Supporting Information Analysis of the Magnetic Exchange Interactions in Yttrium(III) Complexes Containing Nitronyl Nitroxide Radicals

Julie Jung,^{†,‡} Marin Puget,[¶] Olivier Cador,[†] Kevin Bernot,^{*,¶} Carmen J.

Calzado, $^{*, \S}$ and Boris Le Guennic $^{*, \dagger}$

Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Cedex Rennes, France, Max Planck Institut für

Chemische Energiekonversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany,

INSA, Institut des Sciences Chimiques de Rennes UMR CNRS 6226, 35708 Rennes,

France, and Departamento de Química Física. Universidad de Sevilla. c/ Prof. García González, s/n. 41012 Sevilla, Spain

E-mail: kevin.bernot@insa-rennes.fr; calzado@us.es; boris.leguennic@univ-rennes1.fr

 $^{\ddagger} \mathrm{Present}$ address: Max Planck Institut für Chemische Energiekonversion

^{*}To whom correspondence should be addressed

[†]Université de Rennes

[¶]INSA de Rennes

[§]Universidad de Sevilla

A. X-ray Crystallographic data



Figure S 1: Superposition of powder X-ray diffraction patterns of $\mathbf{1}$ (red line), and simulated from structural data file of the dysprosium derivative $\mathbf{1}$ '.

	2
CCDC number	CCDC-1519220
Formula	C45 H45 F18 N4 O12 Y1
$M (g.mol^{-1})$	1264.78
Crystal system	Triclinic
Space group	$P\overline{1}$
Cell parameters	12.260(4)
	14.227(5)
	17.551(6)
	98.051(5)
	103.729(1)
	111.370(1)
Volume $Å^3$	2681.10(16)
Cell formula units	2
Т / К	150(2)
λ (Å)	0.71073
θ range	2.15 – 27.52
Number of	58867
reflections	
Independent	12334
reflections	
Fo $> 4\sigma$ Fo	10374
Number of	721
variables	
μ	1.212
Goof, R_1 , wR_2	1.049, 0.0403, 0.09891

Table S 1: X-ray Crystallographic data for compound **2**.

	3b
CCDC number	CCDC-1519219
Formula	C43 H41 F18 N4 O12 Y1
$M (g.mol^{-1})$	1236.71
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell parameters	19.885(5)
	12.056(3)
	22.643(4)
	90
	104.130(5)
	90
Volume $Å^3$	5264(3)
Cell formula units	4
T/K	150(2)
λ (Å)	0.71073
θ range	1.06 - 27.52
Number of	41013
reflections	
Independent	12086
reflections	
Fo $> 4\sigma$ Fo	7580
Number of	703
variables	
μ	1.232
Goof, R_1 , wR_2	1.073, 0.0472, 0.1051

Table S 2: X-ray Crystallographic data for compound **3b**.

Table S 3: Continuous Shape Measurements $(CSM)^1$ of the reported compounds.

Compound	Best site symmetry – CSM value	2^{nd} symmetry and CSM value
1'	Triangular do decahedron $\mathrm{D}_{2d}-0.079$	Square antiprism $D_{4d} - 2.123$
2	Triangular dodecahedron $D_{2d} - 0.326$	Square antiprism $D_{4d} - 1.452$
3a	Triangular dodecahedron $D_{2d} - 0.265$	Square antiprism $D_{4d} - 1.635$
3b	Triangular dodecahedron $D_{2d} - 0.298$	Square antiprism $D_{4d} - 1.477$

Compound	$d(Ln-O_1); d(Ln-O_2)$	$d(N_{1,2}\!\!-\!\!O_{1,2})$	$d(N_{3,4}\!-\!O_{3,4})$	$d(O_1 – O_2)$
1'	2.330 - 2.334	1.293 - 1.304	1.271 - 1.259	4.365
2	2.315 – 2.351	1.296 - 1.314	1.258 - 1.275	4.364
3a	2.302 - 2.307	1.307 - 1.313	1.278 - 1.280	4.292
3b	2.293 - 2.305	1.305 - 1.317	1.268 - 1.272	4.275

Table S 4: Characteristic bonds lengths (Å) according to the labeling described in Figure 1. Ln = Dy for 1'; Ln = Y for 2, 3a and 3b.

Table S 5: Characteristic angles (°) according to the labeling described in Figure 1. Ln = Dy for 1'; Ln = Y for 2, 3a and 3b. The NIT–NIT angle corresponds to the angle between the straight lines that connects the two O atoms of each ligands (*i.e.* O_1 to O_3).

Compound	O ₁ -Ln-O ₂	$Ln-O_{1,2}-N_{1,2}$	NIT-NIT
1'	138.8	141.1 - 141.5	141.0
2	138.5	136.2 - 133.9	120.3
3a	137.3	138.7 - 141.1	138.1
3b	136.8	136.4 - 136.9	133.3

B. Ab initio calculations

The NIT-Y-NIT model

To ensure that the structural changes (*i.e.* replacing the $-CF_3$ groups of the hfac⁻ ligands, and the -R group in position -2- of the imidazole backbone by H atoms) made in the *NIT*-*Y-NIT* model do not interfere with the computed coupling constants, calculations with and without these changes were performed. The corresponding models are shown in Figure S2. The computed *J* values for the different models using the SA-7:3 singlet MOs as starting orbitals are shown in Table S6.



Figure S 2: The three NIT-Y-NIT models employed to evaluate the changes in the calculated coupling constants for the *through-bond* NIT-NIT interaction in the particular case of **1** with respect to the above mentioned structural simplifications.

Table S 6: Calculated exchange coupling constants J (cm⁻¹) at various levels of calculation for the different *NIT-Y-NIT* models shown in Figure S2.

	model 1	model 2	model 3
CASCI	-1.8	-1.3	-1.5
CAS+S	-3.8	-3.4	-3.1
DDC2	-5.3	-4.8	-4.1
DDCI	-8.8	-8.5	-8.4

From these results, it appears that the *through-bond* J value is slightly reduced when

keeping either the $-CF_3$ groups of the hfac⁻ ligand (model 2) or the first phenyl ring of the -PhOPh group in position -2- of the imidazole backbone of the NIT radical (model 3) with respect to model 1. Though, this reduction is not significant, and allows for considerable reduction of the computational cost, since replacing the CF_3 groups of the hfac⁻ by H atoms diminishes the number of determinant in the DDCI calculation by 164 millions while simply replacing the phenyl rings of model 3 by H atoms diminishes the number of determinant in the DDCI calculation by 82 millions. Model 1 is thus used throughout the rest of the study.

Through-bond NIT-NIT interaction



Figure S 3: CAS(2/2)SCF MOs of the singlet ground state for the *NIT-Y-NIT* model in compound **1**.



Figure S 4: Spin density associated to the CAS(2/2) triplet (top) and CAS(6/6) triplet orbitals (botom). While the spin density is null on the C(sp2) from the CAS(2/2) calculations, it is not from the CAS(6/6) calculations. This feature is most likely due to spin-polarization brought in by π - π * excitations which are included in the CAS(6/6) calculation.



Through-space $NIT \cdots NIT$ interactions

Figure S 5: CAS(2,2)SCF SA-7:3 singlet MOs (ϕ_1 and ϕ_2) for the *through-space* interaction along Pathways #1 (i), #2 (ii) and #3 (iii) for compound **1**. For Pathway #2 orbitals are shown when the phenyl rings connected to the NIT radicals are neglected (ii, top) and when they were taken into account (ii, bottom).

The $Y(NO_3)_3(NIT-triazol)_2$ compound



Figure S 6: Structure of the $Y(NO_3)_3(NITtriazol)_2$ compound.² Grey, light blue, red, white and pink spheres correspond to C, N, O, H and Y atoms, respectively.

Table S 7: Calculated magnetic coupling constant J_{bond} (cm⁻¹) for the *NIT-Y-NIT* model of Y(NO₃)₃(NITtriazol)₂. In parenthesis, the values obtained with a CAS(2/2) using the CASSCF(6/6) MOs. Experimental value taken from Ref. 2.

CAS		Singlet MOs	Triplet MOs	SA-7:3 singlet MOs
(2/2)	CASCI	-0.16	-0.09	+0.21
	CAS+S	-0.30	+0.29	-0.99
	DDC2	-0.38	+0.17	-1.82
	DDCI	-0.62	-0.17	-2.09
(6/6)	CASCI	-0.40 (-0.42)	-0.17 (-0.23)	
	CAS+S	-0.78 (-0.58)	-0.80 (-0.55)	
	DDC2	-1.10 (-0.83)	-1.22(-1.04)	
	DDCI	- (-1.26)	- (-1.42)	
J_{exp}			-3.1	



Figure S 7: Magnetic orbitals for the NIT-Y-NIT model of $Y(NO_3)_3(NITtriazol)_2$. (a) CAS(2/2)SCF orbitals of the triplet state. The CAS(2/2)SCF orbitals of the ground singlet state have basically the same shape. (b) CAS(2/2)SCF orbitals of the SA 7:3 singlet state. (c) CAS(6/6)SCF singly occupied orbitals of the triplet state. The CAS(6/6)SCF orbitals of the ground singlet state have basically the same shape as those of the triplet state.

Extension to complexes 2, 3a and 3b



Scheme 1: Schematic orbital overlap between π -type orbitals of the NIT radical ligands and the central hfac⁻ moiety.

C. Treatment of the magnetic data

The Hatfield and AF/F 1D alternating chain models

For a 1D chain of 1/2 spins interacting isotropically with alternating coupling constants J_1 and J_2 related by α such as $J_1 = \alpha J_2$ described by the Hatfield model, the magnetic susceptibility χ of the system is given by the following formula:

$$\chi = \frac{2N \cdot g^2 \cdot \beta^2}{kT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3}$$
(1)

for $0.4 < \alpha \le 1.0$

$$\begin{split} x &= |J|/kT \\ A &= 0.25 \\ B &= -0.068475 + 0.13194\alpha \\ C &= 0.0042563 - 0.031670\alpha + 0.12278\alpha^2 - 0.29943\alpha^3 + 0.21814\alpha^4 \\ D &= 0.035255 + 0.65210\alpha \\ E &= -0.00089418 - 0.10209\alpha + 0.87155\alpha^2 - 0.18472\alpha^3 \\ F &= 0.045230 - 0.0081910\alpha + 0.83234\alpha^2 - 2.6181\alpha^3 + 1.92813\alpha^4 \end{split}$$

$$\begin{aligned} x &= |J|/kT \\ A &= 0.25 \\ B &= -0.062935 + 0.11376\alpha \\ C &= 0.0047778 - 0.033268\alpha + 0.12742\alpha^2 - 0.32918\alpha^3 + 0.25203\alpha^4 \\ D &= 0.053860 + 0.70960\alpha \\ E &= -0.00071302 - 0.10587\alpha + 0.54883\alpha^2 - 0.20603\alpha^3 \\ F &= 0.047193 - 0.0083778\alpha + 0.87256\alpha^2 - 2.7098\alpha^3 + 1.9798\alpha^4 \end{aligned}$$

For a 1D chain of 1/2 spins interacting isotropically with alternating coupling constants J_1 and J_2 related by α such as $J_2 = \alpha J_1$ where J_1 is assumed antiferromagnetic and J_2 ferromagnetic, the molar magnetic susceptibility χ_M of the system is given by the following formula:³

$$\chi_M = \frac{2\chi_r N g^2 \beta^2}{4|J_1|} \tag{2}$$

with:

$$\chi_r = \frac{AT_r^3 + BT_r^2 + CT_r + D}{T_r^4 + ET_r^3 + FT_r^2 + GT_r + H}$$
(3)

and

$$T_r = \frac{kT}{|J_1|} \tag{4}$$

for $0.0 \le \alpha \le 2.0$

$$\begin{split} A &= 1 \\ B &= 5 \\ C &= -1 \\ D &= 0.05 \\ E &= 5.2623 - 0.33021\alpha \\ F &= 0.44976686 - 0.99234827\alpha - 0.00881524\alpha^2 + 0.15481517\alpha^3 \\ G &= 0.18948031 + 0.36766434\alpha + 0.51001414\alpha^2 - 0.2795751\alpha^3 \\ H &= 0.28437797 - 0.16749925\alpha - 0.18725364\alpha^2 + 0.09374817\alpha^3 \end{split}$$

for $2.0 \le \alpha \le 8.0$

A = 1

B = 5

$$\begin{split} C &= 18.49535656 - 6.1326194\alpha + 1.63540894\alpha^2 - 0.114937\alpha^3 \\ D &= -1.476022 + 0.238098\alpha - 0.0394290\alpha^2 + 0.001851\alpha^3 \\ E &= 5.3195744 - 0.25251758\alpha \\ F &= 20.12902219 - 7.98423527\alpha + 1.827504022\alpha^2 - 0.116829819\alpha^3 \\ G &= -2.696851543 + 2.7164805741\alpha - 0.310485224\alpha^2 + 0.008341925\alpha^3 \end{split}$$

 $H = 5.1120826687 - 2.478242688\alpha + 0.457077363\alpha^2 - 0.02686769\alpha^3$



Figure S 8: Plots of χ_M and $\chi_M T$ as a function of temperature for compound **2** with simulated curves using the Hatfield model and the calculated J values (green curve; $J_{bond} = -10.2 \text{ cm}^{-1}$, $J_{space} = -0.5 \text{ cm}^{-1}$) and J * 1.5 values (blue curve; $J_{bond} = -15.3 \text{ cm}^{-1}$ and $J_{space} = -0.75 \text{ cm}^{-1}$). Both curves have been simulated using the experimental g value (g = 1.93).



Figure S 9: Plots of χ_M and $\chi_M T$ as a function of temperature for compound **3b** with simulated curves using the numerical model given in Ref³ and the calculated J values (green curve; $J_{bond} = -10.2 \text{ cm}^{-1}$, $J_{space} = 19.6 \text{ cm}^{-1}$) and J * 1.5 values (blue curve; $J_{bond} = -15.3 \text{ cm}^{-1}$ and $J_{space} = 29.4 \text{ cm}^{-1}$). Both curves have been simulated using the experimental gvalue (g = 1.75) and paramagnetic impurities.

References

- Llunell, M.; Casanova, D.; Cirera, J.; Bofill, J. M.; Alemany, P.; Alvarez, S. SHAPE (Version 2.1). Universitat de Barcelona, Barcelona, Spain, 2013.
- Sutter, J.-P.; Kahn, M. L.; Gohlen, S.; Ouahab, L.; Kahn, O. Synthesis and magnetic behavior of rare-earth complexes with N,O-chelating nitronyl nitroxide triazole ligands: example of a [Gd^{III}organic radical₂] compound with an S = 9/2 ground state. *Chem. Eur. J.* 1998, 4, 571–576.
- Borras-Almenar, J. J.; Coronado, E.; Curely, J.; Georges, R.; Gianduzzo, J. C. Alternating chains with ferromagnetic and antiferromagnetic interactions. Theory and magnetic properties. *Inorg. Chem.* 1994, 33, 5171–5175.