New tetranuclear manganese clusters with [MnII3MnIII] and [MnII2MnIII2] metallic cores exhibiting the low and high spin ground state

M. Sobocińska,[a]* M. Antkowiak,[b] M. Wojciechowski,[c] G. Kamieniarz,[b] J. Utko[a] and T. Lis[a]

[a] Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383, Wrocław, Poland
[b] Faculty of Physics, A. Mickiewicz University, Umultowska 85, 61-614, Poznań, Poland
[c] Institute of Physics, University of Zielona Góra, Szafrana 4a, 65-516 Zielona Góra, Poland

* Correspondence e-mail: maria.sobocinska@chem.uni.wroc.pl

Electronic Supplementary Information (ESI)

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1. Supplementary tables

Table S1. Crystallographic data for complexes: 1 and 2.

	Complex **1**	Complex **2**
Empirical formula	$C_{98}H_{96}ClMn_4N_{1.60}O_{16}$	$C_{18}H_{42}Cl_4Mn_4O_{12}$
Formula weight [g/mol]	1807.37	812.07
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature [K]	100(2)	100(2)
Wavelenght [Å]	0.71073	0.71073
Unit cell dimensions		
a, b, c [Å]	22.483(5), 14.057(3), 29.614(6)	11.252(3), 13.134(4), 11.161(3)
β [°]	111.74(2)	105.16(2)
Volume [Å^3]	8694(3)	1592.0(8)
Z	4	2
Crystal size [mm]	0.57 x 0.42 x 0.39	0.15 x 0.14 x 0.07
Reflections collected	59724	17276
Independent reflections	20876	4717
Reflections observed ($I > 2\sigma(I)$)	15370	3868
Absorption correction	Analytical	Analytical
Absorption coefficient [mm^{-1}]	0.67	1.96
Data / restraints / parameters	20876 / 0 / 1126	4717 / 0 / 175
R_{int}	0.040	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.674	0.727
No. of reflections	20876	4717
No. of parameters	1126	175
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.45	0.66, −0.51

The highest residual electron density of 0.76 e Å^{-3} was located 0.06 Å from Mn2 for the complex **1**, whereas in the complex **2** the highest residual electron density of 0.66 e Å^{-3} was located 0.73 Å from Cl2.

Table S2. Selected interatomic distances [Å] for complex **1**.

Mn1···Mn4	3.1698(9)	Mn2–O1A	2.2617(15)
Mn1···Mn2	3.1761(7)	Mn2–O2M	2.2948(15)
Mn1···Mn3	3.2064(7)	Mn2–Cl	2.3931(7)
Mn1–O1M	1.8643(14)	Mn3–O1D	2.0828(15)
Mn1–O1O	1.8756(14)	Mn3–O2C	2.0932(14)
Mn1–O2A	1.9731(14)	Mn3–O1O	2.2419(14)
Mn1–O1P	2.0092(14)	Mn3–O1P	2.2581(14)
Mn1–O1C	2.1368(14)	Mn3–N1	2.2855(19)
Mn1–O1N	2.2567(14)	Mn3–O2O	2.3709(15)
Mn3···Mn4	3.6275(8)	Mn3–O2P	2.5553(6)
Mn2···Mn4	3.7107(8)	Mn4–O2B	2.0443(15)
Mn2···Mn3	5.987(1)	Mn4–O2D	2.0725(14)
Mn2–O1M	2.1683(14)	Mn4–O1N	2.1070(14)
Mn2–O1N	2.1716(14)	Mn4–O1P	2.1662(14)
Mn2–O1B	2.2070(15)	Mn4–O2N	2.2374(15)

Table S3. Bond valence sums (BVS) for manganese atoms in complex **1**.

Atom	Mn(II)	Mn(III)	Mn(IV)
Mn1	3.34	3.10	3.04
Mn2	2.10	1.87	1.80
Mn3	2.00	1.76	1.70
Mn4	2.04	1.80	1.75

Table S4. Hydrogen-bond geometry in complex **1.**

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	<(D–H···A) [º]
C3O–H3O1···N1	0.98	2.58	3.224(3)	123.5
C2G–H2G···O2C	0.95	2.32	2.986(3)	126.5
C2K–H2K···O2D	0.95	2.30	2.953(3)	127.5
C6C–H6C···O1A	0.95	2.34	3.007(3)	126.5
C3P–H3P1···N1	0.98	2.66	3.264(3)	119.9
C2R–H2R2···Cl^{ii}	0.98	2.87	3.532(3)	125.7
C2R–H2R2···O1A^{ii}	0.98	2.63	3.475(3)	144.5

Symmetry code: (ii) x, 1 + y, z.

Table S5. Geometry of C–H···π interaction in complex **1**.

C–H···π	H···Cg [Å]	C···Cg [Å]	<(C–H···Cg) [º]
C4L–H4L···Cg1^{i}	2.97	3.59	140

Symmetry code: (i) 0.5 – x, –0.5 + y, 0.5 – z.

Centroid of aromatic ring: Cg1: [C1J/C2J/C3J/C4J/C5J/C6J].

Table S6. Selected interatomic distances [Å] for complex **2**.

Mn1···Mn1^{i}	3.2380(9)	Mn1–O2C^{i}	2.2820(13)
Mn1···Mn2	3.3447(9)	Mn2–O1A	2.1177(13)
Mn1–O1B	1.8840(12)	Mn2–O1B^{i}	2.1332(12)
Mn1–O1A	1.8925(12)	Mn2–O2B^{i}	2.2941(13)
Mn1–O1C^{i}	2.0127(12)	Mn2–O2A	2.3313(14)
Mn1–O1C	2.2341(12)	Mn2–O1C	2.3442(12)
Mn1–Cl1	2.2642(7)	Mn2–Cl2	2.3755(7)

Symmetry code: (i) –x + 1, –y + 1, –z + 1

Table S7. Bond valence sums (BVS) for manganese atoms in complex **2**.

Atom	Mn(II)	Mn(III)	Mn(IV)
Mn1	3.27	3.08	3.02
Mn2	2.06	1.88	1.78

Table S8. Hydrogen-bond geometry in complex **2**.

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	<(D–H···A) [°]
C1A–H1A1···Cl1^{ii}	0.99	2.83	3.761(2)	157.0
C1A–H1A2···O2C^{i}	0.99	2.51	3.094(2)	117.6
C2A–H2A1···Cl1	0.99	2.79	3.4758(19)	126.6
C3A–H3A2···Cl2	0.98	2.77	3.441(2)	126.1
C1B–H1B2···Cl1	0.99	2.67	3.2134(19)	115.0
C1C–H1C2···O1A^{i}	0.99	2.51	2.999(2)	110.3
C2C–H2C2···Cl2	0.99	2.68	3.548(2)	146.8

Symmetry codes: (i) –x + 1, –y + 1, –z + 1; (ii) –x + 1, y – 0.5, –z + 1.5.

Table S9. The DFT total energies calculated of **1** without the SO interaction. Energy is related to the lowest value. M_{tot} is the total magnetic moment of a single molecule. The symbols ± correspond to spin orientation of manganese ions at specific positions, i.e. +-+- means that Mn1 spin is "up", Mn2 spin is "down", Mn3 spin is "up" and Mn4 spin is "down".

spin configuration	++++	--+-	-+++	+-+-
E (meV)	124.3	73.2	53.7	0.0
M_{tot} (μ_B)	19.00	-11.00	9.00	-1.00
Mn1 (μ_B)	4.42	-4.42	-4.39	4.39
Mn2 (μ_B)	4.45	-4.44	4.43	-4.42
Mn3 (μ_B)	3.63	3.54	3.61	3.56
Mn4 (μ_B)	4.46	-4.45	4.45	-4.44

Table S10. The DFT total energies of **1** calculated with the SO interaction taken into account. Energy is related to the lowest value. Quantization axis is expressed in basis of cell vectors (Miller index notation). M_{tot} is the total magnetic moment of a single molecule. The symbols ± correspond to spin orientation of manganese ions at specific positions, i.e. +-+- means that Mn1 spin is "up", Mn2 spin is "down", Mn3 spin is "up" and Mn4 spin is "down".

quantization axis	(0 0 1)		(0 1 0)		(1 0 0)	
spin configuration	++++	+-+-	++++	+-+-	++++	+-+-
E (meV)	124.4	0.0	124.7	0.3	125.3	0.9
M_{tot} (μ_B)	19.00	-1.00	19.00	-1.00	19.00	-1.00
Mn1 (μ_B)	4.42	4.39	4.42	4.39	4.42	4.39
Mn2 (μ_B)	4.45	-4.42	4.45	-4.42	4.45	-4.42
Mn3 (μ_B)	3.63	3.56	3.63	3.56	3.63	3.56
Mn4 (μ_B)	4.46	-4.44	4.46	-4.44	4.46	-4.44

Table S11. Precise electric charges and magnetic moments of **1** obtained without the SO interaction (see chapter **Computational details**). The symbols ± correspond to spin orientation of manganese ions at specific positions, i.e. +-+- means that Mn1 spin is "up", Mn2 spin is "down", Mn3 spin is "up" and Mn4 spin is "down".

spin configuration	atomic sphere	Q_{up} (e)	Q_{down} (e)	Q_{tot} (e)	M (μ_B)
++++ ferromagnetic	Mn1	13.876346	9.456615	23.332961	4.419731
	Mn2	13.853849	9.404693	23.258542	4.449156
	Mn3	13.620033	9.985053	23.605086	3.634980
	Mn4	13.854931	9.391738	23.246668	4.463193
--+-	Mn1	9.458237	13.875541	23.333777	-4.417304
	Mn2	9.409145	13.849112	23.258258	-4.439967
	Mn3	13.573043	10.036758	23.609801	3.536285
	Mn4	9.397902	13.849282	23.247184	-4.451380
-+++	Mn1	9.474713	13.862113	23.336825	-4.387400
	Mn2	13.847015	9.412073	23.259088	4.434942
	Mn3	13.606567	9.997704	23.604271	3.608863
	Mn4	13.849835	9.397308	23.247143	4.452527
+-+- ferrimagnetic	Mn1	13.862614	9.473344	23.335959	4.389270
	Mn2	9.416738	13.841633	23.258371	-4.424895
	Mn3	13.586615	10.023602	23.610217	3.563013
	Mn4	9.403742	13.84429	23.248032	-4.440548

Table S12. Precise electric charges and magnetic moments of **1** obtained with the SO interaction taken into account (see chapter **Computational details**). The symbols ± correspond to spin orientation of manganese ions at specific positions, i.e. +-+- means that Mn1 spin is "up", Mn2 spin is "down", Mn3 spin is "up" and Mn4 spin is "down".

spin configuration / quantization axis	atomic sphere	Q_{up} (e)	Q_{down} (e)	Q_{tot} (e) $Q_{up} + Q_{down}$	M (μ_B) $Q_{up} - Q_{down}$
++++ (0 0 1)	Mn1	13.875728	9.457283	23.333011	4.418445
	Mn2	13.853166	9.405287	23.258453	4.447879
	Mn3	13.618793	9.986325	23.605117	3.632468
	Mn4	13.854405	9.392304	23.246708	4.462101
+-+- (0 0 1)	Mn1	13.861987	9.474026	23.336014	4.387961
	Mn2	9.417246	13.841059	23.258305	-4.423813
	Mn3	13.585368	10.024818	23.610185	3.560550
	Mn4	9.404363	13.843668	23.248031	-4.439305
++++ (0 1 0)	Mn1	13.87574	9.457272	23.333013	4.418468
	Mn2	13.853155	9.405294	23.258449	4.447861
	Mn3	13.618848	9.986275	23.605122	3.632573
	Mn4	13.854448	9.392258	23.246705	4.462190
+-+- (0 1 0)	Mn1	13.862000	9.474017	23.336017	4.387983
	Mn2	9.417265	13.841026	23.258292	-4.423761
	Mn3	13.585439	10.024756	23.610195	3.560683
	Mn4	9.404323	13.843700	23.248023	-4.439377
++++ (1 0 0)	Mn1	13.875776	9.457227	23.333003	4.418549
	Mn2	13.853151	9.405296	23.258447	4.447855
	Mn3	13.619049	9.986075	23.605123	3.632974
	Mn4	13.854459	9.392245	23.246704	4.462214
+-+- (1 0 0)	Mn1	13.862039	9.473966	23.336005	4.388073
	Mn2	9.417255	13.841044	23.258300	-4.423789
	Mn3	13.585645	10.024544	23.610189	3.561101
	Mn4	9.404316	13.843709	23.248024	-4.439393

2. Supplementary figures

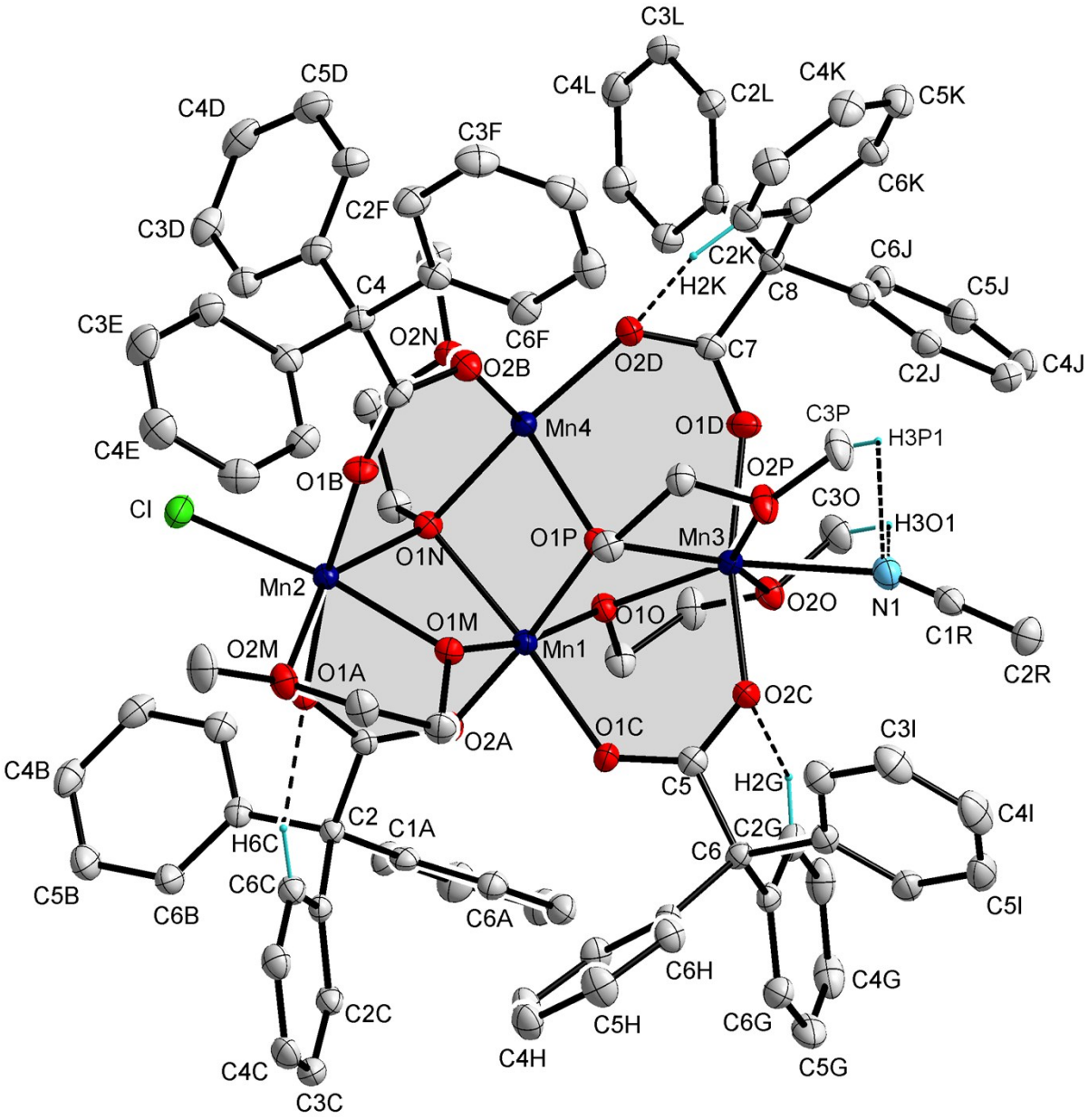

Figure S1. Intramolecular hydrogen bonds drawn with dashed lines in the molecular structure of complex **1**. H atoms not involved in hydrogen bonds have been omitted for clarity.

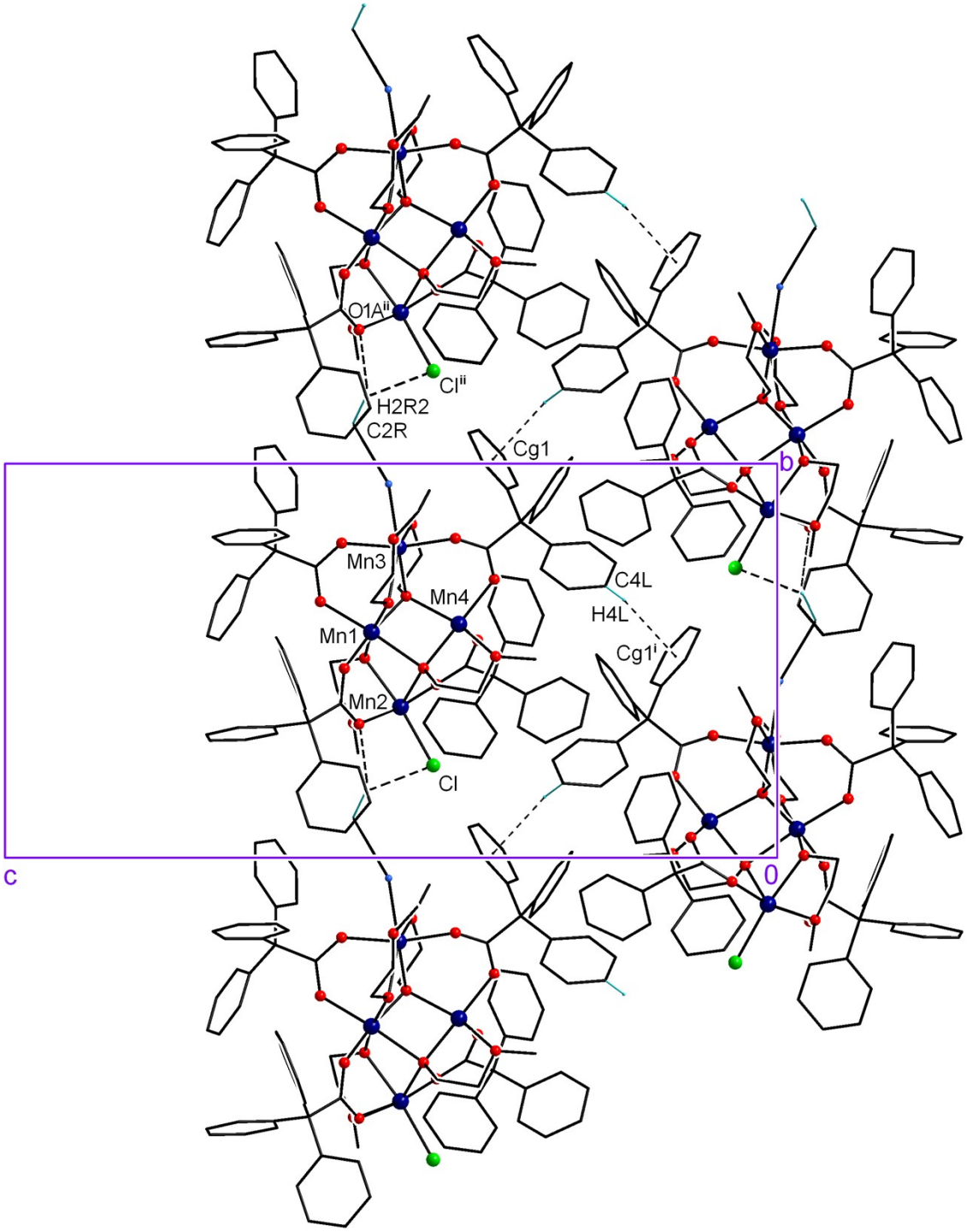

Figure S2. Double chain spreads along *b*-axis. Symmetry codes: (i) 0.5 – x, –0.5 + y, 0.5 – z, (ii) x, 1 + y, z. Centroid of aromatic ring: Cg1: [C1J/C2J/C3J/C4J/C5J/C6J]. Intramolecular hydrogen bonds have been omitted for clarity.

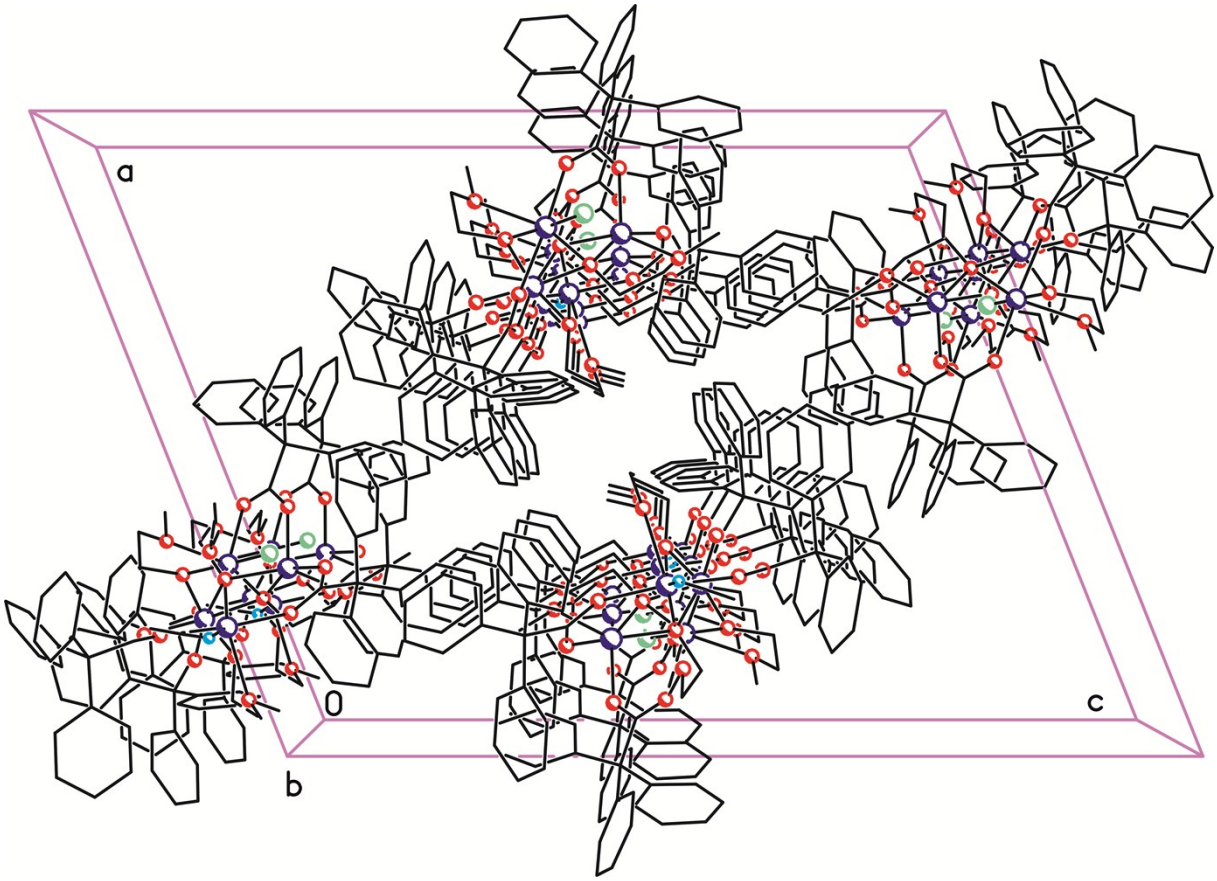

Figure S3. Layer architecture in **1**; viewed down *b*-axis. Hydrogen atoms have been omitted for clarity. Intra- and intermolecular interactions are not shown in this picture.

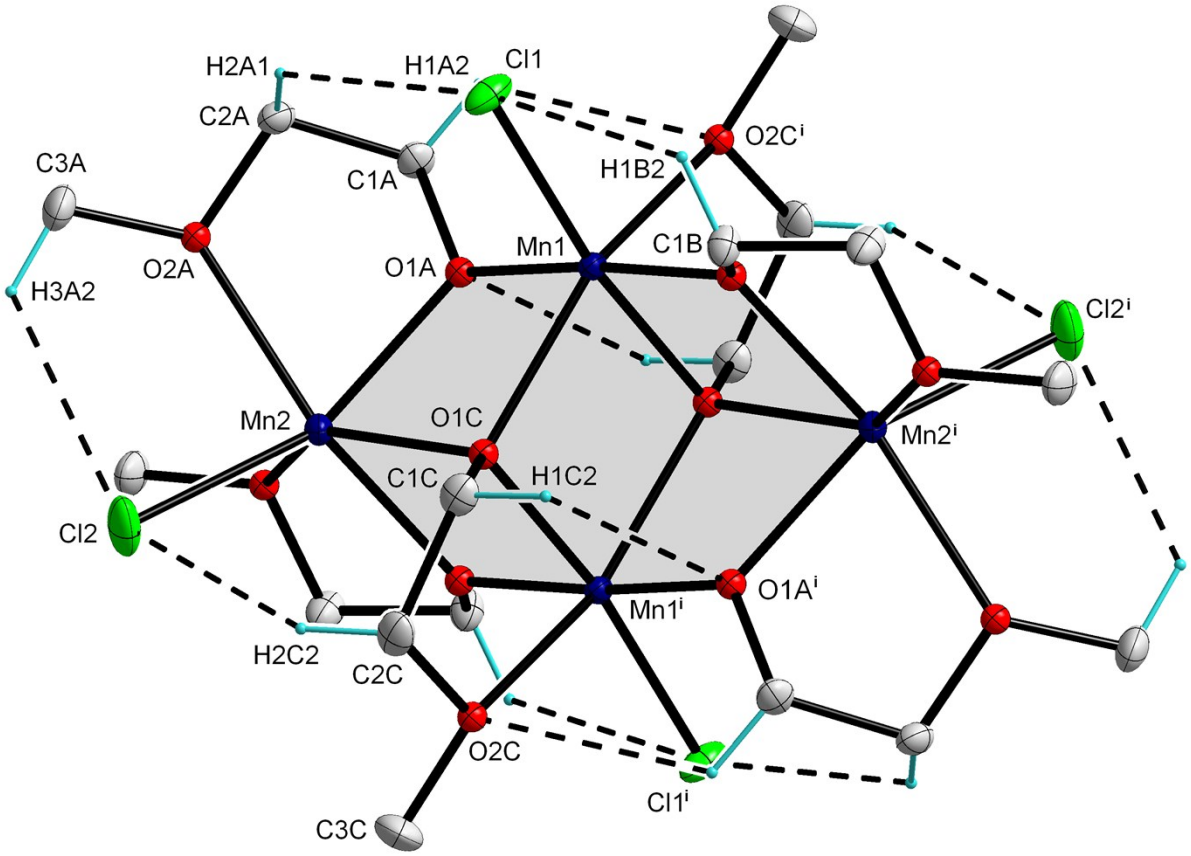

Figure S4. Intramolecular hydrogen bonds drawn with dashed lines in the molecular structure of complex **2**. H atoms not involved in hydrogen bonds have been omitted for clarity. Symmetry code: (i) 1 – x, 1 – y, 1 – z.

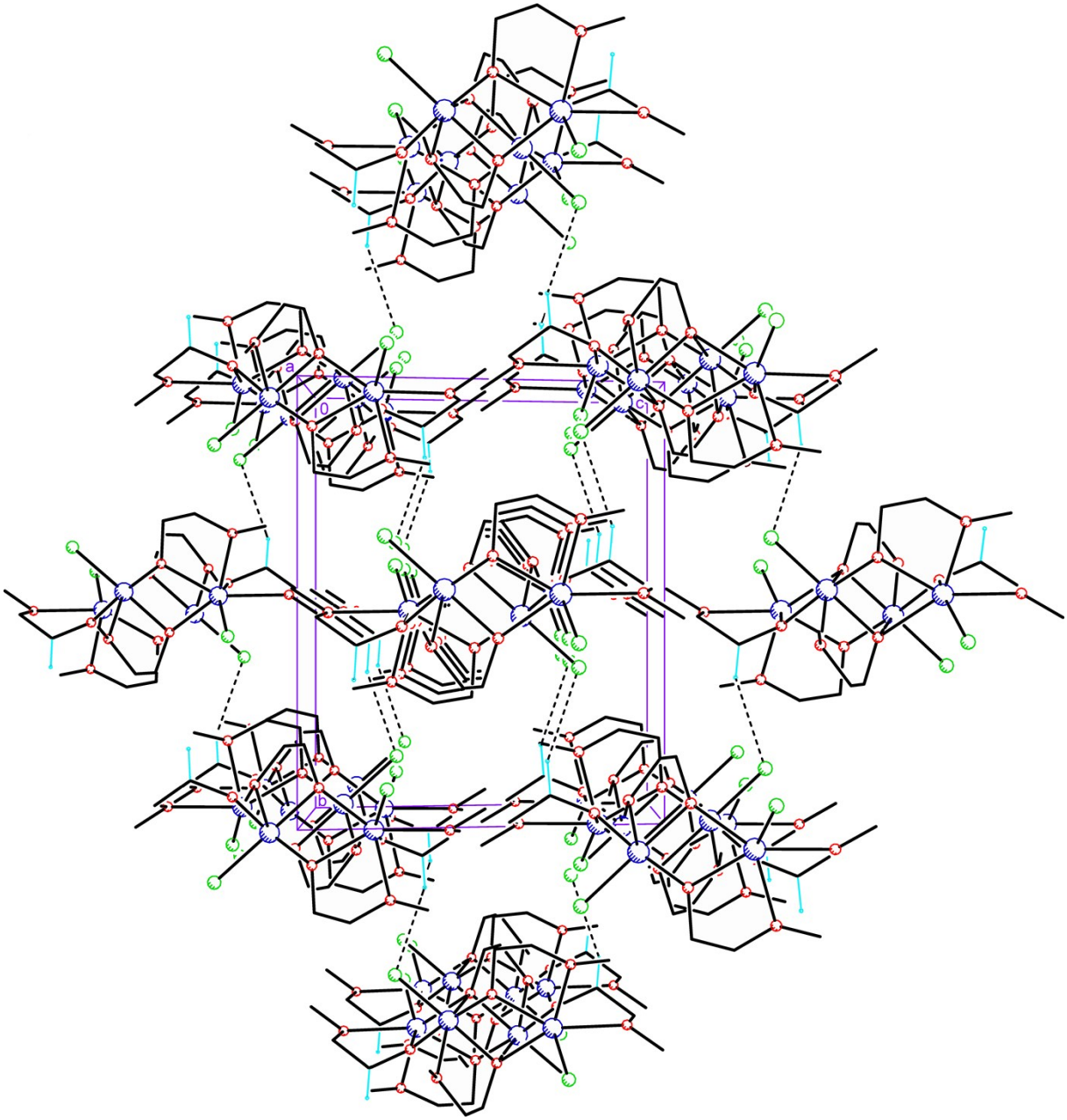

Figure S5. Layer architecture in **2**; viewed down *a*-axis. H atoms not involved in hydrogen bonding have been omitted. Dashed lines represent C–H···Cl hydrogen bonds between adjacent molecules.

3. Crystal Structures

H-bonding and C–H··· π interactions in complex 1

Structure of the complex has twofold character: presence of oxygen atoms within the molecule causes hydrophilic interior surrounded by hydrophobic sphere build up from triphenylacetate ligands. This leads to a creation of intramolecular hydrogen bonds of type C–H···O and C–H···N (nitrogen atom comes from coordinated CH_3CN molecule). The first type occurs between carbon atom of phenyl ring and oxygen atom of carboxylate arm from the same triphenylacetate ligand. The second type is observed between carbon atom of methyl group of 2-methoxyethanolate ligand and nitrogen atom of acetonitrile coordinated to the same manganese centre. In this case nitrogen atom participates as an acceptor in two specific interactions composing bifurcated hydrogen bond. These intramolecular hydrogen bonds are shown in Fig. S1. Crystal packing is dictated by C–H···Cl, C–H···O hydrogen bonding as well as C–H···π interactions. Hydrogen atom H2R2 belonged to methyl group of coordinated acetonitrile is involved in interactions with two electronegative atoms of adjacent molecule, generating bifurcated hydrogen bond. In one case, terminal chlorine atom bonded to Mn(II) centre, plays a role of H-acceptor, while in the second case, this function is assigned to oxygen atom O1A of the carboxylic ligand also bonded to the same manganese ion, giving the separation between two acceptors of 3.352(2) Å. Intermolecular hydrogen bonds and C–H···π interactions cause the formation of double-chain architecture that is extended along *[010]* direction (Fig. S2). Crystal packing is shown in Fig. S3. Geometric parameters of intra- and intermolecular hydrogen bonds are shown in Table S3, whereas Table S4 contains geometric parameters of intermolecular C–H···π interaction.

H-bonding in complex 2

Electronegative atoms such as oxygen and chlorine atoms, and carbon atoms present in the complex may display H-donoric behavior. Within the compound **2** the bifurcated hydrogen bonds are observed (Figure S4). Every chlorine atom interacts specifically with two hydrogen atoms comming from two different 2-methoxyethanolate ligands bonded to the same manganese ion as chlorine atom. In the molecule there are also existing C–H···O interactions between atoms of various ligands. Crystal structure of **2** is stabilized by C–H···Cl hydrogen bonds created between adjacent molecules (Figure S5). Carbon atom of 2-methoxyethanolate ligand acts as a H-donor, while chlorine atom of neighbouring molecule is an acceptor. Geometric parameters of intra- and intermolecular hydrogen bonds are listed in Table S7.

4. Computational details

For both compounds **1** and **2** the DFT calculations were performed using all electron linearized augmented plane wave (LAPW) method[1,2] implemented in WIEN2k computational package[3,4,5]. We account for the exchange and correlation effects using the generalized gradient approximation (GGA) as implemented in Perdew, Burke and Ernzerhof (PBE) functional[6]. The parameters defining the basis set are GMAX = 20 and RKMAX = 3.0 for **1** and RKMAX = 2.5 for **2**.

Within WIEN2k the core and valence states are treated separately. In our calculations we define manganese core states as those from argon configuration (1s, 2s, 2p, 3s and 3p). This leaves us with the states 3d and 4s which are considered valence. Core states are treated fully relativistically[7]. Relativistic effects are also included for valence electrons by scalar relativistic treatment when no spin-orbit (SO) interaction is present[8] or with the second variational method when SO coupling is included[9].

The LAPW method incorporates muffn-tin radii (RMT) approximation[10]. According to this approximation around each atom in the structure there is a spherical area called atomic sphere. All electrons within atomic spheres are considered to belong to atoms around which those spheres are described. Atomic spheres cannot overlap and cannot be too small, so that the core electrons do not “leak out”. This is very important, because within atomic spheres electrons are described with wave functions that can be expressed as a product of spherically symmetrical radial function R(r) and spherical harmonics Y_{lm}. Area outside atomic spheres is called interstitial region and all electrons in it are described with plain wave functions. The values of the RMT parameters which have been chosen for different elements are the same for both compounds, i.e. 2.27, 2.00, 1,24, 1.15, 1.00 and 0.83 Bohrs for Mn, Cl, O, N, C and H, respectively.

In terms of electronic density, WIEN2k considers two of them - one for spin channel “up” and one for spin channel “down”. Quite self explanatory, the “up” density is generated for those electrons which spin is oriented “up” and “down” density is for those electrons, for which spin projection is “down”. Through integration of these densities (expressed in units of e/Bohr^3) for specific atoms within appropriate atomic spheres one can calculate electric charges (expressed in units of e). By integrating “up” and “down” densities we obtain Q_{up} and Q_{down} charges. Total electric charges Q_{tot} are obtained by summing the result ($Q_{tot} = Q_{up} + Q_{down}$). In a similar fashion magnetic moments M (expressed in units of μ_B) can be calculated

as a difference of charges ($M = Q_{up} - Q_{down}$). Precise values of Q_{up}, Q_{down}, Q_{tot} and M for manganese in complex **1** are presented in table S10 and S11.

For complex **1** the so called "hydrogen saturation" was performed[11,12]. Each $C(C_6H_5)_3$ group in the bridges between manganese ions was replaced with single hydrogen atom. The lengths of C-H bonds for these hydrogen atoms were set to 0.99 Å. This action does not change the electronic and magnetic properties of the compound, however it speeds up calculations by reducing the number of atoms in a cell and consequently number of electrons. For complex **2** no modification of the structure was performed.

[1] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975)

[2] D.J. Singh, **Planewaves Pseudopotentials and the LAPW Method**, Kluwer Academic Publishers (1994)

[3] P. Blaha, K. Schwarz, G.H.K. Madsen, D. Kvasnicka, J. Luitz, **WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties**, Karlheinz Schwarz, Techn. Universität Wien (1999)

[4] E. Sjöstedt, L. Nordström, D.J. Singh, Solid State Commun. **114**, 15 (2000)

[5] G.K.H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, L. Nordström, Phys. Rev. B **64**, 195134 (2001)

[6] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)

[7] J.P. Desclaux, Comp. Phys. Commun. **1**, 216 (1969)

[8] D.D. Koelling, B.N. Harmon, J. Phys. C: Sol. St. Phys. **10**, 3107 (1977)

[9] A.H. MacDonald, W.E. Pickett, D.D. Koelling, J. Phys. C **13**, 2675 (1980)

[10] J.C. Slater, Phys. Rev. **51**, 846 (1937)

[11] T. Ślusarski, B. Brzostowski, D. Tomecka, G. Kamieniarz, J. Nanosci. Nanotechnol. **11**, 9080 (2011)

[12] V. Bellini, A. Olivieri, F. Manghi, Phys. Rev. B **73**, 184431 (2006)