Table 1

Compound reference	Complex **1**	Complex **2**
Chemical formula	$C_{56}H_{70}Mn_6N_{12}O_{22}$•10($CH_3OH$)	$C_{66.37}H_{75.75}Mn_8N_{16}O_{22.5}$•5.25($CH_3OH$)•9.45($H_2O$)
Formula Mass	1913.30	2251.67
Crystal system	Triclinic	Triclinic
a/Å	11.514(3)	16.608(5)
b/Å	11.767(4)	17.907(5)
c/Å	17.730(6)	19.811(6)
α/°	95.80(5)	78.12(4)
β/°	105.73(5)	65.89(4)
γ/°	99.28(5)	75.79(3)
Unit cell volume/Å^3	2255.3(15)	5176(3)
Temperature/K	100(2)	85(2)
Space group	*P*-1	*P*-1
No. of formula units per unit cell, *Z*	1	2
No. of reflections measured	25491	51148
No. of independent reflections	11459	27840
R_{int}	0.0530	0.0543
Final R_1 values ($I > 2\sigma(I)$)	0.0679	0.0498
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1751	0.1102
Final R_1 values (all data)	0.1390	0.1136
Final $wR(F^2)$ values (all data)	0.1942	0.1179

Data were collected on an Xcalibur PX diffractometer with CCD Onyx and Mo-Kα radiation (λ = 0.71073 Å) at 100 K and 85 K for **1** and **2** respectively. Structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 (SHELX).[1]
In both structures the non-hydrogen atoms, except disordered atoms, were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model.
In the structure of **1** acetate anion was disordered over two position with occupation factors 0.56/0.46. Also one of the methanol solvent molecules was splitted into two positions due to disorder.
In the structure of **2** one of the coordination sites of Mn7 atom consists of disordered over two positions methanol (67%, 20%) and water (13%) molecules. Some other water and methanol molecules were refined with partial occupation due to disorder.

[1] G.M. Sheldrick, *Acta Cryst.* (2008) **A64** 112.

Synthesis

$[Mn^{III}_6O_2$(phamidox)$_6$(OAc)$_2$(MeOH)$_4]$·10MeOH (1·10H_2O**)**. $Mn(OAc)_2$·4H_2O (1 mmol, 245 mg), phamidoxH_2 (1 mmol, 166 mg) and NEt_3 (2 mmol) were stirred in MeOH (20 ml) for a period of 35 minutes to form a dark brown solution. After filtration the solution was left to slowly evaporate and black crystals were formed during ~4 days. The crystals were collected by filtration, washed with Et_2O (2 x 5 mL), and dried in vacuo; yield, ~40%.

$[Mn^{III}_8O_4$(phamidox)$_8$(MeOH)$_2$(H_2O)]·5.25MeOH·9.45H_2O (2· 5.25MeOH·9.45H_2O**).** $MnBr_2$·4H_2O (1 mmol, 286 mg), phamidoxH_2 (1 mmol, 166 mg) and NEt_3 (2 mmol) were stirred in MeOH (20 ml) for a period of ~45 minutes to form a dark brown solution. The solution was filtered and allowd to evaporate slowly. Black crystals were formed during ~5

days and were collected by filtration, washed with Et_2O (2 x 5 mL), and dried in vacuo; yield, ~30%.

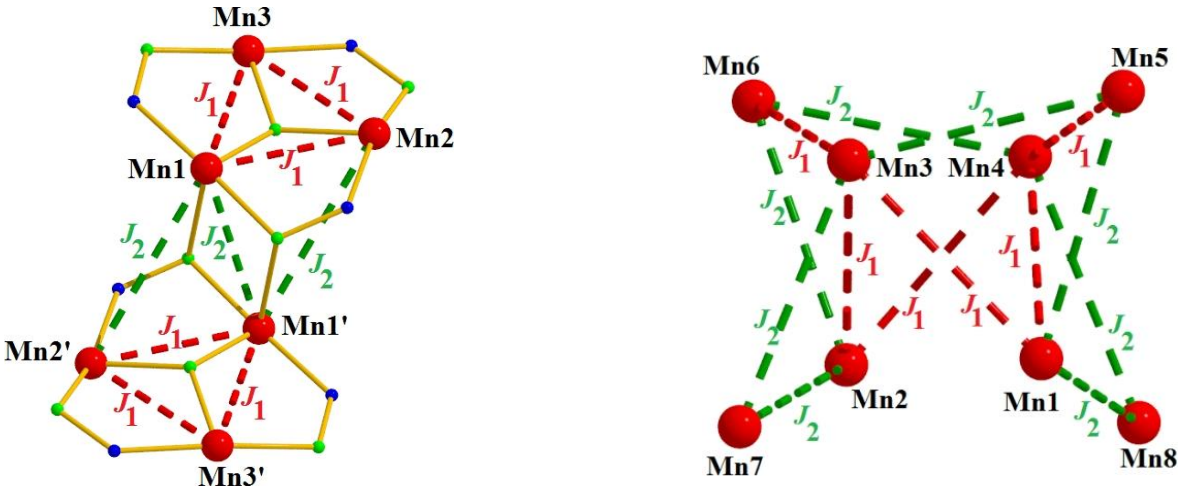

Fig. S1. Interaction schemes for complexes **1** (left) and **2** (right).