Supporting Information for "*Manganese clusters derived from 2-pyridylcyanoxime: new topologies and large spin ground state in pyridyloximate chemistry*".

Structural information for compound 2b

Table S1. Selected interatomic distances (Å) and angles (deg.) for compound **2b**.

Mn(1)-O(11)	2.109(2)	Mn(2)-O(21)	2.130(2)
Mn(1)-O(12)	2.125(2)	Mn(2)-O(22)	2.096(2)
Mn(1)-N(11)	2.308(3)	Mn(2)-N(21)	2.288(3)
Mn(1)-N(13)	2.300(3)	Mn(2)-N(23)	2.304(3)
Mn(1)-N(14)	2.264(3)	Mn(2)-N(24)	2.265(3)
Mn(1)-N(16)	2.293(3)	Mn(2)-N(26)	2.255(3)
Mn(1)-N(13)-O(12')-Mn(1')	27.9(3)	Mn(2)-N(14)-O(21')-Mn(2')	33.2(3)
Mn(1)-N(16)-O(11')-Mn(1')	32.3(3)	Mn(2)-N(26)-O(22')-Mn(2')	37.9(3)

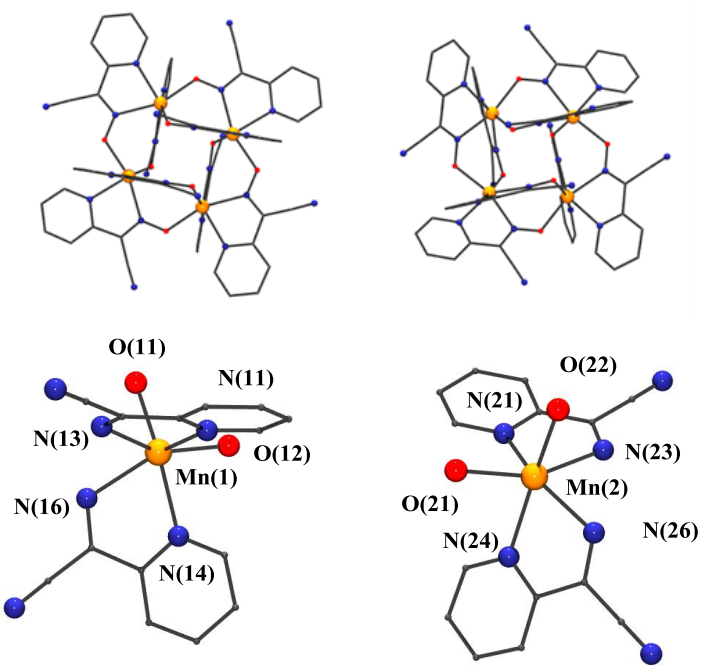

Fig. S1 Top, view of the two non-equivalent molecules found in the structure of **2b**. Bottom, partially labeled asymmetric unit.

Table S2. BSV parameters for complexes **3**, **4** and **5**.

Cluster 3	BSV value	Assigned valence	**Cluster 5**	BSV value	Assigned valence
Mn(1)	2.83	3^+	Mn(1)	4.01	4^+
Mn(2)	2.86	3^+	Mn(2)	2.95	3^+
Mn(3)	1.92	2^+	Mn(3)	3.03	3^+
Mn(4)	1.97	2^+	Mn(4)	2.89	3^+
			Mn(5)	2.88	3^+
Cluster 4			Mn(6)	2.89	3^+
Mn(1)	1.95	2^+	Mn(7)	2.83	3^+
Mn(2)	2.93	3^+	Mn(8)	2.06	2^+
Mn(3)	3.17	3^+	Mn(9)	2.08	2^+
Mn(4)	3.18	3^+	Mn(10)	2.06	2^+
Mn(5)	3.96	4^+			

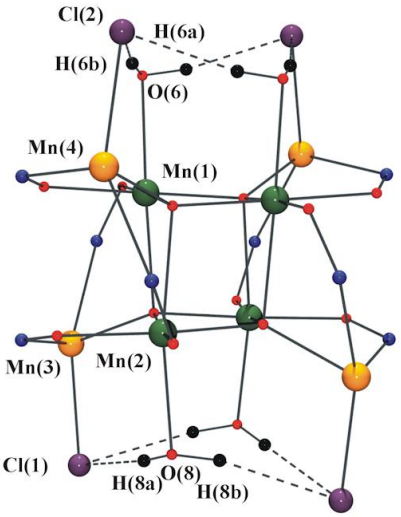

Fig. S2 Core of **3** showing the set of the H-bond parameters between the water molecules and the chloride atoms.

Table S3. Parameters for the intramolecular H-bonds found in complex **3**.

	O-H (Å)	H···Cl (Å)	O···Cl (Å)	O-H···Cl (deg.)
O(6)-H(6a)···Cl(2)	0.89(3)	2.25(4)	3.127(3)	170(4)
O(8)-H(8a)···Cl(1)	0.90(2)	2.3823)	3.223(4)	155(3)
O(6)-H(6b)···Cl(2)	0.87(3)	2.25(3)	3.106(4)	167(5)
O(8)-H(8b)···Cl(1)	0.900(18)	2.34(2)	3.222(5)	165(5)

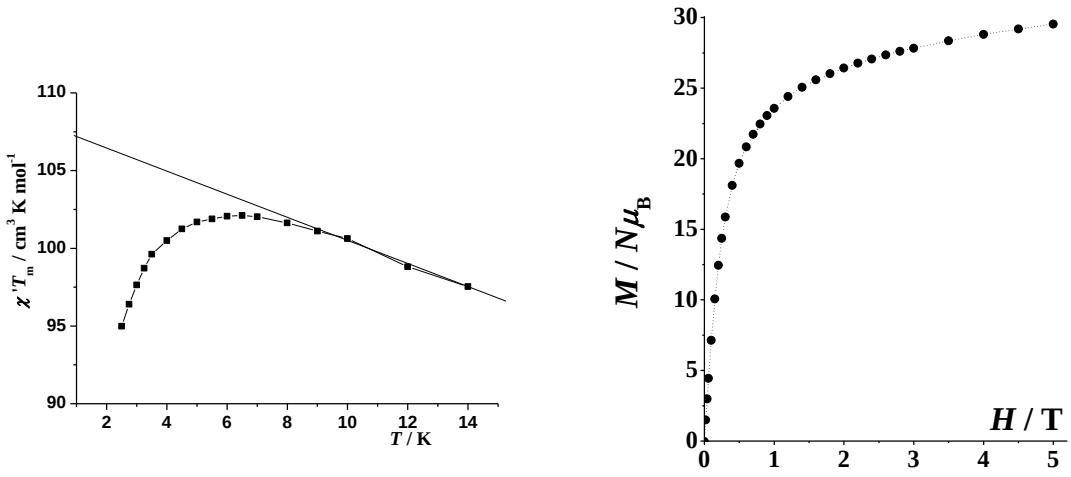

Fig. S3 Left, plot of the $\chi_M T$ *vs.* *T* for compound **5** showing the low T extrapolation value. Right, isothermal magnetization at 2 k for compound **5**, showing the fast magnetization at low fields and the unsaturated value under the maximum external field of 5 T.