Table S1: Density functional dependence of calculated Mn–Mn distances for tri-μ-oxo-protonated and non-protonated forms of the WOC model structure **I**.

Functional	spin state	coupling	Mn–Mn Distances / Ångstroms [a]					
			Mn(1)–Mn(2)	Mn(2)–Mn(3)	Mn(1)–Mn(3)	Mn(3)–Mn(4)	Mn(1)–Mn(4)	
			2.64	**2.70**	**3.29**	**3.24**	**5.43**	**(2.9 Å**
			2.80	**2.90**	**3.29**	**2.94**	**4.98**	**1.9 Å XRD**
			2.69—2.74 [b]	**2.69—2.74** [b]				**EXAFS**
BP	$S = 8$	AAAA [c]	3.10 / 2.76	3.06 / 2.86	3.69 / 3.52	3.12 / 3.14	5.69 / 5.48	
	$M_S = 0$	ABAB [c]	3.07 / 2.74	3.01 / 2.81	3.66 / 3.47	3.07 / 2.92	5.78 / 5.37	
	$M_S = 0/1$ [d]	ABBA [c,d]	3.07 / 2.73	3.10 / 2.84	3.71 / 3.47	2.93 / 2.93	6.21 / 5.39	
B3-LYP	$S = 8$	AAAA [c]	3.10 / 2.75	3.08 / 2.86	3.73 / 3.51	3.16 / 3.18	5.76 / 5.45	
	$M_S = 0$	ABAB [c]	3.11 / 2.74	3.08 / 2.84	3.72 / 3.50	3.14 / 3.10	5.79 / 5.42	
	$M_S = 0/1$ [d]	ABBA [c,d]	3.10 / 2.74	3.10 / 2.85	3.73 / 3.50	3.13 / 3.11	5.79 / 5.44	
PBE0	$S = 8$	AAAA [c]	3.05 / 2.73	3.04 / 2.83	3.71 / 3.43	3.11 / 3.13	5.70 / 5.29	
	$M_S = 0$	ABAB [c]	3.07 / 2.72	3.05 / 2.81	3.69 / 3.42	3.09 / 3.06	5.75 / 5.26	
	$M_S = 0/1$ [d]	ABBA [c,d]	3.06 / 2.72	3.07 / 2.82	3.71 / 3.42	3.09 / 3.07	5.76 / 5.28	

Notes:

a Mn–Mn distances displayed as protonated/non-protonated values.

b Range of data from Yachandra et al[40] and Dau et al.[41] for the two 'close' Mn–Mn vectors in S_1.

c Coupling scheme, where, for example, 'ABAB' denotes the consistently-antiferromagnetic (αβαβ) coupling mode.

d $M_S = 0$ (protonated) or $M_S = 1$ (non-protonated) 'ABBA' (αββα) coupling.