Supporting Information

for the manuscript

Syntheses, Crystal Structures and Magnetic Properties of Five New Manganese(II) Complexes: Influence of the Conformation of Different Alkyl/Aryl Substituted Malonate Ligands.

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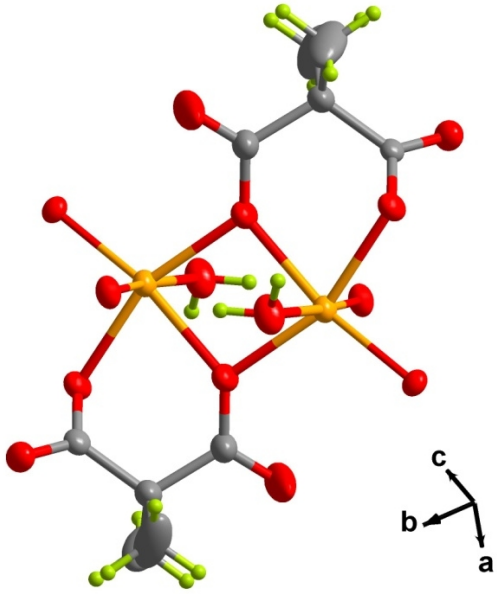
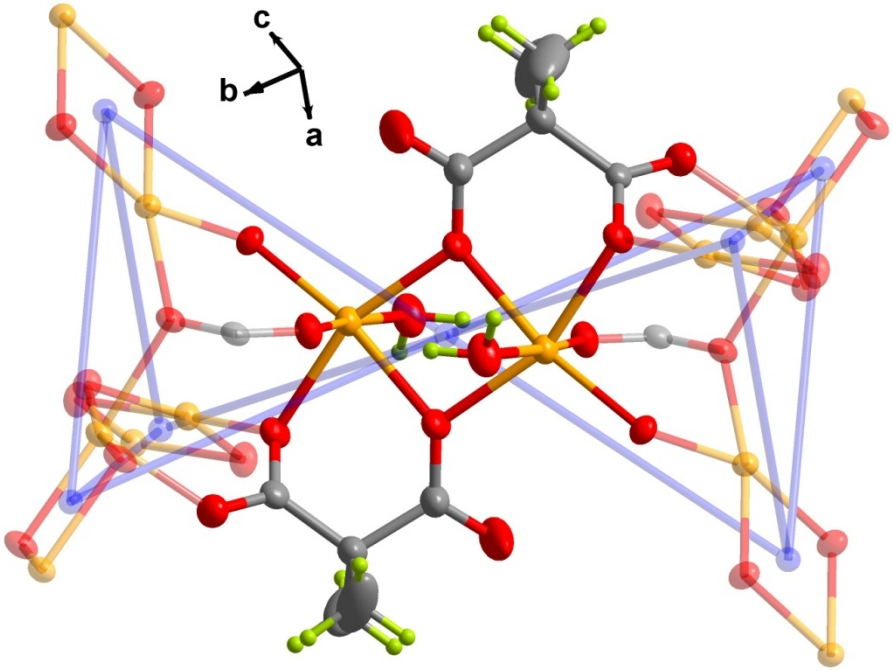


(a)



(b)

Figure S1. (a) Detail of the dinuclear units present in complex **2**. (b) Bonding of the dinuclear units with the other six ones. The blue spheres shows the center of each dinuclear entitie.

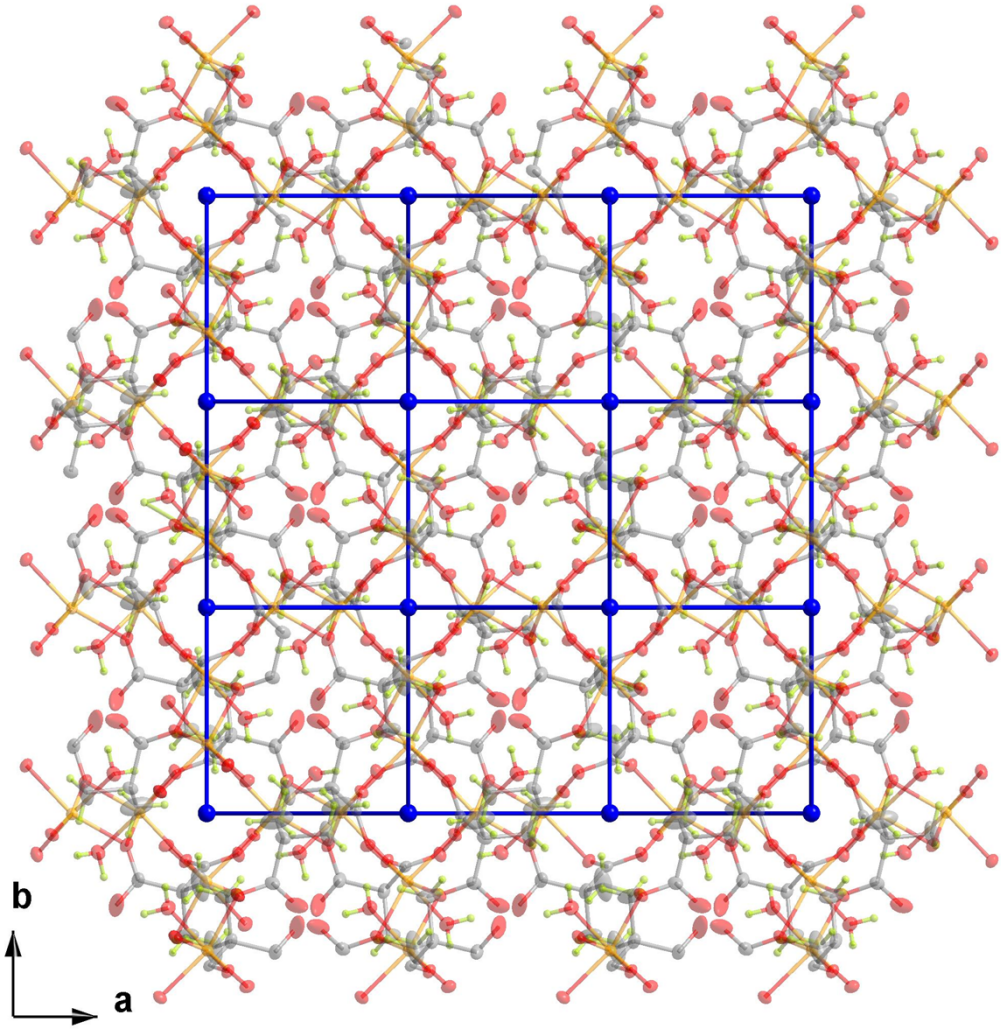


Figure S2. A view along the *c* axis of the topological **dia**-net of **2**, represented with the actual strutucture.

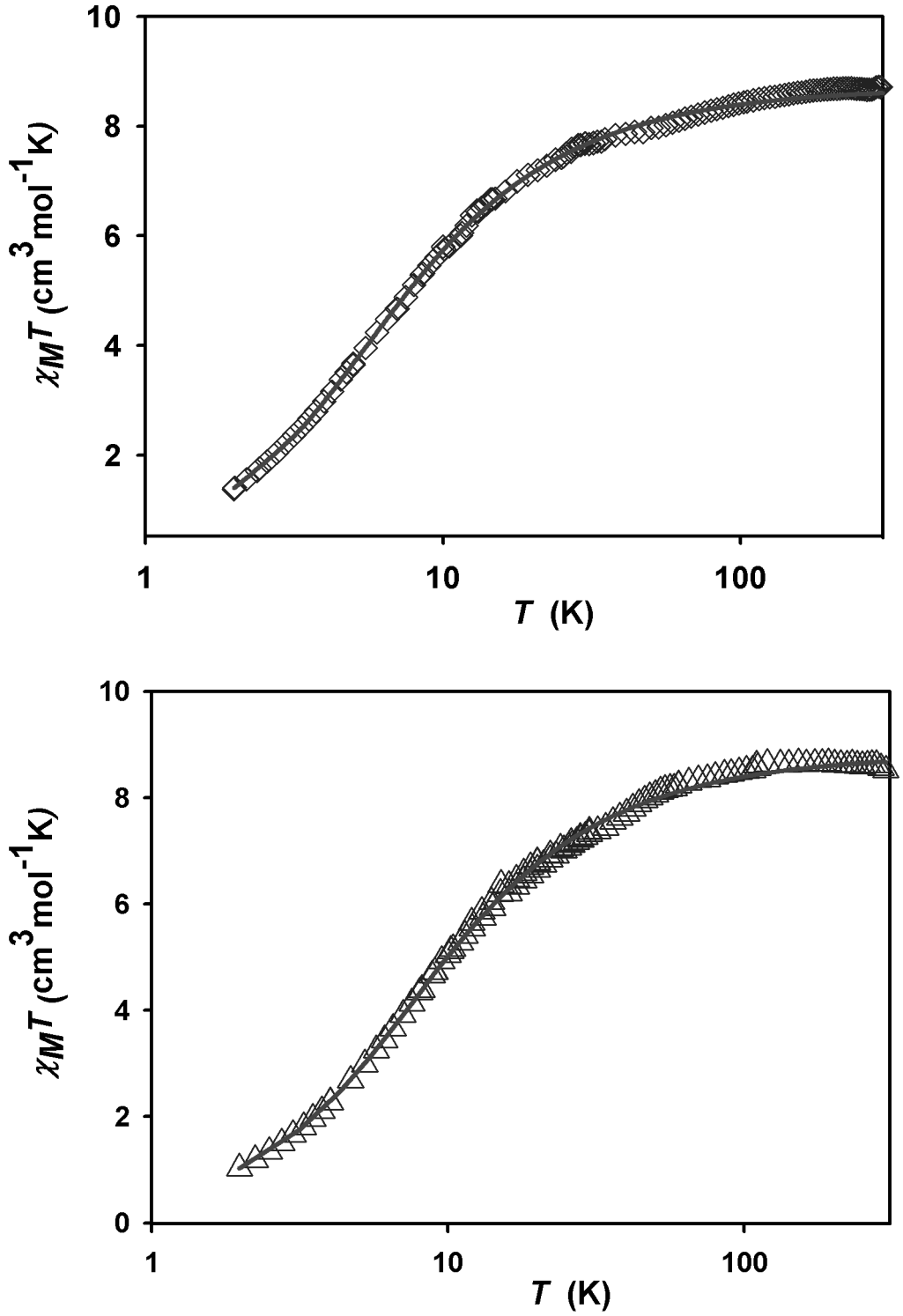


Figure S4. $\chi_M T$ *vs*. T plots for complex **4** (diamonds) and **5** (triangles) in logarithmic scale of T to highlight the low temperature region. The solid line corresponds to the best-fit.

Table S1. Selected Bond Distances (Å) and Angles (deg) and Intermolecular Interactions (Å, deg) for Complex **1.**[a]

1					
Mn(1)-O($1a_1$)	2.1120(17)	O(1 a_1)-Mn(1)-O($3b_1$)	88.71(7)	O(2)-Mn(1)-O(1W)	92.87(8)
Mn(1)-O(2)	2.1093(19)	O($1a_1$)-Mn(1)-O(4)	85.19(6)	O(3 b_1)-Mn(1)-O(4)	99.66(6)
Mn(1)-O($3b_1$)	2.2566(17)	O($1a_1$)-Mn(1)-O($4b_1$)	93.87(6)	O(3 b_1)-Mn(1)-O(4 b_1)	57.15(5)
Mn(1)-O(4)	2.1482(15)	O($1a_1$)-Mn(1)-O(1W)	93.79(8)	O(3 b_1)-Mn(1)-O(1W)	154.53(7)
Mn(1)-O($4b_1$)	2.2991(14)	O(2)-Mn(1)-O($3b_1$)	89.30(7)	O(4)-Mn(1)-O(4 b_1)	156.81(6)
Mn(1)-O(1W)	2.113(2)	O(2)-Mn(1)-O(4)	84.00(6)	O(4)-Mn(1)-O(1W)	105.80(7)
O($1a_1$)-Mn(1)-O(2)	168.51(7)	O(2)-Mn(1)-O($4b_1$)	94.55(6)	O(4 b_1)-Mn(1)-O(1W)	97.38(7)
D-H ⋯ A[b]		D-H (Å)	H ⋯ A (Å)	D ⋯ A (Å)	D-H ⋯ A (º)
O(1W)-H(1WA) ⋯ O($1c_1$)		0.84(2)	2.15(2)	2.903(3)	149(3)
O(1W)-H(1WB) ⋯ O($2c_1$)		0.84(2)	2.24(2)	2.988(2)	149(2)
O(1W)-H(1WB) ⋯ O($3d_1$)		0.84(2)	1.90(2)	2.731(3)	169(5)

[a] Symmetry code: (a_1) = -*x*+1/2, *y*-1/2, *z*+1/2; (b_1) = *x*-1/2, -*y*+1/2, *z*; (c_1) = -*x*, -*y*+1, *z*+1/2; (d_1) = -*x*+1, -*y*+1, *z*+1/2.
[b] D and A stand for donor and acceptor, respectively.

Table S2. Selected Bond Distances (Å) and Angles (deg) and Intermolecular Interactions (Å, deg) for Complex **2.**[a]

2				
Mn(1)-O($1a_2$)	2.1900(12)	O($1a_2$)-Mn(1)-O($2b_2$)	99.06(5)	
Mn(1)-O(2)	2.2151(12)	O($1a_2$)-Mn(1)-O(4)	84.66(5)	
Mn(1)-O($2b_2$)	2.1434(12)	O($1a_2$)-Mn(1)-O($4c_2$)	91.66(5)	
Mn(1)-O(4)	2.2075(13)	O($1a_2$)-Mn(1)-O(1W)	170.18(5)	
Mn(1)-O($4c_2$)	2.1627(12)	O(2)-Mn(1)-O($2b_2$)	89.80(5)	
Mn(1)-O(1W)	2.1616(13)	O(2)-Mn(1)-O(4)	78.81(4)	
O($1a_2$)-Mn(1)-O(2)	94.24(5)	O(2)-Mn(1)-O($4c_2$)	158.57(5)	
D-H ⋯ A[b]	D-H (Å)	H ⋯ A (Å)	D ⋯ A (Å)	D-H ⋯ A (º)
O(1W)-H(1WA) ⋯ O($3d_2$)	0.87(2)	1.73(2)	2.601(2)	176(3)
O(1W)-H(1WB) ⋯ O($1e_2$)	0.85(2)	2.13(2)	2.946(2)	161(3)

[a] Symmetry code: (a_2) = -*x*+1, -*y*+3/2, *z*; (b_2) = *y*-1/4, -*x*+5/4, -*z*+1/4; (c_2) = -*x*+1, -*y*+1, -*z*; (d_2) = *y*+1/4, -*x*+5/4, *z*+1/4; (e_2) = *x*, *y*-1/2, -*z*.
[b] D and A stand for donor and acceptor, respectively.

Table S3. Selected Bond Distances (Å) and Angles (deg) and Intermolecular Interactions (Å, deg) for Complex **3.**[a]

3					
Mn(1)-O($1a_3$)	2.1371(18)	O($1a_3$)-Mn(1)-O(2)	168.52(7)	O(2)-Mn(1)-O($2d_3$)	84.77(10)
Mn(1)-O(2)	2.1649(17)	O($1a_3$)-Mn(1)-O(1W)	83.05(7)	O(2)-Mn(1)-O(1W)	87.17(7)
Mn(1)-O(1W)	2.278(2)	O($1a_3$)-Mn(1)-O($1Wc_3$)	80.98(6)	O(2)-Mn(1)-O($1Wc_3$)	110.15(7)
O($1a_3$)-Mn(1)-O($1b_3$)	95.97(12)	O(1)b4-Mn(1)-O(2)	88.76(8)	O(1W)-Mn(1)-O($1Wc_3$)	156.03(7)
D-H ⋯ A[b]	D-H (Å)	H ⋯ A (Å)	D ⋯ A (Å)	D-H ⋯ A (º)	
O(1W)-H(1WA) ⋯ O($2e_3$)	0.87(2)	1.99(2)	2.767(2)	149(3)	

[a] Symmetry code: (a_3) = -*x*+1, *y*-1/2, -*z*+1/2; (b_3) = *x*, *y*-1/2, -*z*+1/2; (c_3) = -*x*+1, *y*+1/2, -*z*+1/2; (d_3) = -*x*+1, *y*, *z*; (e_3) = *x*, -*y*, -*z*+1. [b] D and A stand for donor and acceptor, respectively.

Table S4. Selected Bond Distances (Å) and Angles (deg) and Intermolecular Interactions (Å, deg) for Complex **4.**[a]

4					
Mn(1)-O($1a_4$)	2.115(2)	O($1a_4$)-Mn(1)-O($3b_4$)	88.61(8)	O(2)-Mn(1)-O(1W)	102.55(9)
Mn(1)-O(2)	2.125(2)	O($1a_4$)-Mn(1)-O(4)	165.77(8)	O($3b_4$)-Mn(1)-O(4)	84.77(8)
Mn(1)-O($3b_4$)	2.246(2)	O($1a_4$)-Mn(1)-O($4c_4$)	115.69(8)	O($3b_4$)-Mn(1)-O($4c_4$)	85.02(8)
Mn(1)-O(4)	2.266(2)	O($1a_4$)-Mn(1)-O(1W)	105.24(9)	O($3b_4$)-Mn(1)-O(1W)	164.21(9)
Mn(1)-O($4c_4$)	2.216(2)	O(2)-Mn(1)-O($3b_4$)	85.96(8)	O(4)-Mn(1)-O($4c_4$)	76.32(8)
Mn(1)-O(1W)	2.192(2)	O(2)-Mn(1)-O(4)	82.26(7)	O(4)-Mn(1)-O(1W)	83.27(9)
O(1^a_4)-Mn(1)-O(2)	84.72(8)	O(2)-Mn(1)-O($4c_4$)	157.41(8)	O($4c_4$)-Mn(1)-O(1W)	82.17(8)
D-H ⋯ A[b]	D-H (Å)	H ⋯ A (Å)	D ⋯ A (Å)	D-H ⋯ A (º)	
O(1W)-H(1WA) ⋯ O($1d_4$)	0.87(2)	2.07(2)	2.882(3)	156(3)	
O(1W)-H(1WB) ⋯ O($3e_4$)	0.88(2)	2.04(2)	2.919(3)	171(5)	

[a] Symmetry code: (a_4) = *x*+1/2, -*y*+3/2, *z*; (b_4) = -*x*+1/2, *y*-1/2, -*z*; (c_4) = -*x*+1, -*y*+2, -*z*; (d_4) = *x*+1, *y*, *z*; (e_4) = *x*+1/2, -*y*+5/2, *z*.
[b] D and A stand for donor and acceptor, respectively.

Table S5. Selected Bond Distances (Å) and Angles (deg) and Intermolecular Interactions (Å, deg) for Complex **5.**[a]

5					
Mn(1)-O($3a_5$)	2.2835(18)	O($1c_5$)-Mn(1)-O($3a_5$)	87.14(7)	O(1W)-Mn(1)-O(2)	80.59(6)
Mn(1)-O(4)	2.2928(16)	O(2)-Mn(1)-O($3a_5$)	83.82(7)	O($1c_5$)-Mn(1)-O($4b_5$)	116.38(7)
Mn(1)-O($4b_5$)	2.1964(17)	O(1W)-Mn(1)-O($3a_5$)	165.04(7)	O(2)-Mn(1)-O($4b_5$)	157.88(7)
Mn(1)-O($1c_5$)	2.1292(18)	O($3a_5$)-Mn(1)-O(4)	86.51(6)	O($4b_5$)-Mn(1)-O(1W)	84.73(7)
Mn(1)-O(2)	2.1118(17)	O($4b_5$)-Mn(1)-O(4)	78.17(7)	O(2)-Mn(1)-O($1c_5$)	82.22(7)
Mn(1)-O(1W)	2.2143(19)	O($1c_5$)-Mn(1)-O(4)	163.56(7)	O($1c_5$)-Mn(1)-O(1W)	107.28(8)
O($4b_5$)-Mn(1)-O($3a_5$)	85.24(7)	O(2)-Mn(1)-O(4)	82.03(6)	O(2)-Mn(1)-O(1W)	101.72(8)
D-H ⋯ A[b]	D-H (Å)	H ⋯ A (Å)	D ⋯ A (Å)	D-H ⋯ A (º)	
O(1W)-H(1WA) ⋯ O($3d_5$)	0.88(2)	2.03(2)	2.910(3)	172(4)	
O(1W)-H(1WB) ⋯ O($1e_5$)	0.88(2)	2.15(3)	2.938(3)	148(5)	
O(1W)-H(1WB) ⋯ O($2c_5$)	0.88(2)	2.29(4)	2.896(2)	125(4)	

[a] Symmetry code: (a_5) = x+1/2, -y+1/2, -z+1; (b_5) = -x+1, -y, -z+1; (c_5) = -x+3/2, y-1/2, z; (d_5) = -x+1/2, y-1/2, z; (e_5) = x, y-1, z.
[b] D and A stand for donor and acceptor, respectively.