Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Table S1 Bond valence sum analysis of Mn ions for **1**.

	Bond Valence Sum		
	Mn^{II}	**Mn^{III}**	**Mn^{IV}**
Mn1	4.28	3.94	**3.87**
Mn2	3.35	**3.09**	3.03
Mn3	3.43	**3.16**	3.10
Mn4	3.41	**3.14**	3.09
Mn5	3.34	**3.08**	3.02
Mn6	**1.90**	1.75	1.72
Mn7	**1.99**	1.84	1.80
Mn8	**1.80**	1.66	1.63
Mn9	3.24	**2.98**	2.93
Mn10	**2.02**	1.86	1.82

Table S2 Bond valence sum analysis of inorganic O atoms for **1**.

	BVS	Asgmt.
O1	1.95	**O^{2-}**
O2	2.05	**O^{2-}**
O4	2.00	**O^{2-}**
O5	2.01	**O^{2-}**
O3	1.98	**O^{2-}**
O6	1.35	**OH^{-}**
O7	1.24	**OH^{-}**

Table S3 Bond valence sum analysis of Mn ions for **2**.

	Bond Valence Sum						
	Mn^{II}	Mn^{III}	Mn^{IV}		Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	3.30	**3.04**	2.99	Mn7A	3.20	**2.95**	2.89
Mn2A	3.45	**3.18**	3.12	Mn7B	3.31	**3.05**	2.99
Mn2B	3.38	**3.11**	3.06	Mn8A	3.36	**3.09**	3.04
Mn3A	3.32	**3.06**	3.00	Mn8B	3.42	**3.15**	3.09
Mn3B	3.41	**3.15**	3.09	Mn9A	**1.91**	1.76	1.73
Mn4A	3.24	**2.98**	2.93	Mn9B	**1.91**	1.76	1.73
Mn4B	3.28	**3.03**	2.97	Mn10	3.24	**2.99**	2.94
Mn5A	3.40	**3.14**	3.08	Mn11	3.40	**3.14**	3.08
Mn5B	3.42	**3.15**	3.09	Mn12	**2.22**	2.04	2.00
Mn6A	**1.97**	1.82	1.79	Mn13	**2.15**	1.98	1.95
Mn6B	**1.93**	1.78	1.75				

Table S4 Bond valence sum analysis of inorganic O atoms for **1**.

	BVS	Asgmt		BVS	Asgmt
O1	2.20	**O^{2-}**	O9	1.89	**O^{2-}**
O2	1.91	**O^{2-}**	O10	1.77	**O^{2-}**
O3	2.06	**O^{2-}**	O11	1.98	**O^{2-}**
O4	1.90	**O^{2-}**	O12	2.06	**O^{2-}**
O5	1.89	**O^{2-}**	O13	1.12	**OH^{-}**
O6	1.96	**O^{2-}**	O14	1.13	**OH^{-}**
O7	2.16	**O^{2-}**	O15	1.15	**OH^{-}**
O8	2.14	**O^{2-}**	O16	1.19	**OH^{-}**

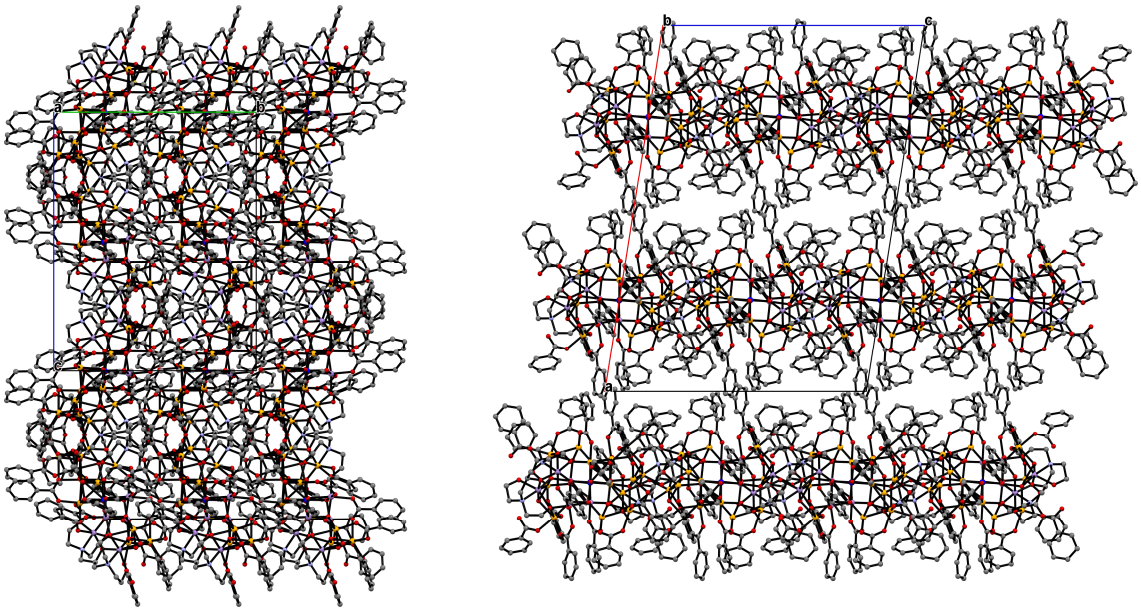

Figure S1 Packing diagrams of **1**·4H_2O viewed along the a-(left) and b-axis (right). All solvent molecules are omitted for clearly.

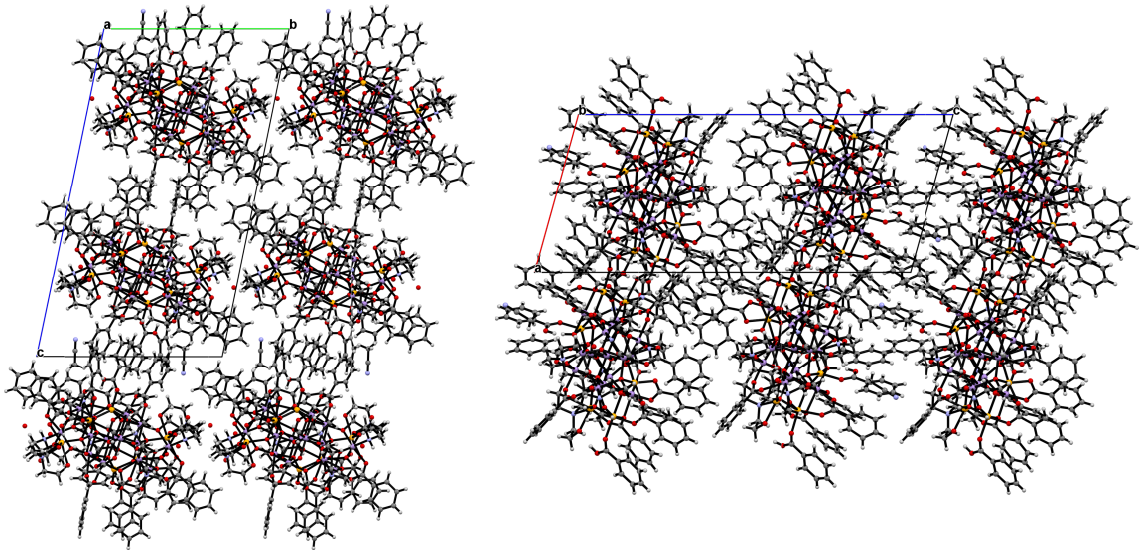

Figure S2 Packing diagrams of **2**·7H_2O viewed along the a-(left) and b-axis (right). All solvent molecules are omitted for clearly.

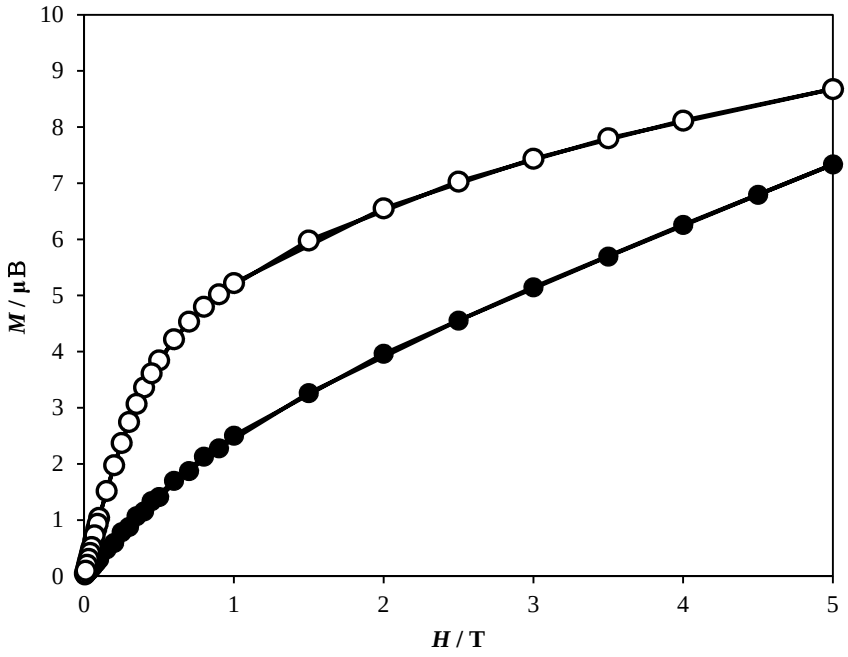

Figure S3 *M vs. H* plots for **1**·4H_2O (●) and **2**·7H_2O (○) measured at 1.8 K.

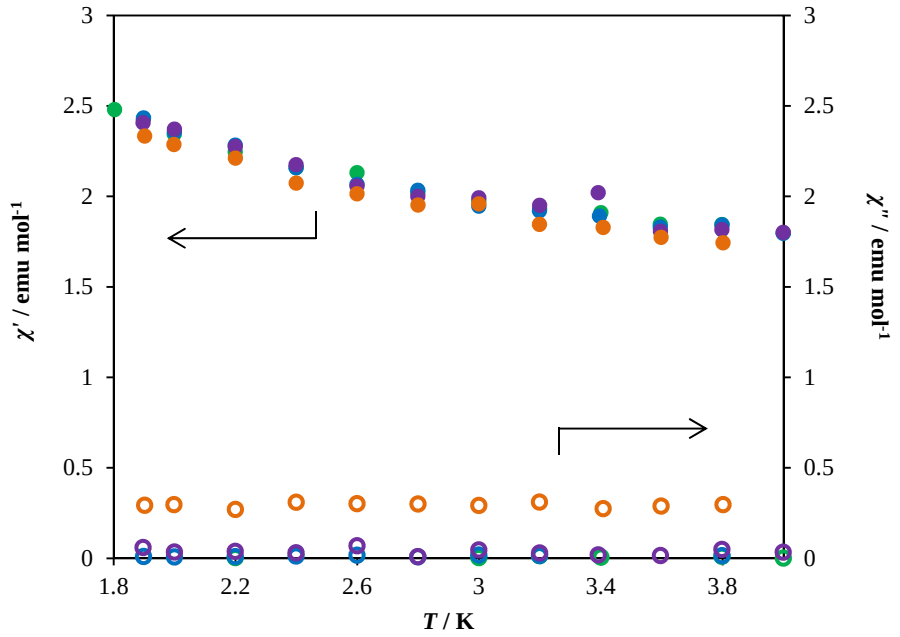

Figure S4 Temperature dependence of the in-phase (χ', filled circle) and out-of-phase (χ", open circle) ac magnetic susceptibilities of **1**·4H_2O measured at 1 (green), 10 (blue), 100 (purple) and 1000 Hz (orange) under zero dc field.

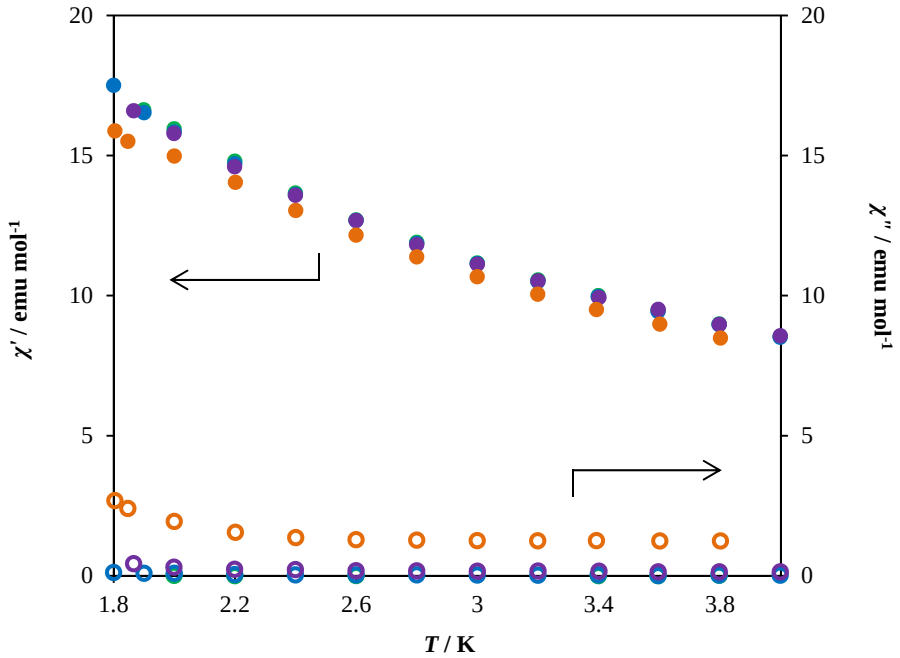

Figure S5 Temperature dependence of the in-phase (χ', filled circle) and out-of-phase (χ", open circle) ac magnetic susceptibilities of **2**·7H_2O measured at 1 (green), 10 (blue), 100 (purple) and 1000 Hz (orange) under zero dc field.