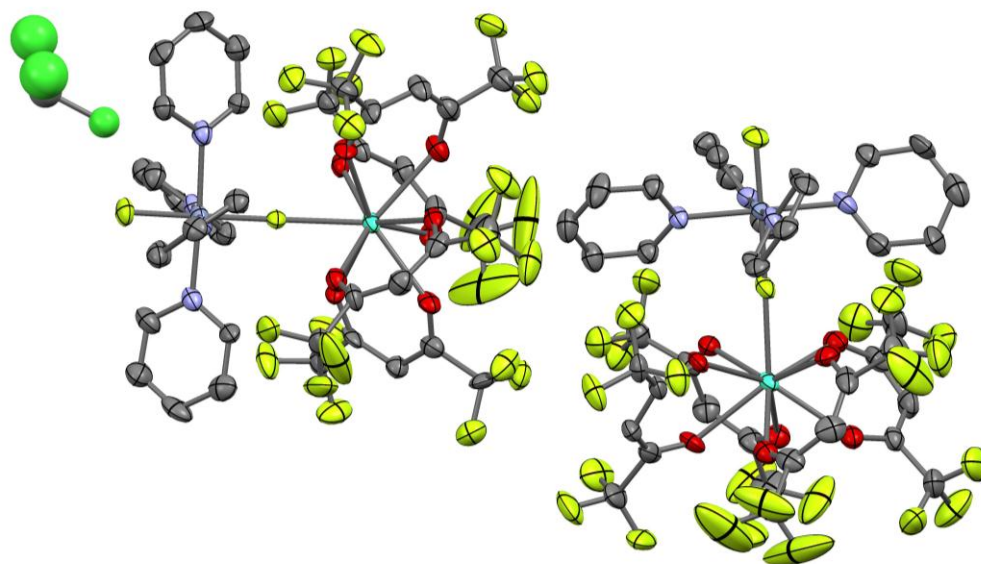

Fig. S1. Thermal ellipsoid plot (50 % probability level) of the asymmetric unit of **1**. Colour code: Gd, turquoise; Cr, dark blue; Cl, light green; F, yellow; O, red; N, blue; C, grey. Hydrogen atoms have been omitted for clarity.

Electronic Supporting Information

Table S1. Crystallographic data for **1**.

	1
Formula	$(C_{40}H_{24}CrGdF_{26}N_4O_8)\cdot0.35(CHCl_3)$
M_r	1433.66
Color, shape	Pink, prism
crystal size/mm	$0.11 \times 0.08 \times 0.04$
Crystal system	triclinic
Space group	$P\bar{1}$
T/K	122
a/Å	12.575(9)
b/Å	19.91 (3)
c/Å	21.36 (4) Å
α/°	85.44 (13)
β/°	81.52 (11)
γ/°	86.29 (10)°
V/Å^3	5264(13)
Z	4
ρ_{calc}/g cm^{-3}	1.65
F_{000}	2793
μ(Mo $K\alpha$)/mm^{-1}	1.65
θ range/°	2.0–25.2
collected reflns	150717
unique reflns	18466
params/restraints	1458/3
reflns ($I > 2\sigma(I)$)	11906
GoF	1.02
$R1^a$($I > 2.00\sigma(I)$)	0.089
$R1^a$(all data)	0.1471
$wR2^b$(all data)	0.239
max/min $\Delta\rho_r$/ e Å^{-3}	4.35 /−3.14

$^aR1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|.$ $^bwR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Electronic Supporting Information

Magnetic measurements

All magnetic measurements were performed on a Quantum Design MPMS-XL equipped with a 5 T dc magnet. The susceptibility was approximated as $\chi = M/H_{dc}$ where $H_{dc} = 1000$ Oe. Magnetization measurements were performed with fields from 1 to 5 T and at selected temperatures. All data were corrected for diamagnetic contributions from the sample (by means of Pascal constants) and from the sample holder and crystallite-immobilizing 1-octadecene oil.
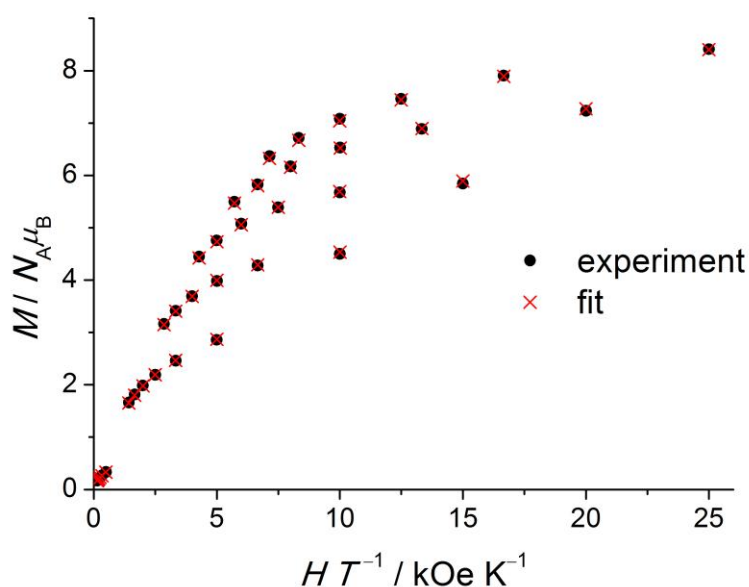

Fig. S2. Magnetization data and best-fit for **1** as described in the main text.

Inelastic neutron scattering

INS experiments on **1** were performed at the direct geometry time-of-flight spectrometer IN5 located at Institut Laue-Langevin (Grenoble, France). The time-of-flight to energy conversion and data reduction were performed using the LAMP package [iv]. Around 2 g of non-deuterated **1** was loaded in a double-wall aluminum can and placed in a standard ILL orange cryostat. The intensity was summed over the complete Q range. INS spectra were simulated with the "ins" program developed by Dr. Høgni Weihe (University of Copenhagen).

Electronic Supporting Information

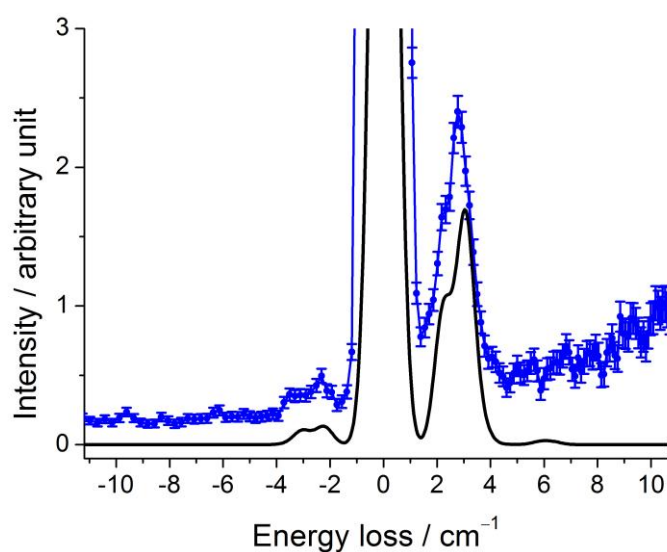**Fig. S3.** INS spectrum of **1** obtained with $\lambda_i = 4.8$ Å and $T = 1.5$ K. The calculated spectrum utilized $J = 0.87$ cm^{-1} and $D_{Cr} = 0.50$ cm^{-1}.

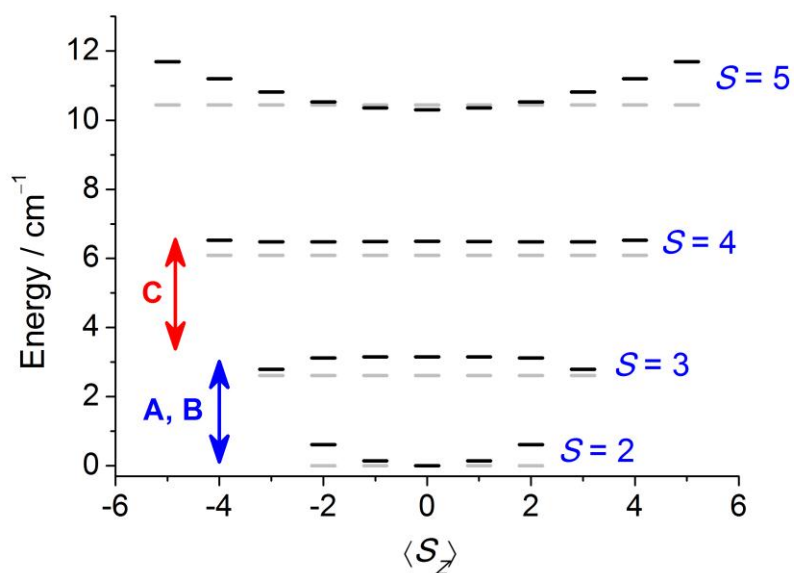**Fig. S4.** Black lines: Calculated energy levels with $J = 0.87$ cm^{-1} and $D_{Cr} = 0.50$ cm^{-1}. Grey lines: $J = 0.87$ cm^{-1} and $D_{Cr} = 0$.
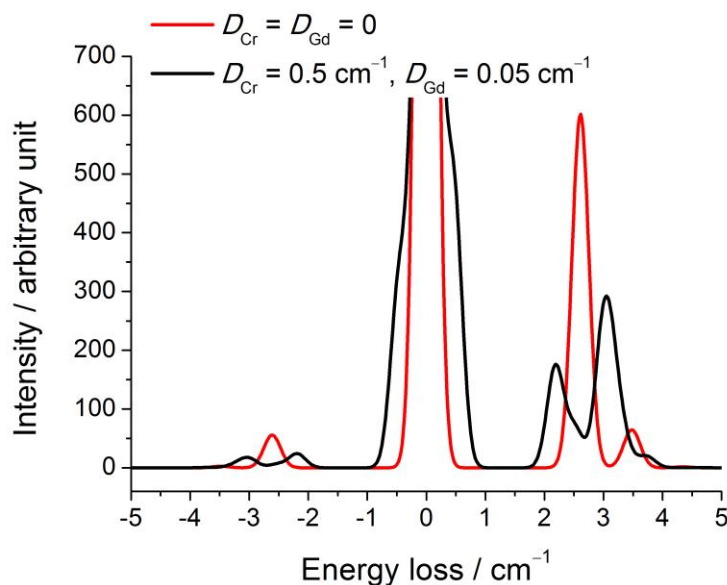
Electronic Supporting Information

Fig. S5. Calculated INS spectra with and without inclusion of the zero-field splitting terms for Cr[III] and Gd[III]. In both cases is $J = 0.87$ cm^{-1}.

Computational Details

The spin Hamiltonian which is used for to estimate the magnetic interaction between Cr[III] and Gd[III] ions is described here,

$$\hat{H} = J \cdot S_{Gd} \cdot S_{Cr}$$

Here J is the isotropic exchange coupling constant and S_{Gd} and S_{Cr} are the spins on Gd[III] (S=7/2) and Cr[III] (S=3/2) atoms respectively. The DFT calculations combined with Broken Symmetry (BS) approach[v] has been employed to compute the J values. The BS method has a proven record of yielding good numerical estimates of J constants for a variety of complexes.[vi-vii] A detailed technical discussion on computational details on the evaluation of J values using broken symmetry approach on dinuclear as well polynuclear complexes can be found elsewhere.[viii] We have performed most of calculations using the Gaussian 09 suite of programs.[ix] We have employed a hybrid B3LYP functional[x] along with a double-zeta quality basis set employing Cundari-Stevens (CS) relativistic effective core potential on Gd atom[xi] and TZV basis set on Cr[xii] and the rest of the atoms. A comprehensive method assessment performed earlier on {Cu-Gd} complexes by us, reveal that this combination yield good estimate of the J constants. A very tight SCF (1x10^{-8}Eh) convergence has been employed throughout. All magneto-structural calculations have been performed by varying the specific structural parameters and performing single point calculations on the modified structure.

Electronic Supporting Information

Table S2. DFT computed energies of high spin (HS) and broken symmetry (BS) state, $<S^2>$ values for the parent dinuclear {Cr-Gd} complex.

Complex	Total Energy		$<S^2>$ values		J values / cm^{-1}
	HS	BS	HS	BS	
1	-6112.56625531	-6112.56630034	30.0279	9.0280	0.82

Table S3. DFT computed spin densities on **1** in HS and the BS states. Atom numbers refer to the numbering provided in the picture of **1** below:
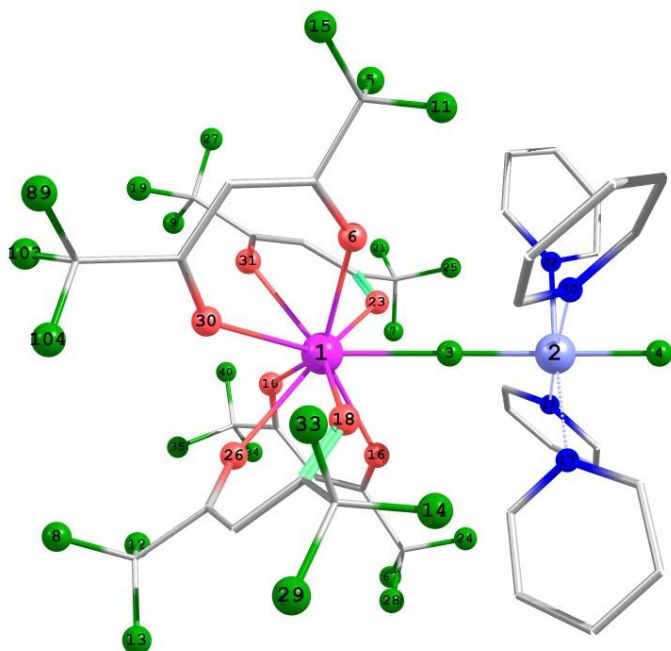
1	Gd	7.028167		1	Gd	7.027730
2	Cr	3.090067		2	Cr	-3.092583
3	F	0.016876		3	F	-0.017468
4	F	0.033375		4	F	-0.033694

Electronic Supporting Information

5	F	0.000008		5	F	0.000007
6	O	-0.003007		6	O	-0.002844
7	F	-0.000007		7	F	-0.000007
8	F	-0.000029		8	F	-0.000026
9	F	-0.000041		9	F	-0.000039
10	O	-0.001783		10	O	-0.001848
11	F	0.000054		11	F	0.000017
12	F	0.000006		12	F	0.000006
13	F	-0.000014		13	F	-0.000017
14	F	0.000043		14	F	0.000008
15	F	-0.000042		15	F	-0.000048
16	O	-0.002811		16	O	-0.002713
17	N	-0.068182		17	N	0.068004
18	O	-0.002751		18	O	-0.002649
19	F	0.000007		19	F	0.000007
20	N	-0.069340		20	N	0.069222
21	F	-0.000034		21	F	-0.000038
22	N	-0.069563		22	N	0.069421
23	O	-0.002394		23	O	-0.002205
24	F	0.000050		24	F	0.000010
25	F	0.000049		25	F	0.000011
26	O	-0.001977		26	O	-0.002057
27	F	0.000001		27	F	-0.000002
28	F	0.000010		28	F	0.000007
29	F	-0.000037		29	F	-0.000042
30	O	-0.002010		30	O	-0.002100
31	O	-0.001968		31	O	-0.002067
32	N	-0.073187		32	N	0.073028
33	F	0.000000		33	F	-0.000001
34	F	-0.000028		34	F	-0.000029
35	F	-0.000009		35	F	-0.000007
36	C	0.021627		36	C	-0.021663
37	H	-0.000787		37	H	0.000778
38	C	0.020477		38	C	-0.020440
39	H	-0.000996		39	H	0.000894
40	F	0.000028		40	F	0.000028
41	C	0.022747		41	C	-0.022799
42	H	0.000171		42	H	-0.000212
43	C	0.000395		43	C	0.000379
44	H	0.000013		44	H	0.000008
45	C	-0.000494		45	C	-0.000493
46	C	-0.000492		46	C	-0.000494
47	C	0.000294		47	C	0.000351
48	H	0.000013		48	H	0.000005
49	C	-0.013858		49	C	0.013910
50	H	0.000452		50	H	-0.000460

Electronic Supporting Information

51	C	0.000207	51	C	0.000192
52	H	0.000019	52	H	0.000014
53	C	0.017994	53	C	-0.018011
54	H	-0.000854	54	H	0.000853
55	C	-0.000768	55	C	-0.000822
56	C	-0.000577	56	C	-0.000540
57	C	0.019113	57	C	-0.019017
58	H	-0.000145	58	H	-0.000009
59	C	-0.011768	59	C	0.011805
60	H	0.000361	60	H	-0.000367
61	C	0.019619	61	C	-0.019658
62	H	-0.000837	62	H	0.000830
63	C	0.000388	63	C	0.000341
64	H	0.000016	64	H	0.000013
65	C	-0.000437	65	C	-0.000433
66	C	-0.001110	66	C	-0.001206
67	F	-0.000035	67	F	-0.000045
68	C	-0.000993	68	C	-0.001046
69	C	-0.001028	69	C	-0.001062
70	C	-0.012484	70	C	0.012499
71	H	0.000364	71	H	-0.000368
72	C	-0.011089	72	C	0.011109
73	H	0.000464	73	H	-0.000465
74	C	0.021109	74	C	-0.020984
75	H	-0.000468	75	H	0.000293
76	C	-0.000052	76	C	-0.000051
77	C	-0.000031	77	C	-0.000035
78	C	-0.012018	78	C	0.012040
79	H	0.000530	79	H	-0.000530
80	C	0.019019	80	C	-0.019057
81	H	-0.000981	81	H	0.000972
82	C	-0.000459	82	C	-0.000514
83	C	-0.000526	83	C	-0.000494
84	C	-0.010251	84	C	0.010273
85	H	0.000452	85	H	-0.000453
86	C	-0.011157	86	C	0.011178
87	H	0.000452	87	H	-0.000452
88	C	-0.000154	88	C	-0.000151
89	F	-0.000031	89	F	-0.000033
90	C	0.018064	90	C	-0.018078
91	H	-0.000867	91	H	0.000867
92	C	-0.011922	92	C	0.011973
93	H	0.000365	93	H	-0.000371
94	C	-0.000287	94	C	-0.000297
95	C	-0.000420	95	C	-0.000420
96	C	0.017208	96	C	-0.017227

Electronic Supporting Information

97	H	-0.000863		97	H	0.000862
98	C	0.018954		98	C	-0.018994
99	H	-0.000831		99	H	0.000822
100	C	0.021099		100	C	-0.021117
101	H	-0.001016		101	H	0.001015
102	C	-0.000453		102	C	-0.000454
103	F	-0.000004		103	F	-0.000002
104	F	0.000027		104	F	0.000026

Electronic Supporting Information

Table S4. DFT computed spin densities on metal ions and bridged fluoride ions at several different bond angles.
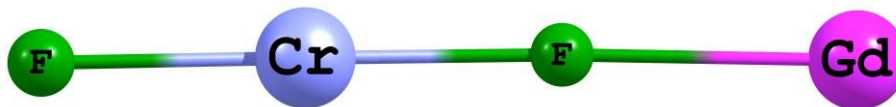

Bond Angle	Spin densities			
	Gd	Cr	F-bridging	F-Terminal
180	7.028	3.090	0.016	0.033
170	7.028	3.090	0.016	0.033
160	7.028	3.093	0.015	0.033
150	7.029	3.095	0.014	0.033
140	7.031	3.096	0.012	0.034
135	7.031	3.099	0.011	0.034

Table S5. Computed Overlap Integral for Cr-Gd pairs at higher and lower angle.

| Bond Angle-178.3			$J = 0.82$ cm^{-1}	Bond Angle-135			$J = -0.12$ cm^{-1}
Gd- forbitals	Cr (d_{xz})	Cr (d_{yz})	Cr (d_{xy})	Gd- forbitals	Cr (d_{xz})	Cr (d_{yz})	Cr (d_{xy})
	331	332	333		329	330	331
387	0.003	0.006	0.001	378	-0.003	0.001	-0.001
391	0.006	0.003	0.002	381	-0.003	0.001	-0.002
393	0.006	0.000	0.001	382	0.004	-0.001	0.003
395	-0.002	0.006	0.001	385	0.003	0.006	0.002
397	0.001	-0.007	-0.005	386	0.001	0.006	0.005
398	0.008	-0.005	0.003	387	0.004	-0.003	0.001
399	-0.005	0.004	0.002	392	-0.004	0.006	-0.003

Electronic Supporting Information

Figure S6. The four representative d-f-orbitals (a spin on left (Cr^{III}) and b on right (Gd^{III})), which show the strongest overlap at angles close to 180. The isodensity surface represented corresponds to a value of 0.03 e⁻/bohr³.
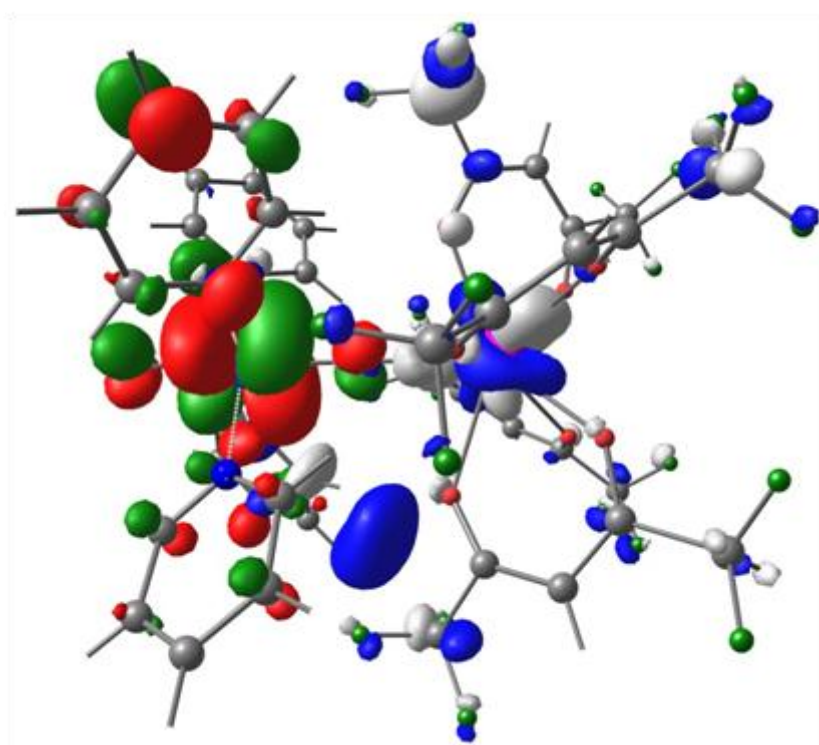
331 Cr - 398 Gd

331 Cr - 391 Gd
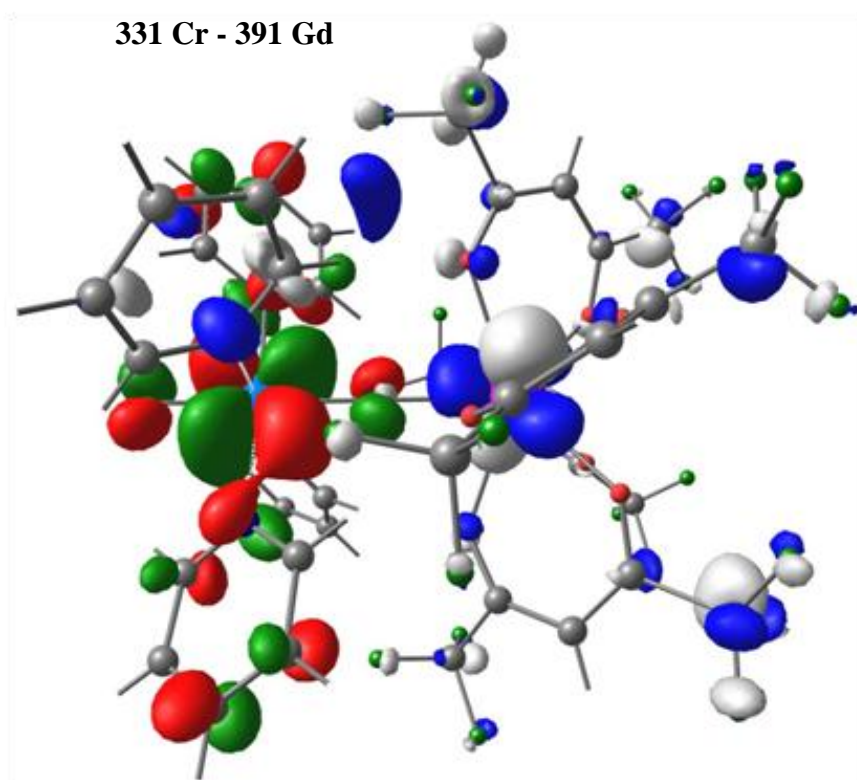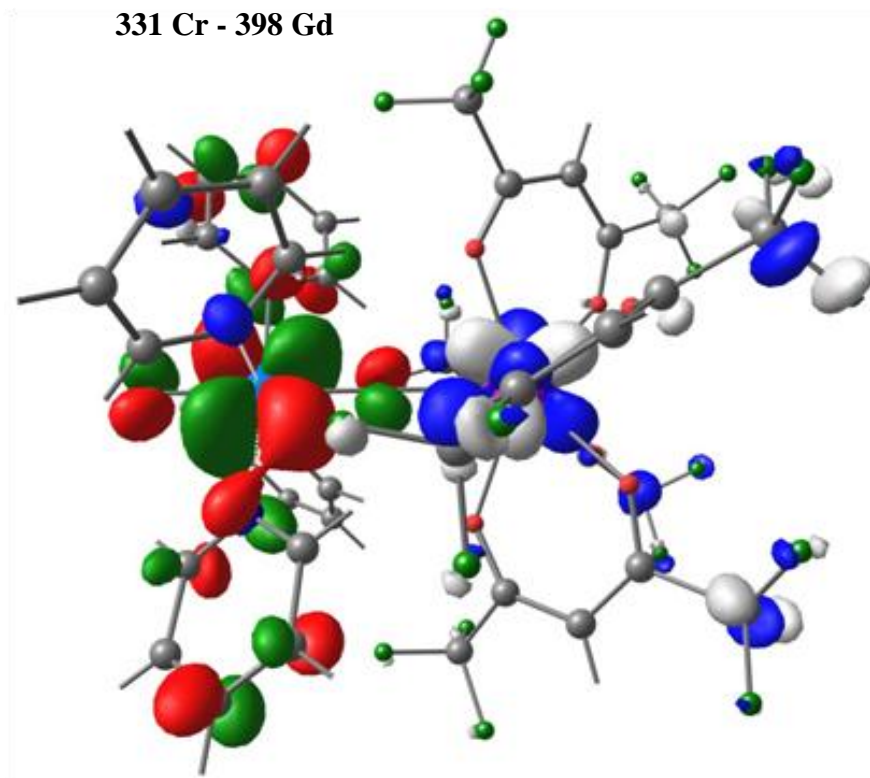
Electronic Supporting Information

331 Cr - 393 Gd
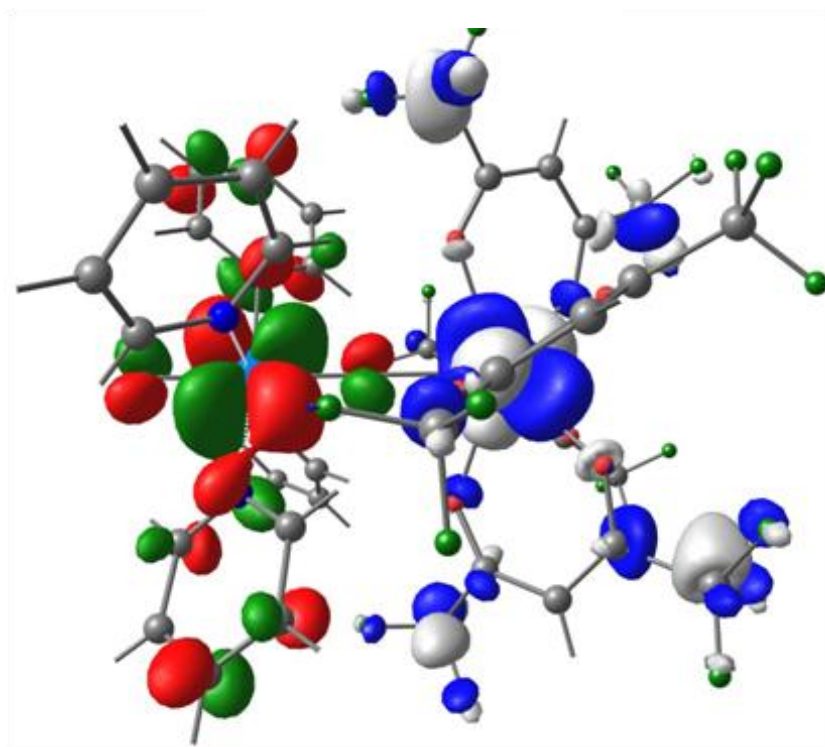
332 Cr - 397 Gd

Electronic Supporting Information

Table S6. Computed NBO occupation for the {CrGd} pair at minimum and maximum bond angles.

Orbitals	Angle 135	Angle 180
6s	0.20	0.20
4f	7.01	7.01
5d	0.38	0.35

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