Supplementary information

1. Methodology

For any binuclear system of interacting spin centres, *J* parametrises the energy difference between the coupled high-spin state (HS, all spins paired in the same direction) and the appropriate low-spin states – if the system is isotropic, the energy difference between different pairs of states should be proportional to *J* (Landé interval rule). Importantly, these states are eigenstates not only of the electronic Hamiltonian of the system but also the total spin-operator Hamiltonian ($\hat{S}^2$) and its z-component ($\hat{S}_z$). As such, the wavefunctions describing these states must be spin-adapted, limiting the computational methodology to formalisms based on a multiconfigurational description like CASSCF. An alternative at a much lower computational cost, which is the one our methodology relies on, employs density functional theory (DFT) to calculate the so-called *broken symmetry* determinants (BS, as they are not spin-adapted) to recover the spin-adapted ones following a mapping approach.[1] For systems involving more magnetic centres, the computation of the couplings is even more complicated but it has recently been generalised in DFT. [2]
The present series of compounds implies three magnetic centres (labelled Gd1, Gd2 and σ) and their coupling is described by the Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian $\hat{H}^{\mathrm{HDvV}} = -2J_{\mathrm{Gd}_1-\sigma}\hat{S}_{\mathrm{Gd}_1}\hat{S}_{\sigma} - 2J_{\sigma-\mathrm{Gd}_2}\hat{S}_{\sigma}\hat{S}_{\mathrm{Gd}_2} - 2J_{\mathrm{Gd}_1-\mathrm{Gd}_2}\hat{S}_{\mathrm{Gd}_1}\hat{S}_{\mathrm{Gd}_2}$. The decomposition of the magnetic exchange coupling is based on successive calculations of HS and BS determinants. The scheme starts with the computation of the HS state in the restricted open-shell (RO) or *quasi*-restricted open-shell formalism ($\Phi_{\mathrm{Gd}_1\text{-}\sigma\text{-}\mathrm{Gd}_2,\mathrm{RO}}$). This first determinant defines a set of unpolarised doubly occupied core orbitals and *n* singly occupied molecular orbitals (SOMOs) associated with the *n* unpaired electrons of the system. The SOMOs are then localised to define the *n* magnetic orbitals. Here, the spin quantum number associated with the gadolinium and the electron on the $5d_{z^2}$ orbital are S=7/2 and S=1/2, respectively (figure 1).

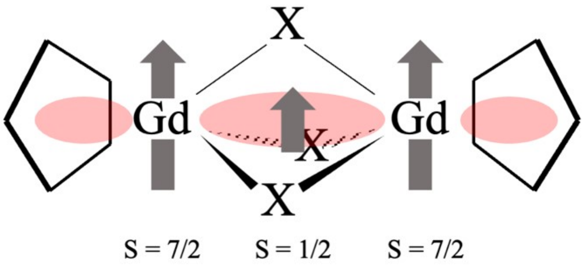

Figure S1: Schematic representation of the three spin centres (arrows) and of the σ-like orbital (red lobes)

The first contribution extracted is the direct exchange J_0 which corresponds to the exchange integral between the magnetic centres and which is ferromagnetic, favouring a parallel alignment of the spin of electrons. The extraction of this contribution in the case of 3-centre systems requires the computation of three non-optimised (NOpt) BS determinants defined from the HS RO state by flipping the spin of all electrons of one centre (labelled with a top bar), leading to $\Phi_{\mathrm{Gd}_1\text{-}\sigma\text{-}\bar{\mathrm{Gd}}_2,\mathrm{NO}}$, $\Phi_{\mathrm{Gd}_1\text{-}\bar{\sigma}\text{-}\mathrm{Gd}_2,\mathrm{NO}}$ and $\Phi_{\bar{\mathrm{Gd}}_1\text{-}\sigma\text{-}\mathrm{Gd}_2,\mathrm{NO}}$. These three determinants allow for defining three energy differences with the HS RO determinant,

$$E[\Phi_{\mathrm{Gd}_1\text{-}\sigma\text{-}\bar{\mathrm{Gd}}_2,\mathrm{NO}pt}] - E[\Phi_{\mathrm{Gd}_1\text{-}\sigma\text{-}\mathrm{Gd}_2,\mathrm{RO}}] = 4S_{\mathrm{Gd}_1}S_{\mathrm{Gd}_2}J_0^{\mathrm{Gd}_1-\mathrm{Gd}_2} + 4S_{\sigma}S_{\mathrm{Gd}_2}J_0^{\sigma-\mathrm{Gd}_2}$$

$$E[\Phi_{\mathrm{Gd}_1\text{-}\bar{\sigma}\text{-}\mathrm{Gd}_2,\mathrm{NO}pt}] - E[\Phi_{\mathrm{Gd}_1\text{-}\sigma\text{-}\mathrm{Gd}_2,\mathrm{RO}}] = 4S_{\mathrm{Gd}_1}S_{\sigma}J_0^{\mathrm{Gd}_1-\sigma} + 4S_{\sigma}S_{\mathrm{Gd}_2}J_0^{\sigma-\mathrm{Gd}_2}$$

$$E[\Phi_{\bar{\mathrm{Gd}}_1\text{-}\sigma\text{-}\mathrm{Gd}_2,\mathrm{NO}pt}] - E[\Phi_{\mathrm{Gd}_1\text{-}\sigma\text{-}\mathrm{Gd}_2,\mathrm{RO}}] = 4S_{\mathrm{Gd}_1}S_{\sigma}J_0^{\mathrm{Gd}_1-\sigma} + 4S_{\mathrm{Gd}_1}S_{\mathrm{Gd}_2}J_0^{\mathrm{Gd}_1-\mathrm{Gd}_2}$$

The individual contributions are then determined by solving this set of equations.

The computation of the spin polarisation ΔJ_{SP} contribution is substantially similar to that of the direct exchange contribution. This mechanism corresponds to the different responses of the core orbitals to the spin distribution in the different spin states. To extract this contribution, the magnetic orbitals are kept frozen (frozen magnetic orbitals – FroMag) whilst the core orbitals are relaxed in the different determinants used for the direct exchange. To extract ΔJ_{SP} only, the direct exchange must be retrieved, resulting in a set of equations with two energy differences,

$$E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\bar{\mathrm{Gd}}_2,FroMag}] - E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,FroMag}] - (E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\bar{\mathrm{Gd}}_2,\mathrm{NO}pt}] - E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,\mathrm{RO}}])$$

$$= 4S_{\mathrm{Gd}_1}S_{\mathrm{Gd}_2}\Delta J^{\mathrm{Gd}_1-\mathrm{Gd}_2}_{\mathrm{SP}} + 4S_{\sigma}S_{\mathrm{Gd}_2}\Delta J^{\sigma-\mathrm{Gd}_2}_{\mathrm{SP}}$$

$$E[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,FroMag}] - E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,FroMag}] - (E[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,\mathrm{NO}pt}] - E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,\mathrm{RO}}])$$

$$= 4S_{\mathrm{Gd}_1}S_{\sigma}\Delta J^{\mathrm{Gd}_1-\sigma}_{\mathrm{SP}} + 4S_{\sigma}S_{\mathrm{Gd}_2}\Delta J^{\sigma-\mathrm{Gd}_2}_{\mathrm{SP}}$$

$$E[\Phi_{\bar{\mathrm{Gd}}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,FroMag}] - E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,FroMag}] - (E[\Phi_{\bar{\mathrm{Gd}}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,\mathrm{NO}}] - E[\Phi_{\mathrm{Gd}_1\text{ - }\sigma\text{ - }\mathrm{Gd}_2,\mathrm{RO}}])$$

$$= 4S_{\mathrm{Gd}_1}S_{\sigma}\Delta J^{\mathrm{Gd}_1-\sigma}_{\mathrm{SP}} + 4S_{\mathrm{Gd}_1}S_{\mathrm{Gd}_2}\Delta J^{\mathrm{Gd}_1-\mathrm{Gd}_2}_{\mathrm{SP}}$$

solved similarly to the direct exchange. This contribution may be positive or negative depending on the coupling considered but in couplings based on transition metal or lanthanide ions it is expected negligible due to the local nature of the magnetic orbitals.

The last contribution corresponds to the kinetic exchange and results from the relaxation of the magnetic orbitals in the BS determinants, being then a negative contribution. Its computation relies on the extraction of the *t* and *U* Hubbard Hamiltonian parameters (see below), which proceeds by successively allowing the relaxation of one centre to another, denoted with an asterisk *. In the case of Gd to σ one gets

$$t_{\mathrm{Gd}_1\to\sigma} = \left(E\left[\Phi_{\mathrm{Gd}_1{}^*\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,\mathrm{FC}}\right] - E\left[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,\mathrm{NO}}\right]\right)\sqrt{\frac{\alpha}{1-\alpha}}$$

$$U_{\mathrm{Gd}_1\to\sigma} = \left(E\left[\Phi_{\mathrm{Gd}_1{}^*\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,\mathrm{FC}}\right] - E\left[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,\mathrm{NO}}\right]\right)\frac{2\alpha-1}{\alpha-1}$$

With,

$$\alpha = 1 - \left(\langle\hat{S}^2\rangle_{Gd_1-\bar{\sigma}-Gd_2,NO} - \langle\hat{S}^2\rangle_{Gd_1{}^*-\bar{\sigma}-Gd_2,FC}\right)$$

while the expressions for the other process (σ to Gd) are,

$$t_{\mathrm{Gd}_1\leftarrow\sigma} = \left(E\left[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}^*\text{ - }\mathrm{Gd}_2,\mathrm{FC}}\right] - E\left[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,\mathrm{NO}}\right]\right)\sqrt{\frac{\alpha}{1-\alpha}}$$

$$U_{\mathrm{Gd}_1\leftarrow\sigma} = \left(E\left[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}^*\text{ - }\mathrm{Gd}_2,\mathrm{FC}}\right] - E\left[\Phi_{\mathrm{Gd}_1\text{ - }\bar{\sigma}\text{ - }\mathrm{Gd}_2,\mathrm{NO}}\right]\right)\frac{2\alpha-1}{\alpha-1}$$

with,

$$\alpha = 1 - \left(\langle\hat{S}^2\rangle_{Gd_1-\bar{\sigma}-Gd_2,NO} - \langle\hat{S}^2\rangle_{\mathrm{Gd}_1\text{ - }\bar{\sigma}^*-Gd_2,FC}\right)$$

The kinetic exchange contribution to the Gd- σ coupling may then be determined by,

$$4S_{\mathrm{Gd}_1}S_{\sigma}\Delta J^{\mathrm{Gd}_1-\sigma}_{\mathrm{KE}} = -\left(\frac{t_{\mathrm{Gd}_1\to\sigma}{}^2}{U_{\mathrm{Gd}_1\to\sigma}} + \frac{t_{\mathrm{Gd}_1\leftarrow\sigma}{}^2}{U_{\mathrm{Gd}_1\leftarrow\sigma}}\right)$$

The on-site repulsion *U* parameter strongly depends on the definition of the magnetic orbitals, the more diffused they are, the lower the on-site repulsion is. It then results in a larger kinetic exchange. The hopping *t* integral depends more on the bridging ligand, with may ease or not the relaxation of the orbitals, regarding its length and its chemical nature.[3] Hence, a larger *t* results in a larger antiferromagnetic contribution.

Finally, the overall magnetic coupling may be defined by summing these three contributions,

$$J_{\Sigma} = J_0 + \Delta J_{\mathrm{SP}} + \Delta J_{\mathrm{KE}}$$

The reader may refer to Ref. [2] for further details about the methodology.

2. Computational details

To perform the decomposition, the B3LYP functional[4] has been employed with the 2nd order Douglas-Kroll Hamiltonian to account for relativistic effects, whilst the D3 scheme has been used for dispersion corrections.[5] DKH-def2-TZVP, DKH- def2-SVP, old-DKH-TZVP and SARC-DKH-TZVP basis sets have been employed for carbon, hydrogen, halogens and gadolinium, respectively.[6] All calculations have been performed using a modified ORCA 4.2 version.[7] The local self-consistent field (LSCF) method has been used for the selective relaxation of the orbitals.[8] The quasi-restricted open-shell formalism[9] has been employed due to the use of RIJCOSX and SARC/J approximations to speed up the calculations.

X-ray diffraction geometry has been used to perform the decomposition on the original $\mathrm{Cp^{iPr5}Gd_2I_3}$ and served as a reference structure to make the three distortions (the variations of the Gd-Gd distance, the Gd-σ-Gd angle and the Gd-Cp angle). In addition, this structure has also been used to investigate the role of the halogen substitutions without geometry optimisation, where the iodine has simply been changed with another halogen and these structures are labelled as "constrained geometry".

Geometry optimisations for the F, Cl and Br analogues were performed in gas-phase with Gaussian09d[10] suite of programs. Given the impossibility of optimising these structures with gadolinium ions, they have been substituted by yttrium, which is justified by their similar ionic radii and the fact that these derivatives are widely found to be structural analogues. B3LYP[4] hybrid functional has been employed with cc-pVTZ[11] basis set for all coordinating atoms, cc-pVDZ[4] for the rest of non-metal atoms, the Stuttgart RSC 1997[12] effective core potential (ECP) for the 28 core electrons of yttrium and the corresponding valence basis set for the remaining valence electrons, and Grimme's dispersion corrections.[13-14] Calculation of normal modes was performed by explicit calculation of the Hessian at the optimized geometry, making sure that the forces and displacements are zero and that all frequencies are positive.

3. Results

Table S1: Decomposition (J_0, ΔJ_{KE} and ΔJ_{SP}) and the total coupling J_Σ for the constrained and optimised $\mathrm{Cp^{iPr5}Gd_2X_3}$ with X=Iodine, Bromine, Chlorine, and Fluorine in $\mathrm{cm^{-1}}$.

	X	J_0	ΔJ_{KE}	ΔJ_{SP}	J_Σ
	I	350	-17	0	333
Constrained geometry	Br	374	-17	-4	365
	Cl	388	-17	-8	375
	F	418	-25	-13	398
Relaxed geometry	Br	389	-37	-6	347
	Cl	406	-41	-8	356

Table S2: Decomposition (J_0, ΔJ_{KE} and ΔJ_{SP}) and the total coupling J_Σ (in $\mathrm{cm^{-1}}$) for the distortion of $\mathrm{(Cp^{iPr5})_2Gd_2I_3}$ according to the Gd-Gd distance, the CpGd-σ-GdCp angle and the Gd-x-Cp angle. [a] Initial $\mathrm{(Cp^{iPr5})_2Gd_2I_3}$ values.

Gd-Gd distance					CpGd-σ-GdCp angle					Gd-x-Cp angle				
Dist (Å)	J_0	ΔJ_{KE}	ΔJ_{SP}	J_Σ	Angle (°)	J_0	ΔJ_{KE}	ΔJ_{SP}	J_Σ	Angle (°)	J_0	ΔJ_{KE}	ΔJ_{SP}	J_Σ
3.4	390	-34	1	357	180[a]	350	-17	0	334	90	353	-18	0	336
3.6	367	-26	0	342	176	351	-17	1	334	88	353	-18	0	336
3.8[a]	350	-17	0	333	172	352	-19	0	334	86	354	-19	0	336
4	338	-11	0	327	168	353	-20	1	333	84	354	-19	0	335
4.2	330	-8	-1	321	164	354	-22	1	333	82	354	-19	0	335
4.4	323	-5	-1	317	160	356	-24	1	333	80	354	-20	0	335
4.6	317	-3	-2	312	156	357	-26	2	333	78	353	-20	0	333
4.8	312	-2	-2	308	152	358	-28	2	332	76	352	-20	0	331
5	309	-2	-2	306	148	359	-30	3	332	74	351	-21	0	330

5.2	306	-2	-2	303	144	361	-32	3	332	72	349	-21	0	327
5.4	302	-1	-2	298	140	362	-35	4	331	70	347	-22	0	325

Table S3: Mulliken charge and spin populations of the gadolinium and halogen atoms for the original Cp^{iPr5}Gd$_2$I$_3$, constrained Cp^{iPr5}Gd$_2$$F_3$ and relaxed Cp^{iPr5}Gd$_2$$Cl_3$ structures for the high spin determinants in the quasi-restricted open-shell formalism.

	Cp^{iPr5}Gd$_2$I$_3$		Constrained Cp^{iPr5}Gd$_2$F$_3$		Relaxed Cp^{iPr5}Gd$_2$Cl$_3$	
Atoms	Charge Pop	Spin Pop	Charge Pop	Spin Pop	Charge Pop	Spin Pop
Gd	0.879	7.422	1.333	7.455	0.834	7.443
Gd	0.851	7.425	1.321	7.457	0.832	7.441
X	-0.262	0.022	-0.651	0.003	-0.326	0.018
X	-0.229	0.024	-0.642	0.003	-0.330	0.019
X	-0.233	0.024	-0.641	0.003	-0.330	0.019

4. Orbitals

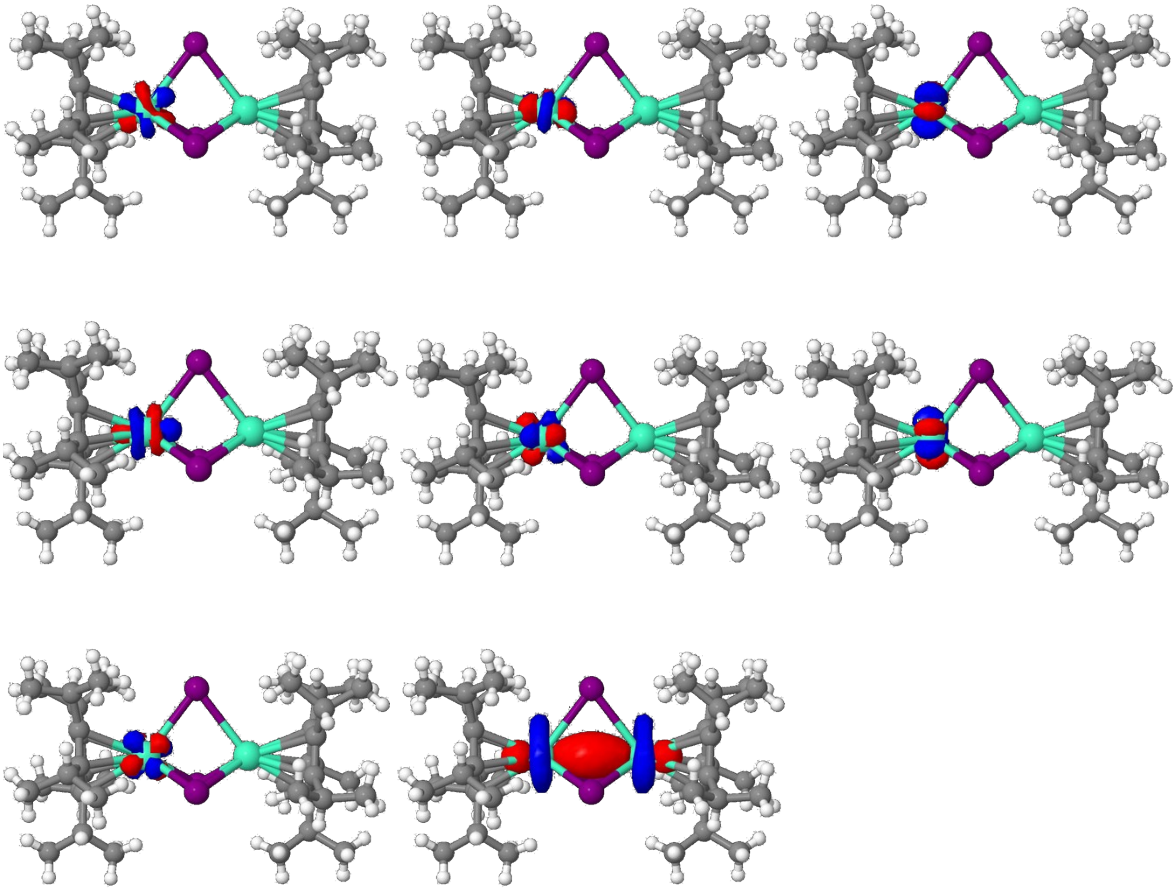

Figure S2: Localised molecular orbitals. Isosurface = 0.05 a.u.

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