Electronic supporting information

Rational Design of Ferromagnetic Coupled Diphenoxocarboxylate Triply Bridged Dinuclear Nickel(II) Complexes: The Role of the Countercomplementarity of the Bridging Ligands

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Table S1. Bond Distances (Å) for compounds 1-4

Table S2. Bond Angles (°)) for compounds 1-4

1	2	3	4	
O1B Ni1 O1A 89.57(6)	O1B Ni1 O1A 90.93(11)	O1A Ni1 O2E 90.53(8)	O1D Ni3 O3B 96.58(8)	O1B Ni1 O1A 90.21(6)
O1B Ni1 O3A 100.33(6)	O1B Ni1 O3A 93.59(11)	O1A Ni1 O3A 75.59(8)	O1D Ni3 O1B 90.05(8)	O1B Ni1 O3A 98.59(7)
O1A Ni1 O3A 76.64(6)	O1A Ni1 O3A 77.33(10)	O2E Ni1 O3A 97.85(8)	O3B Ni3 O1B 76.43(8)	O1A Ni1 O3A 76.29(6)
O1B Ni1 N2A 168.17(7)	O1B Ni1 N2A 168.03(12)	O1A Ni1 N2A 100.19(10)	O1D Ni3 N2B 161.17(9)	O1B Ni1 N2A 166.59(7)
O1A Ni1 N2A 98.94(7)	O1A Ni1 N2A 99.66(12)	O2E Ni1 N2A 167.87(9)	O3B Ni3 N2B 97.17(9)	O1A Ni1 N2A 100.30(7)
O3A Ni1 N2A 89.68(7)	O3A Ni1 N2A 94.16(12)	O3A Ni1 N2A 90.37(10)	O1B Ni3 N2B 105.65(9)	O3A Ni1 N2A 92.03(7)
O1B Ni1 N3A 89.11(7)	O1B Ni1 N1A 91.20(12)	O1A Ni1 N3A 164.72(9)	O1D Ni3 N3B 87.12(9)	O1B Ni1 N3A 87.73(7)
O1A Ni1 N3A 166.06(6)	O1A Ni1 N1A 89.51(12)	O2E Ni1 N3A 86.63(9)	O3B Ni3 N3B 86.23(9)	O1A Ni1 N3A 166.66(7)
O3A Ni1 N3A 89.95(6)	O3A Ni1 N1A 166.05(12)	O3A Ni1 N3A 89.92(9)	O1B Ni3 N3B 162.00(9)	O3A Ni1 N3A 90.98(7)
N2A Ni1 N3A 84.57(7)	N2A Ni1 N1A 83.39(13)	N2A Ni1 N3A 84.46(10)	N2B Ni3 N3B 81.02(10)	N2A Ni1 N3A 83.89(8)
O1B Ni1 N1A 87.95(7)	O1B Ni1 N3A 87.21(12)	O1A Ni1 N1A 90.45(9)	O1D Ni3 N1B 90.05(9)	O1B Ni1 N1A 88.89(7)
O1A Ni1 N1A 88.91(7)	O1A Ni1 N3A 168.33(12)	O2E Ni1 N1A 90.95(9)	O3B Ni3 N1B 162.46(9)	O1A Ni1 N1A 89.73(7)
O3A Ni1 N1A 163.18(7)	O3A Ni1 N3A 91.28(11)	O3A Ni1 N1A 163.49(9)	O1B Ni3 N1B 87.38(9)	O3A Ni1 N1A 164.09(7)
N2A Ni1 N1A 84.04(7)	N2A Ni1 N3A 83.51(13)	N2A Ni1 N1A 83.37(10)	N2B Ni3 N1B 80.54(10)	N2A Ni1 N1A 82.91(8)
N3A Ni1 N1A 104.92(7)	N1A Ni1 N3A 102.04(13)	N3A Ni1 N1A 104.59(10)	N3B Ni3 N1B 110.38(9)	N3A Ni1 N1A 103.40(7)
O1A Ni2 O3A 80.39(6)	O1A Ni2 O2B 97.99(11)	O1A Ni2 O1E 96.85(9)	O1B Ni4 O3B 79.55(8)	O1A Ni2 O3A 79.41(6)
O1A Ni2 O2W 174.18(7)	O1A Ni2 O1M 174.28(12)	O1A Ni2 O3A 78.19(9)	O1B Ni4 O2M 176.79(9)	O1A Ni2 N1C 175.49(8)
O3A Ni2 O2W 105.00(7)	O2B Ni2 O1M 84.91(12)	O1E Ni2 O3A 96.90(9)	O3B Ni4 O2M 102.10(9)	O3A Ni2 N1C 104.88(8)
O1A Ni2 O2B 96.08(6)	O1A Ni2 O3A 80.48(11)	O1A Ni2 O1M 177.46(9)	O1B Ni4 O2D 96.27(9)	O1A Ni2 O2B 93.26(7)
O3A Ni2 O2B 93.30(7)	O2B Ni2 O3A 91.46(11)	O1E Ni2 O1M 85.47(9)	O3B Ni4 O2D 95.71(9)	O3A Ni2 O2B 96.46(7)
O2W Ni2 O2B 85.90(7)	O1M Ni2 O3A 104.44(12)	O3A Ni2 O1M 100.55(9)	O2M Ni4 O2D 86.32(9)	N1C Ni2 O2B 87.68(8)
O1A Ni2 O1W 90.31(7)	O1A Ni2 O1W 91.99(12)	O1A Ni2 O1W 91.64(9)	O1B Ni4 O2W 92.63(9)	O1A Ni2 O1W 90.07(7)
O3A Ni2 O1W 94.59(7)	O2B Ni2 O1W 167.91(12)	O1E Ni2 O1W 167.52(9)	O3B Ni4 O2W 95.73(9)	O3A Ni2 O1W 94.40(7)
O2W Ni2 O1W 87.09(8)	O1M Ni2 O1W 84.58(13)	O3A Ni2 O1W 93.78(9)	O2M Ni4 O2W 84.49(9)	N1C Ni2 O1W 88.22(8)
O2B Ni2 O1W 170.58(7)	O3A Ni2 O1W 96.93(11)	O1M Ni2 O1W 86.23(9)	O2D Ni4 O2W 166.61(9)	O2B Ni2 O1W 169.05(7)
O1A Ni2 O2A 79.35(6)	O1A Ni2 O2A 78.77(11)	O1A Ni2 O2A 78.97(8)	O1B Ni4 O2B 78.79(8)	O1A Ni2 O2A 77.71(6)
O3A Ni2 O2A 158.68(6)	O2B Ni2 O2A 82.94(11)	O1E Ni2 O2A 82.16(9)	O3B Ni4 O2B 158.18(8)	O3A Ni2 O2A 156.46(6)
O2W Ni2 O2A 95.54(7)	O1M Ni2 O2A 96.77(12)	O3A Ni2 O2A 156.86(9)	O2M Ni4 O2B 99.66(9)	N1C Ni2 O2A 98.15(7)
O2B Ni2 O2A 82.34(6)	O3A Ni2 O2A 157.51(11)	O1M Ni2 O2A 102.42(9)	O2D Ni4 O2B 84.10(9)	O2B Ni2 O2A 79.47(7)
O1W Ni2 O2A 92.10(7)	O1W Ni2 O2A 92.39(11)	O1W Ni2 O2A 90.54(9)	O2W Ni4 O2B 87.86(9)	O1W Ni2 O2A 91.08(7)

Table S3.- Degree of distortion of the Ni(II) coordination polyhedra with respect to ideal six-vertex polyhedral for 1-4

Compound 1

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<u>Ni1</u>
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HP-6 1 D6h Hexagon PPY-6 2 C5v Pentagonal pyramid 3 OC-6 Oh Octahedron TPR-6 4 D3h D3h C5v Trigonal prism 5 JPPY-6 Johnson pentagonal pyramid J2 Structure [ML6] (HP-6) (PPY-6) (OC-6) (TPR-6) (JPPY-6)

Ni 9.33910,	26.4	, 1176	32.81198,	22.74939,	1.64181,	
<u>Ni2</u>						
HP-6	1	D6h	Hexagor	1		
PPY-6	2	C5v	Pentago	onal pyramid		
OC-6	3	Oh	Octahed	dron		
TPR-6	4	D3h	Trigona	al prism		
JPPY-6	5	C5v	Johnsor	n pentagonal	pyramid J2	
Structure (JPPY-6)	[ML6]	(HP-6)	(PPY-6)	(OC-6)	(TPR-6)
Ni		,	33.30539,	23.83273,	1.27353,	
12.20711,	27.	. 82038	3			

$\underline{\text{Compound } 2}$

Ni2

1	D6h	Hexagor	n		
2	C5v	Pentago	onal pyramid		
3	Oh	Octahed	dron		
4	D3h	Trigona	al prism		
5	C5v	Johnsor	n pentagonal	pyramid J2	
[ML6]	(HP-6)	(PPY-6)	(OC-6)	(TPR-6)
26	, 99476	33.84813,	22.85815,	1.60116,	
	1 2 3 4 5 [ML6	1 D6h 2 C5v 3 Oh 4 D3h 5 C5v [ML6]	1 D6h Hexagor 2 C5v Pentago 3 Oh Octaheo 4 D3h Trigona 5 C5v Johnson [ML6] (HP-6) , 33.84813, 26 99476	1 D6h Hexagon 2 C5v Pentagonal pyramid 3 Oh Octahedron 4 D3h Trigonal prism 5 C5v Johnson pentagonal [ML6] (HP-6) (PPY-6) , 33.84813, 22.85815, 26 99476	1 D6h Hexagon 2 C5v Pentagonal pyramid 3 Oh Octahedron 4 D3h Trigonal prism 5 C5v Johnson pentagonal pyramid J2 [ML6] (HP-6) (PPY-6) (OC-6) , 33.84813, 22.85815, 1.60116, 26 99476

<u>Ni1</u>

HP-6	1	D6h	Hexagon			
PPY-6	2	C5v	Pentago	nal pyramid		
OC-6	3	Oh	Octahed	ron		
TPR-6	4	D3h	Trigona	l prism		
JPPY-6	5	C5v	Johnson	pentagonal	pyramid J2	
Structure (JPPY-6)	[ML6]	(HP-6)	(PPY-6)	(OC-6)	(TPR-6)
Ni 10.82594,	26.	, 10814	32.15114, 4	22.70149,	1.30576,	

Compound 3

<u>Ni2A</u>

HP-6	1	D6h	Hexagon
PPY-6	2	C5v	Pentagonal pyramid
0C-6	3	Oh	Octahedron
TPR-6	4	D3h	Trigonal prism

JPPY-6 5 C5v Johnson pentagonal pyramid J2 Structure [ML6] (HP-6) (PPY-6) (OC-6) (TPR-6) (JPPY-6) Ni , 33.92565, 23.95292, 1.49937, 11.65322, 27.80757

<u>Ni1A</u>

HP-6	1	D6h	Hexagor	ſ		
PPY-6	2	C5v	Pentago	onal pyramid		
OC-6	3	Oh	Octaheo	dron		
TPR-6	4	D3h	Trigona	al prism		
JPPY-6	5	C5v	Johnsor	n pentagonal	pyramid J2	
Structure	[ML6]	(HP-6)	(PPY-6)	(OC-6)	(TPR-6)
Ni 8.10794,	22.1	, 4333	30.41676,	18.72545,	2.83232,	

<u>Ni1B</u>

HP-6	1	D6h	Hexagon			
PPY-6	2	C5v	Pentago	nal pyramid		
OC-6	3	Oh	Octahed	ron		
TPR-6	4	D3h	Trigona	l prism		
JPPY-6	5	C5v	Johnson	pentagonal	pyramid J2	
Structure (JPPY-6)	[ML6]	(HP-6)	(PPY-6)	(OC-6)	(TPR-6)
Ni 9.42203,	26.3	, 0363	33.13589,	22.59821,	1.69729,	

<u>Ni2B</u>

HP-6	1	D6h	Hexagon			
PPY-6	2	C5v	Pentago	nal pyramid		
OC-6	3	Oh	Octahed:	ron		
TPR-6	4	D3h	Trigonal	l prism		
JPPY-6	5	C5v	Johnson	pentagonal	pyramid J2	
Structure (JPPY-6)	[ML6]	(HP-6)	(PPY-6)	(OC-6)	(TPR-6)
Ni 11.45827,	26.	, 72913	32.51138,	22.84774,	1.70562,	

Compuesto $\mathbf{4}$

Ni2			
HP-6	1	D6h	Hexagon
PPY-6	2	C5v	Pentagonal pyramid
OC-6	3	Oh	Octahedron
TPR-6	4	D3h	Trigonal prism
JPPY-6	5	C5v	Johnson pentagonal pyramid J2

tructure	[ML6]	HP-6	PPY-6	0C-6
TPR-6 diNi	JPPY-6	32.829,	24.008,	1.423,
12.599,	28.056			
Ni1				
Structure	[ML6]	HP-6	PPY-6	0C-6
TPR-6	JPPY-6			
diNi	,	33.028,	22.335,	1.623,
9.538,	25.931			

Table S4.- Variation of the calculated J with the Ni-O_{carboxyalte} distance

J	dNi-O _{carboxylate}
+8.6	2.0
+8.2	2.05
+7.9	2.1
+7.6	2.15
+7.3	2.2

Table S5. Spin density values (in e⁻) on selected atoms for complex **1**.

1 7		
Atoms ^a	Acetate bridge	Replaced bridge by water
Ni1/Ni2	+1.6701/+1.7381	+1.6593/-1.7240
$N1_{amine}^{b}$	+0.0597	+0.0703
O1,2 _{phen-bridge} ^b	+0.0991	-0.0187
O1,2 _{acet-bridge} ^b	+0.0459	
O2 _{methoxo}	+0.0245	-0.0251
O2 _{water} ^b	+0.0319	-0.0391
O1 _{add-water} /O2 _{add-water}		+0.0318/-0.0230

^{*a*} Indexes 1 and 2 refers to the Ni1 (left) and Ni2 (right) moieties, respectively. ^{*b*} Mean value. ^{*c*} No applicable.



Figure S1.- Field dependence of the molar magnetization at 2 K for 1-4.