ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Title:

Indirect effect of the hydrogen bonds on the magnetic coupling on Mn(III) dinuclear compounds

Authors:

J. M. Pagès,[a] L. Escriche-Tur,[a] M. Font-Bardia,[b,c] G. Aullón[a,d*] and M. Corbella[a,e*]

[a.] *Departament de Química Inorgànica i Orgànica (Secció Química Inorgànica), Facultat de Química. Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain.*

[b.] *Departament de Mineralogia, Petrologia i Geologia Aplicada. Facultat de Ciències de la Terra. Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain.*

[c.] *Unitat de Difracció de RX. Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB). Universitat de Barcelona. Solé i Sabarís 1-3. 08028-Barcelona. Spain.*

[d.] *Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Martí i Franquès 1,08028 Barcelona, Spain*

[e.] *Institut de Nanociència i Nanotecnologia (IN2UB), Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain*

Corresponding author

*Montserrat Corbella, e-mail: montse.corbella@ub.edu.

*Gabriel Aullón, e-mail: gabriel.aullon@qi.ub.es

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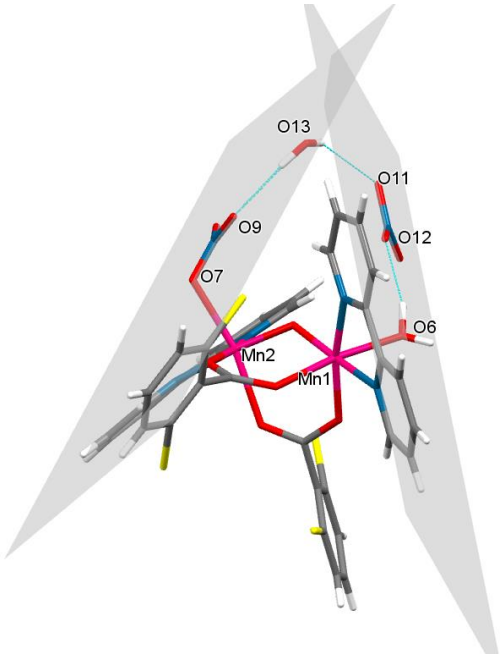

Figure S1. View of the disposition of the planes containing coordinated and non-coordinated nitrate ions for compound **2**.

Table TS1. Magnetic coupling constants *J* and selected structural parameters for [{Mn(L)(NN)}$_2$(μ-O)(μ-*n*-RC$_6$H$_n$COO)$_2$]X$_2$ compounds (n = 4 for monosubstituted carboxylates and n = 3 for 1 and 2).

	Ref.	*n*-R	NN	X	L	J [a] / cm^{-1}	Mn–O–Mn / °	Δ [b]	ρ [c]	ω [d] / °	τ [e] / °	Mn–O–N / °	γ [f] / °
2	*	2,6-Cl$_2$	bpy	NO_3	H_2O/NO_3	–27.3	123.7	12.6	4.1	75.1	90.0	118	33
	1	2-Cl	Phen	ClO_4	H_2O/H_2O	–12.6	122.9	11.2	4.5	77.9	88.3		
	2	2-Cl	Bpy	ClO_4	H_2O/ClO_4 (3/1)	–10.9	122.8	13.3	3.5	56.5	92.6		
1	*	2,6-Cl$_2$	bpy	ClO_4	H_2O/ClO_4	–9.2	124.4	12.6	4.7	73.0	106.2		
	3	2-Me	Bpy	ClO_4	H_2O/ClO_4	–5.6	122.3	13.8	3.7	46.9	101.1		
	3	2-F	Bpy	ClO_4	H_2O/ClO_4	–3.5	124.4	12.7	4.8	19.5	93.6		
	4	2-MeO	Bpy	NO_3	H_2O/NO_3	–2.3	123.5	10.8	5.0	36.2	78.1	140	87
	4	2-MeO	Bpy	ClO_4	H_2O/ClO_4	–0.7	122.8	12.2	4.4	29.2	95.2		
	3	2-Me	Bpy	NO_3	H_2O/NO_3	–0.5	123.1	10.7	4.2	28.8	97.2	120	30
	2	2-Cl	Phen	-	NO_3/NO_3	–0.3	124.4	9.7	4.7	38.1	101.7	127	47
	3	2-F	Bpy	NO_3	H_2O/NO_3	+1.4	125.1	11.2	5.0	18.6	89.2	138	89
	1	2-Cl	Phen	ClO_4	H_2O/H_2O	+2.7	122.9	9.7	4.9	46	102		
	2	2-Cl	Bpy	NO_3	H_2O/NO_3	+3.0	123.0	9.4	5.4	25.4	108.5	126	77
	5	2-COOH	Bpy	NO_3	H_2O/NO_3 (3/1)	+4.7	123.5	11.2	4.6	19.9	96.4	122	40
	6	2-Br	phen	NO_3	H_2O/NO_3	+11.8	124.2	–7.7	–1.6	50.5	96.3	128	69
	7	3-MeO	Bpy	ClO_4	H_2O/ClO_4	+0.5	123.9	12.8	4.4	10.7	102.3		
	7	3-MeO	Bpy	NO_3	H_2O/NO_3	+1.3	124.7	11.8	5.2	11.8	92.8	134	87
	7	3-MeO	Bpy	NO_3	NO_3/NO_3	+1.8	124.5	12.4	4.2	16.9	117.2	131	84
	8	3-Cl	Phen	ClO_4	H_2O/H_2O	+5.7	121.0	11.6	4.7	3.9	120.6		
	8	3-Cl	Bpy	NO_3	H_2O/H_2O	+11.8	122.4	9.0	5.4	5.8	112.7		
	7	4-tBu	Bpy	ClO_4	$EtOH/ClO_4$	–16.0	120.8	13.2	4.1	3.8	73.7		
	9	4-Br	Bpy	ClO_4	$EtOH/ClO_4$	–6.8	122.8	14.6	4.0	10.7	94.1		
	7	4-MeO	Bpy	ClO_4	$EtOH/ClO_4$	–5.2	123.5	15.6	3.5	11.7	95.5		
	6	4-Me	phen	ClO_4	H_2O/H_2O	–1.8	122.2	10.3	4.8	2.9	83.8		
	9	4-Cl	Phen	ClO_4	EtOH/EtOH	0	122.1	11.1	4.1	6.7	88.9		
	10	4-F	Bpy	NO_3	H_2O/H_2O	+1.4	124.4	10.0	5.1	9.3	99		
	10	4-Me	Bpy	NO_3	H_2O/H_2O	+1.5	122.1	10.9	4.4	7.3	112		
	11	H	bpy	NO_3	OH/NO_3	+2.0	124.1	10.8	5.3	10.2	94.9	130	88
	10	4-CF$_3$	Bpy	NO_3	H_2O/H_2O	+5.7	122.2	10.6	4.2	7.5	116		
	12	H	Bpy	-	N_3/N_3	+17.6	122.0	5.3	7.4	5.0	108.1		

** This work ;* [a] $H = -J\cdot(S_1\cdot S_2)$; [b] average Elongation (Eq. 1): $\Delta = (z - \overline{xy}) / \overline{xy}$, $\overline{xy} = (x + y)/2$; [b] average rombicity: $\rho = (y - x) / x$; [d] average O–C$_{carb}$–C$_{ar}$–C$_{ar}$' angle; [e] relative orientation of the O$_h$: L–Mn···Mn–L angle; [f] angle between the equatorial plane of the octahedron N_2O_2 and the NO_3 plane; abbreviations: bpy = 2,2'-bipyridine, phen = 1,10-phenantroline.

Table TS2. Magnetic interaction (J_{cal}), charge (Q) and charge loss (ΔQ) on the perchlorate anions (X), the water ligands (Lw) and in the two manganese ions of the complex (Mn_w and Mn_{Cl}), for different models based on the crystallographic data of [{Mn(bpy)(H_2O)}(μ-2,6-$Cl_2C_6H_3COO$)$_2$(μ-O){Mn(bpy)(ClO_4)}]ClO_4 (**1**) (Mn-w···$(ClO_4)_{1/2}$···w'-Mn'). A scheme for the frame work units in each model is shown in Table 5. ($H = -JS_1 \cdot S_2$)

	X	J_{cal} /cm^{-1}	Q (X_1) /me	Q (X_2) /me	Q (L_W) /me	ΔQ (2X+w) */me*	Q (w') /me	ΔQ *(2X+2w)* */me*	Q (Mn_W) /me	Q (Mn_{Cl}) /me
1A	w·None	–19.9	-	-	-		72	*72*	1563	1545
1B	w·ClO_4^-	–16.7	−963	-	-	*37*	68	*105*	1553	1562
1C	w·ClO_4^-	–16.5	-	–975	-	*25*	63	*88*	1546	1561
1D	w·$(ClO_4^-)_2$	–13.5	–964	–978	-	*58*	65	*123*	1556	1554
1E	w·$(ClO_4^-)_2$·W	–13.1	–956	–963	−26	*55*	67	*122*	1556	1555
1···1'	w·$(ClO_4^-)_2$·w'	–14.5	–953	–953	+61	*(155)/2*	61	*(216)/2*	1554	1559

Table TS3. Magnetic exchange (J_{cal}), charge (Q) and charge loss (ΔQ) and spin density (ρ) on the extra bridge, and charge in the two manganese ions of the complex and the monodentate ligands, for different models based on the crystallographic data of [{Mn(bpy)(H_2O)}(μ-2,6-$Cl_2C_6H_3COO$)$_2$(μ-O){Mn(bpy)(NO_3)}]NO_3·H_2O·CH_3CN (**2**·H_2O·CH_3CN) (Mn-L_N···W···X···L_W-Mn). A scheme for the frame work units in each model is shown in Table 6. ($H = -JS_1 \cdot S_2$)

	X	J_{cal} /cm^{-1}	Q (X) /me	ΔQ (X) /me	Q (W) /me	ΔQ (X+W) /me	Q (X+W) /me	ρ (X) /me	ρ (W) /me	Q (L_N) /me	Q (L_W) /me	Q $(Mn)_W$ /me	Q $(Mn)_N$ /me
2A	None	−31.3								−850	76	1543	1557
2B	$MeNO_2$	−31.2	23	*23*	−10	*13*	13	0	0	−846	54	1553	1554
2C	$HONO_2$	−31.1	19	*19*	−9	*10*	10	0	0	−849	61	1555	1554
2D	NO_2^-	−28.6	−858	*142*	−19	*123*	-877	67	0	−848	55	1545	1552
2	ONO_2^-	−27.6	−943	*57*	−15	*42*	-958	1	0	−849	59	1556	1547
2E	$HOCO_2^-$	−26.5	−939	*61*	−13	*48*	-952	1	0	−848	58	1558	1544
2F	$MeCO_2^-$	−26.3	−923	*77*	−14	*63*	-937	3	0	−846	48	1558	1544

Table TS4. X-ray crystallographic data collection and structure refinement details for compounds [{Mn(bpy)(H_2O)}(μ-2,6-$Cl_2C_6H_3COO$)$_2$(μ-O){Mn(bpy)(ClO_4)}]ClO_4 (**1**) and [{Mn(bpy)(H_2O)}(μ-2,6-$Cl_2C_6H_3COO$)$_2$(μ-O){Mn(bpy)(NO_3)}]NO_3·H_2O·CH_3CN (**2**·H_2O·CH_3CN).

	1	**2**·H_2O·CH_3CN
chemical formula	$C_{34}H_{24}Cl_6Mn_2N_4O_{14}$	$C_{36}H_{26}Cl_4Mn_2N_7O_{13}$
formula weight /g mol-1	1035.15	1016.32
T / K	293	100
λ (Mo Kα) / Å	0.71073	0.71073
crystal system	P21/c (No. 14)	Pca21(Nº21)
space group	Monoclinic	Orthorhombic
a / Å	11.693(2)	18.6545(12)
b / Å	39.642(8)	14.0357(8)
c / Å	9.7135(18)	15.6154(10)
β / deg.	111.005(7)	
V / Å^3	4203.3(14)	4088.6(4)
Z	4	4
ρ_{calcd} / g cm^{-3}	1.636	1.651
μ / mm^{-1}	1.051	0.934
Absorption coefficient / mm^{-1}	1.051	0.934
F(000)	2080	2052
Crystal size /mm	0.344 x 0.090 x 0.056	0.534 x 0.248 x 0.153
Θ range / deg.	1.9 to 28.4	2.5 to 27.2
limiting indices	$-14 \le h \le 15$, $-52 \le k \le 52$, $-12 \le l \le 12$	$-23 \le h \le 23$, $-18 \le k \le 17$, $-20 \le l \le 16$
Independent reflections	88576 / 10480 [*R*(int) = 0.0573]	17365/7592 [*R*(int) = 0.0517]
Completeness to theta / %	99.7	98.5
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6807	0.7455 and 0.5728
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data / restraints / parameters	10480 / 95 / 649	7592 / 14 / 530
goodness-of-fit on F^2	1.057	1.084
final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0497, wR_2 = 0.1198	R_1 = 0.0700, wR_2 = 0.1856
R indices (all data)	R_1 = 0.0637, wR_2 = 0.1266	R_1 = 0.0753, wR_2 = 0.1907

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $\omega R2 = \{\sum[\omega(F_o^2 - F_c^2)^2] / \sum[\omega(F_o^2)^2]\}^{1/2}$, $\omega = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 1.4805P]$, where $P = (F_o^2+2F_c^2) / 3$.

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