Electronic Supplementary Information (ESI) for the paper

Self-assembly and decay of Mn(II) pivalate-phosphonate complexes

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Table S1. Crystal data and structure refinement statistics for manganese(II) compounds.

Parameter	**1**	**2**·2C_7H_{16}·2MeOH	**3**	**3a**
CSD number	951019	951020	975925	982652
Empirical formula	$C_{96}H_{188}Cl_4Mn_{10}O_{44}P_4$	$C_{164}H_{354}Cl_2Mn_{20}O_{88}P_{12}$	$C_{76}H_{156}Mn_4O_{36}P_4$	$C_{76}H_{156}Mn_4O_{36}P_4$
Molecular mass	2861.53	5275.79	1989.64	1989.64
T/K	150(2)	173(2)	184(2)	120(2)
Space group	Tetragonal, *I*–42*m*	Triclinic, *P*–1	Monoclinic, *C*2/*c*	Trigonal, *P*–3
Z	2	1	4	2
a/Å	22.4667(10)	20.016(1)	27.413(17)	16.2519(15)
b/Å	22.4667(10)	20.421(1)	17.073(11)	16.2519(15)
c/Å	14.6274(7)	20.656(1)	26.290(16)	25.431(5)
α/°	90.00	86.268(7)	90.00	90
β/°	90.00	68.581(7)	108.213(10)	90
γ/°	90.00	62.388(7)	90.00	120
V/Å^3	7383.2(7)	6909.1(6)	11688(13)	5817.0(15)
d_{calc}/g·cm^{-3}	1.287	1.268	1.131	1.160
μ/mm^{-1}	1.008	1.037	0.543	0.548
θ/° scanning range	1.28–31.18	2.14–28.70	1.43–26.02	0.80–27.48
Reflections measured	47010	73931	41298	47336
Independent reflections	6132	35351	11482	8921
Reflections with $I>2\sigma_I$	5609	21024	4132	3948
R_{int}	0.0441	0.0412	0.1125	0.1169
Number of refined parameters	199	1434	1012	687
T_{min}/T_{max}	0.707/0.924	0.713/0.886	0.909/0.958	0.875/ 0.942
GooF	1.086	1.011	1.401	1.321
R_1 ($I>2\sigma_I$)	0.0264	0.0619	0.1148	0.0842
wR_2 ($I>2\sigma_I$)	0.0712	0.1631	0.2744	0.2364
R_1 (all data)	0.0350	0.1210	0.2036	0.1827
wR_2 (all data)	0.0851	0.2075	0.2985	0.2927
Flack parameter	0.005(5)			

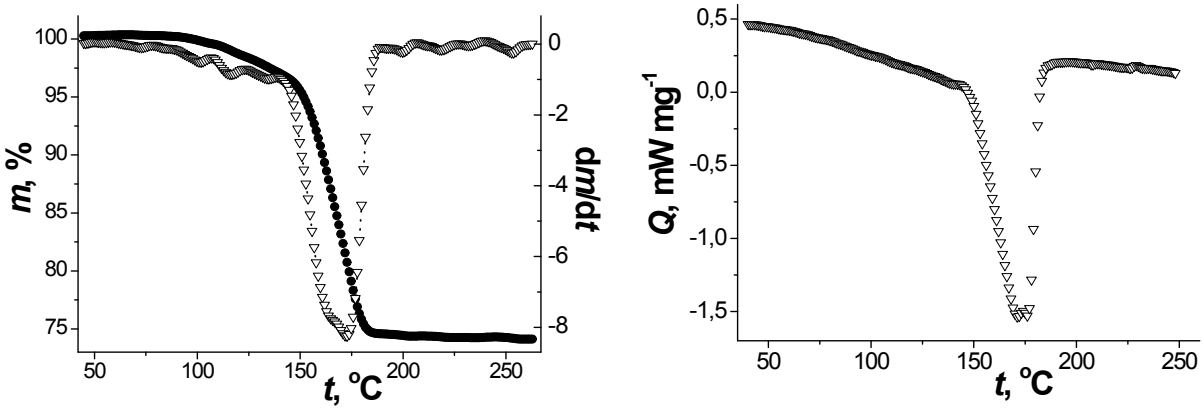
Table S2. Selected bond lengths [Å], bond angles [deg] and H-bonds parameters in manganese compounds.

Parameter	**1***	**2**·2C_7H_{16}·2MeOH**	**3****	**3a*****
Mn–O(μ-OH)	–	2.210(3), 2.135(3)	–	
Mn–Cl(μ-Cl)	2.4721(6)	2.5301(12), 2.5404(12)	–	
Mn–O(μ-Piv)	2.133(3)–2.224(2)	2.055(3)–2.281(3)	–	
Mn–O(O_3PBu^t)	2.110(2)–2.292(2)	2.047(3)– 2.500(3)	2.109(11)–2.169(9)	2.077(10)-2.165(5)
Mn–O(HPiv)	2.292(2)	2.208(5)–2.327(7)	2.272(12)–2.356(13)	2.221(7)-2.386(15)
Mn–O(H_2O)	–	2.094(3)–2.375(2)	–	
P–O	1.534(2)–1.539(2)	1.506(3)–1.551(3)	1.472(11)–1.550(11)	1.404(11)-1.620(11)
O–P–O	104.28(12)–112.74(8)	103.5(2)–114.6(2)	108.3(6)–113.6(7)	105.0(6)-116.5(7)
C–O(Piv)	1.240(4)–1.286(4)	1.239(6)–1.278(5)	–	
C–O(HPiv)	1.213(4), 1.319(5)	1.209(6)–1.323(8)	1.153(9)–1.261(9)	1.162(7)-1.285(8)
O–C–O	122.6(3)–123.9(3)	122.8(4)–126.6(4)	125.0(11)–133.7(12)	122.5(13)-128.8(12)
H-bonds				
O...O	2.603	2.552–2.613	2.505–2.621	2.536–2.591
H...O	1.78	1.72–1.78	1.67–1.80	1.72–1.75
O–H–O	166.0	170.2–173.0	167.0–173.8	163.0–174.6

* Symmetry codes: (*i*) *x*, -*y*+1, -*z*+1; (*ii*) -*x*+1, -*y*+1, *z*; (*iii*) -*x*+1, -*y*+1, *z*; (*iv*) *y*, *x*, *z*; (*v*) *x*, -*y*+1, -*z*+1; (*vi*) -*x*+1, *y*, -*z*+1; (*vii*) -*x*+1, *y*, -*z*+1;
** Symmetry code: (*i*) -*x*+2, -*y*+1, -*z*+1.
*** Symmetry code: (*i*) -*x*, *y*, -*z*+1/2;
**** Symmetry code: (*i*) -*y*+1, *x*-*y*, *z*; (*ii*) -*x*+*y*+1, -*x*+1, *z*

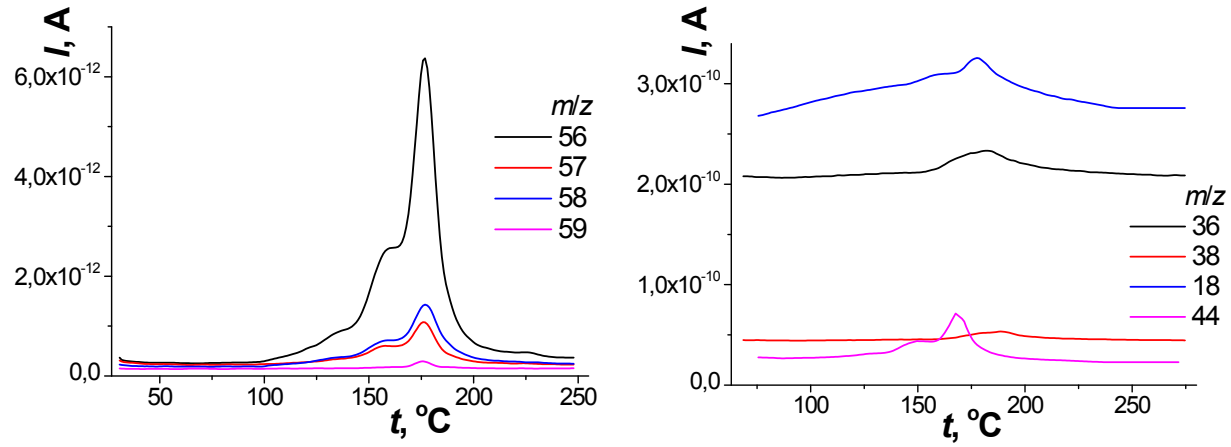
Table S3. Mass spectrum of **1**·$2H_2O$ under TGA experiment conditions.

m/z	Ion	*I*/%	*m*/z	Ion	*I*/%
12	$[C]^+$	3.9	39	$[C_3H_3]^+$	37.4
15	$[CH_3]^+$	0.4	41	$[C_3H_5]^+$, $[C_2HO]^+$	11.3
17	$[OH]^+$	15.8	43	$[C_3H_7]^+$	3.3
18	$[H_2O]^+$	59.1	44	$[CO_2]^+$, $[C_3H_8]^+$	33.5
27	$[C_2H_3]^+$	5.9	45	$[COOH]^+$,$[C_2H_5O]^+$ $[^{13}CO_2]^+$	0.7
28	$[C_2H_4]^+$, $[CO]^+$	28.6	56	$[C_4H_8]^+$	3.1
29	$[C_2H_5]^+$	8.4	57	$[CCOOH]^+$ $[C_4H_9]^+$	0.5
31	$[C_2H_7]^+$	0.4	58	$[HCCOOH]^+$	2.7
35	$[^{35}Cl]^+$	0.2	59	$[H_2CCOOH]^+$	3.2
36	$[H^{35}Cl]^+$	100	87	$[C_3H_7COOH]^+$	0.5
38	$[H^{37}Cl]^+$	22.2	-	-	-



a *b*

Fig. S1. Plots of mass change, first derivative of mass (*a*), and thermal flux *versus* temperature (*b*) for **1**.



a *b*

Fig. S2. Fragments of the mass spectrum (*a* and *b*) of **1** under the conditions of the TGA experiment.

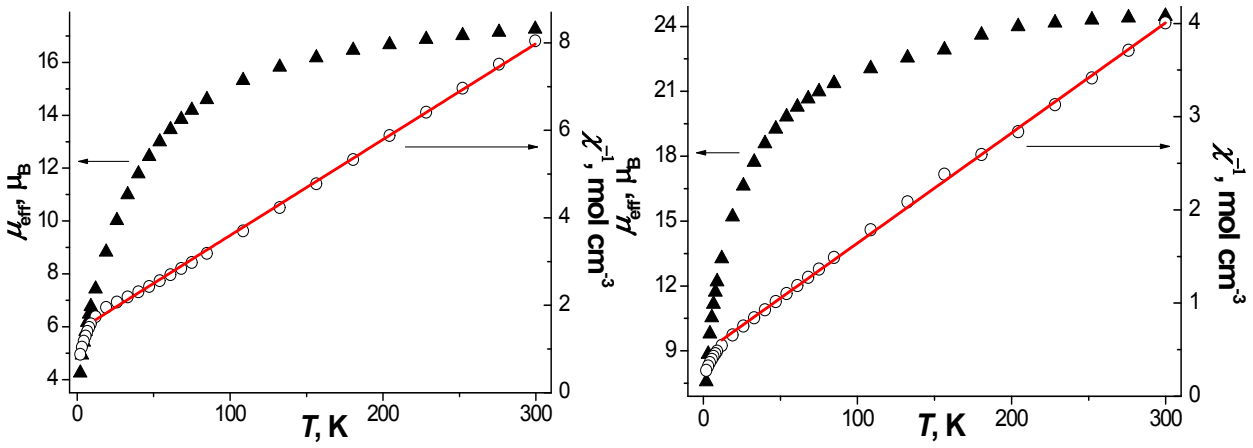


Fig. S3. Magnetic properties of **1** (*a*) and **2** (*b*): $\mu_{eff}(T)$ (□) and $1/\chi(T)$ (○) plots; calculated data (see main text) are shown as lines.

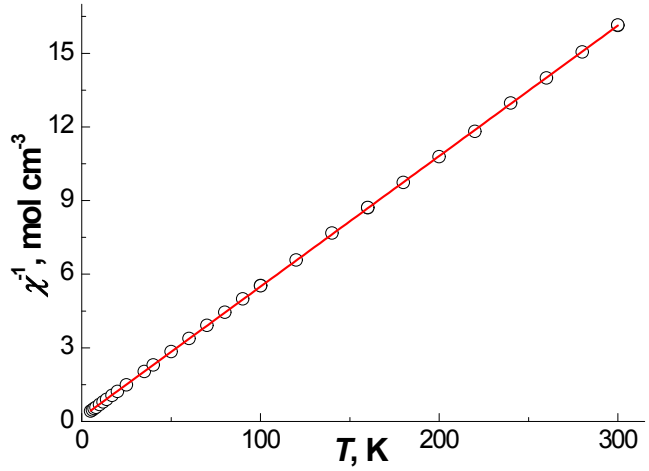


Fig. S4. $1/\chi(T)$ (○) plot and calculated data (line, see main text) for **3**·8H_2O.

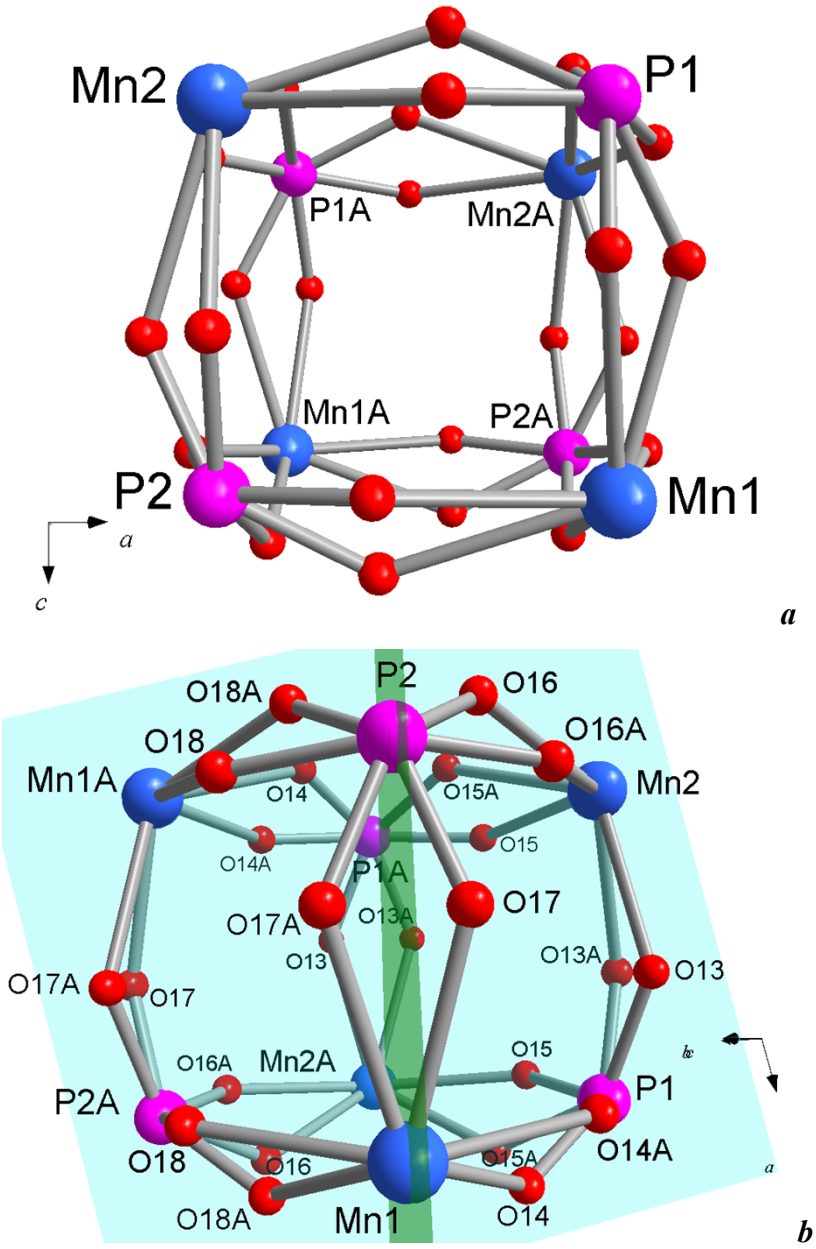


Fig. S5. Disorder of the O_3P fragments in the structure **3** (Piv anions and ^{t}Bu-groups at P atoms are omitted). *b* - Two groups of O atoms (without index and with index "A") correspond to different isomers. Blue and green planes correspond two "non-crystallography" *m*-planes passing through Mn1, Mn2A, P1A, P2 and Mn1A, Mn2, P1, P2A atoms.