Supporting Information

The remarkable influence of *N,O*-ligands in the assembly of mixed valence bis-calix[4]arene-supported Mn clusters

Information comprises:

- Figure S1: Common coordination modes for DEA, its derivatives and L_1.
- Figure S2: Inter-cluster spacing along the *b* axis in the expanded crystal structure of **6**.
- Figure S3: Plot of $\chi_M T$ versus *T* for **6** in the *T* = 5-300 K range in an applied field of *B* = 0.1 T. Inset: VTVB data.
- Figures S4 – S6: Large versions of figures 1 – 3 in the manuscript.
- Table with comparison of bond lengths relevant to discussion of the structure of **6**.
- Bond Valence Sum calculations.

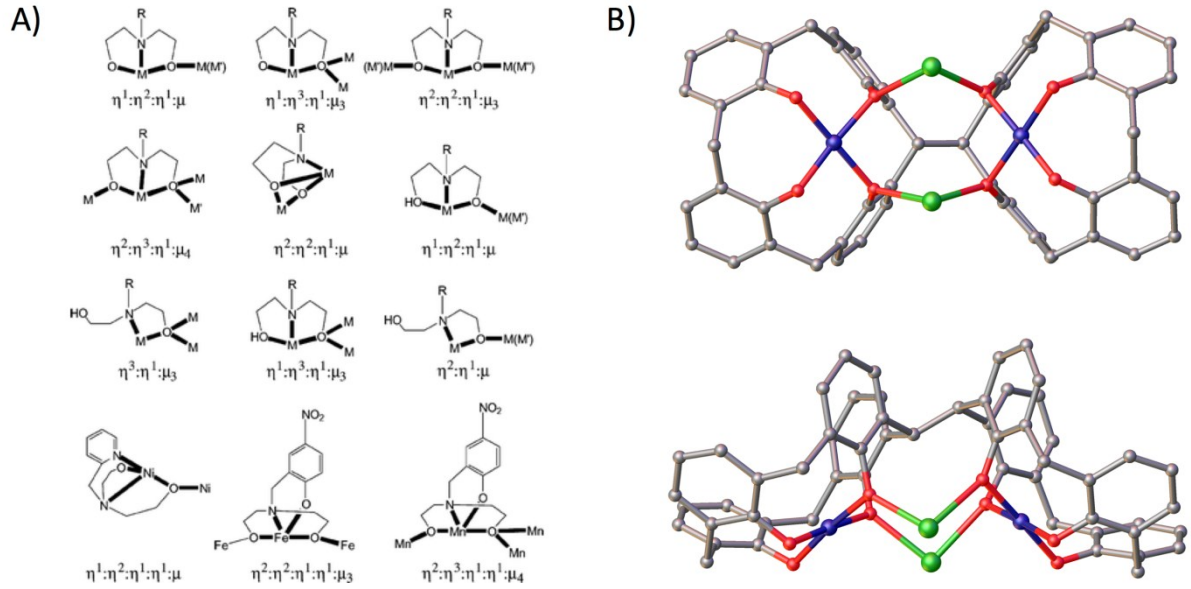

Figure S1. A) Common bridging coordination modes found for DEA and its derivatives, reproduced from source (Royal Society of Chemistry).[S1] B) Typical coordination modes found upon deprotonation of H_8L1 and ligand inversion.[S2]

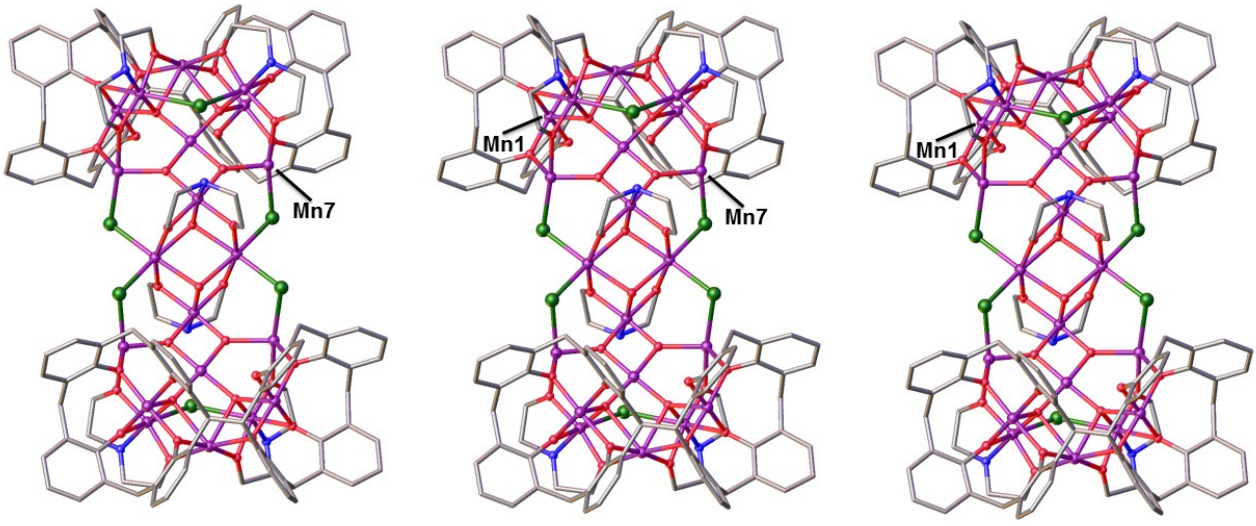

Figure S2. View of the *ac* plane in the extended structure of **6** with closest ions labelled according to discussion. Colour code: Mn – purple; O – purple; N – blue; C – grey; Cl – green. tBu groups, hydrogen atoms, ligated solvent molecules and solvent of crystallisation omitted for clarity.

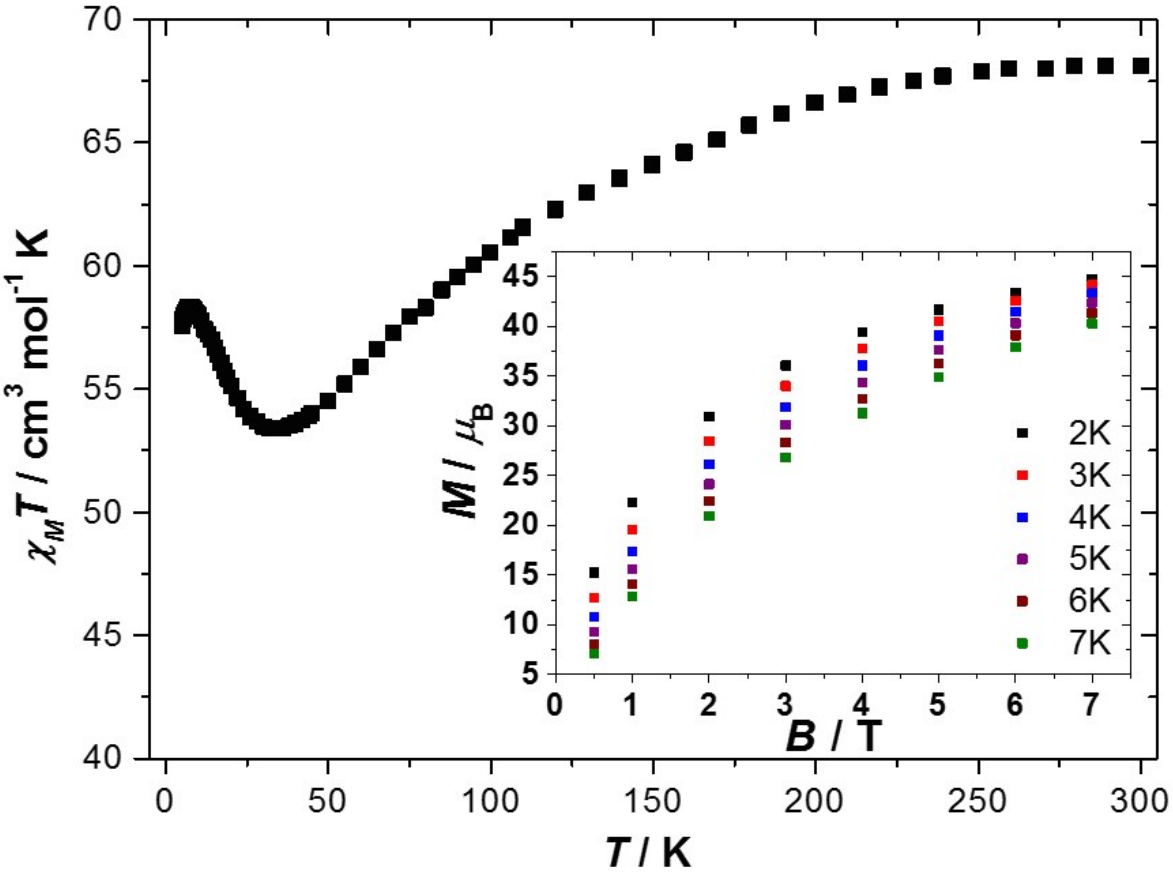

Figure S3. Plot of $\chi_M T$ versus T for **6** in the T = 5-300 K range in an applied field of B = 0.1 T. Inset: VTVB data.

References

S1. A. J. Tasiopoulos and S. P. Perlepes, *Dalton Trans*., 2008, 5537.

S2. R. McLellan, M. A. Palacios, C. M. Beavers, S. J. Teat, S. Piligkos, E. K. Brechin, S. J. Dalgarno, *Chem. Eur. J.*, 2015, **21**, 2804; M. Coletta, R. McLellan, A. Waddington, S. Sanz, K. J. Gagnon, S. J. Teat, E. K. Brechin, S. J. Dalgarno, *Chem. Comm.*, 2016, **52**, 14246; M. Coletta, R. McLellan, S. Sanz, K. J. Gagnon, S. J. Teat, E. K. Brechin, S. J. Dalgarno, *Chem. Eur. J.*, 2017, DOI: 10.1002/chem.201703197.

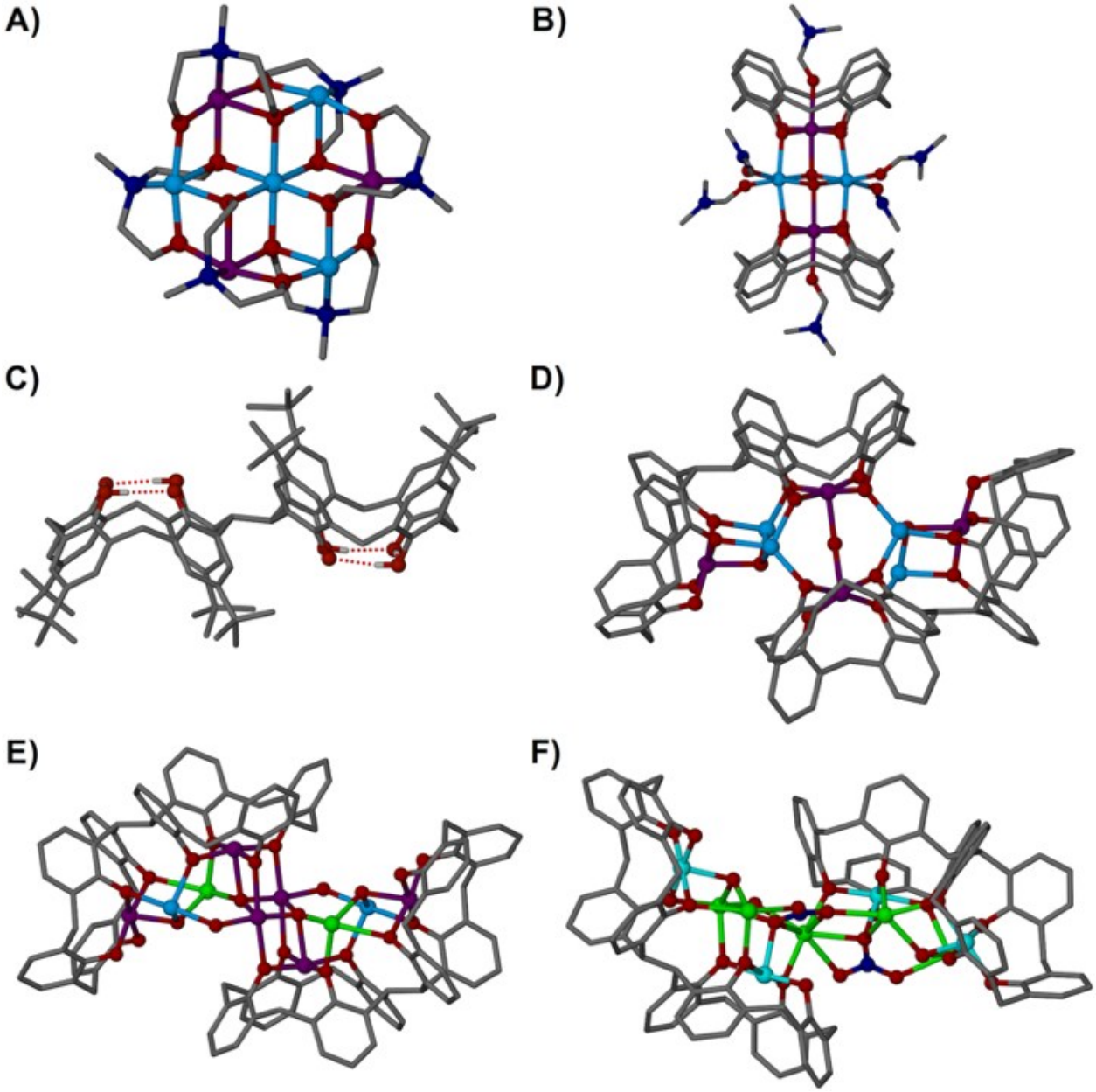

Figure S4. Large version of Figure 1 from manuscript.

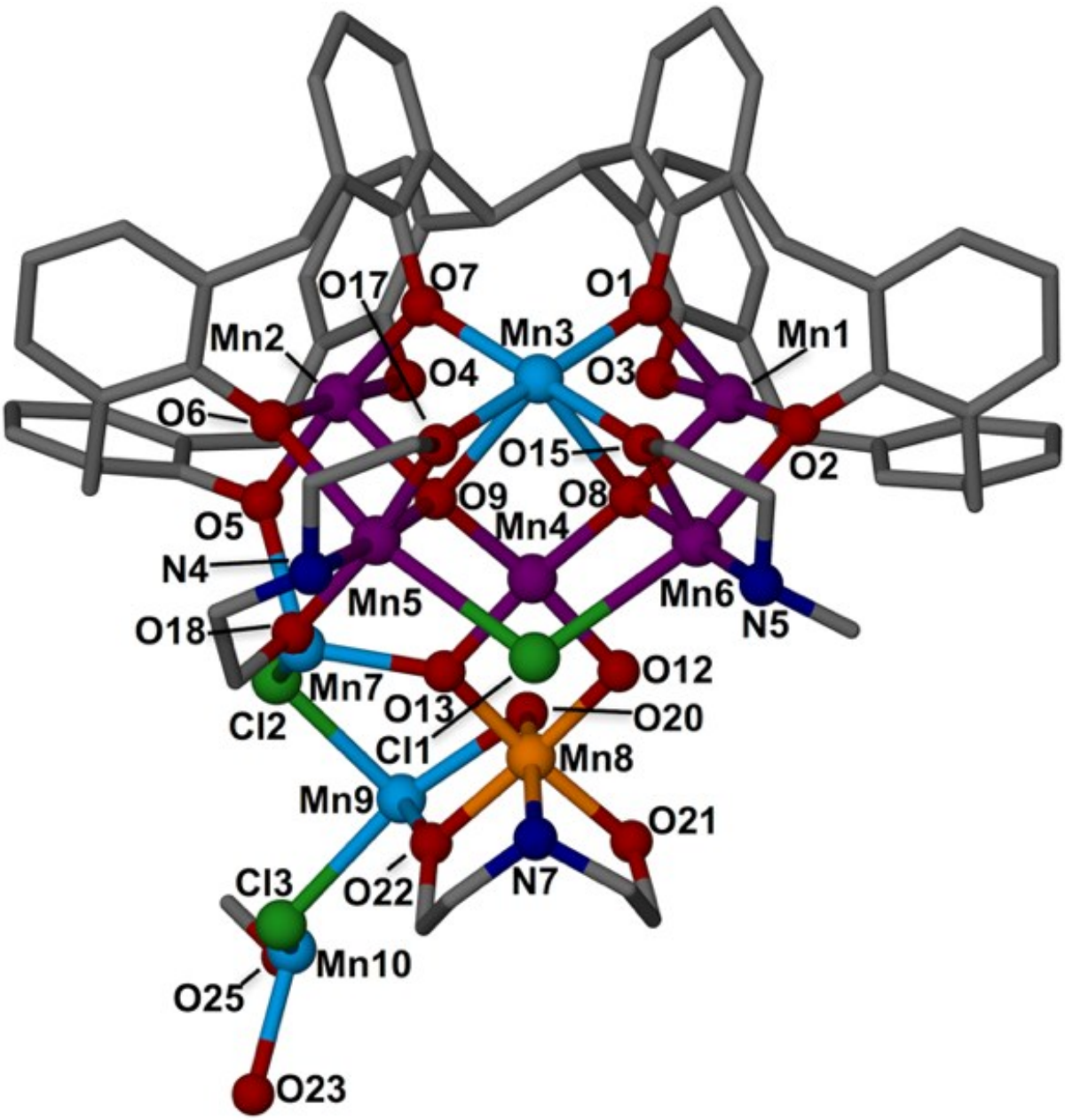

Figure S5. Large version of Figure 2 from manuscript.

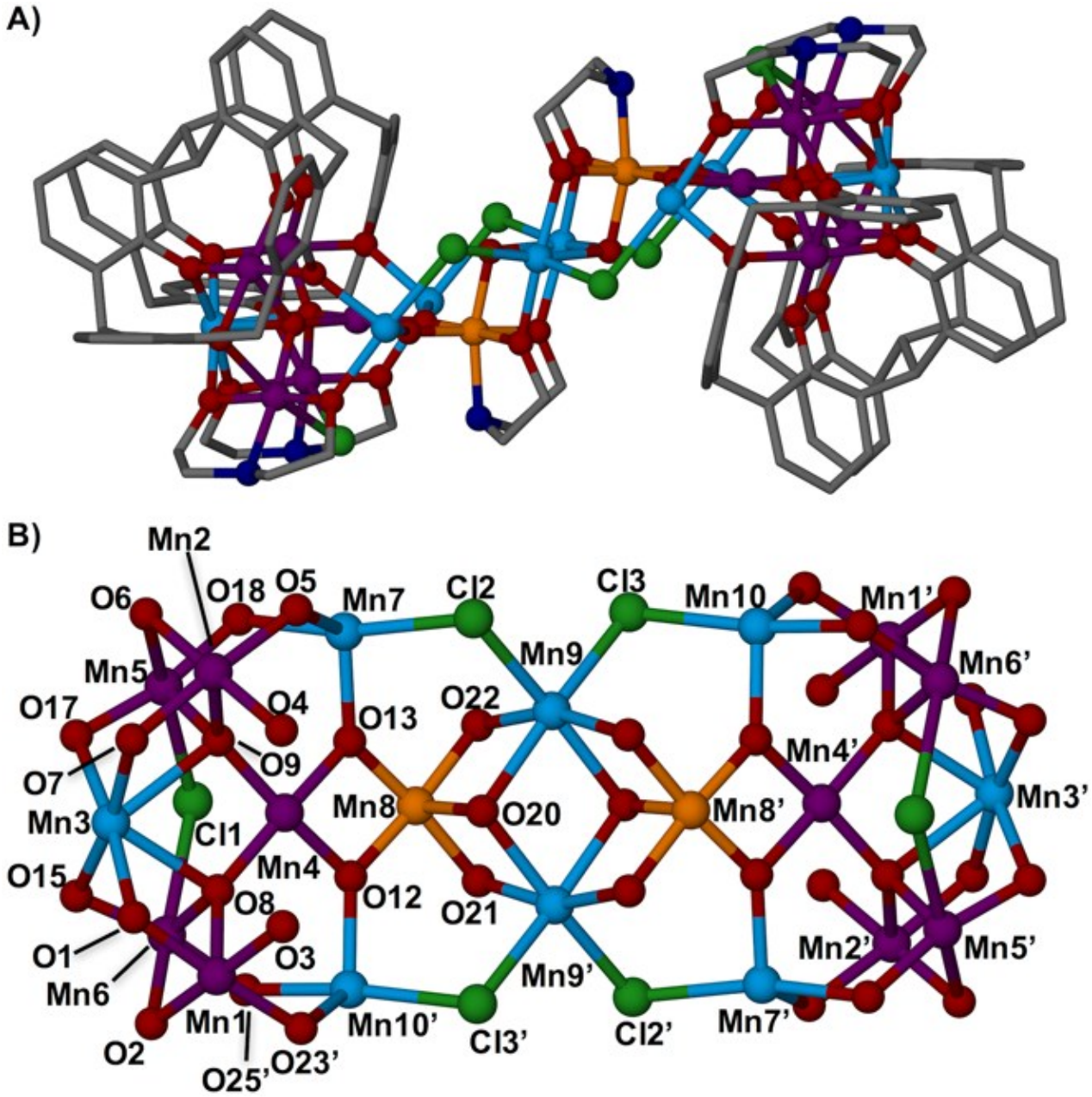

Figure S6. Large version of Figure 3 from manuscript.

Mn1	O1, 1.942(4)	O2, 1.927(4)	O3, 1.890(4)	O23', 1.967(4)	O8, 2.143(3)	O10, 2.240(4)	-
Mn2	O4, 1.897(4)	O5, 1.975(4)	O6, 1.924(4)	O7, 1.957(4)	O9, 2.119(4)	O11, 2.249(4)	-
Mn3	O1, 2.210(4)	O7, 2.209(4)	O8, 2.416(4)	O9, 2.509(4)	O14, 2.200(4)	O15, 2.180(4)	O17 2.168(4)
Mn4	O8, 1.894(3)	O9, 1.885(4)	O12, 1.865(3)	O13, 1.866(3)	O16, 2.281(4)	-	-
Mn5	O6, 2.321(4)	O9, 1.849(4)	O17, 1.866(4)	O18, 1.890(4)	N4, 2.018(4)	Cl1, 2.7804(16)	-
Mn6	O2, 2.295(4)	O8, 1.859(4)	O15, 1.871(4)	O25', 1.891(4)	N5, 2.021(5)	Cl1, 2.8272(16)	-
Mn7	O5, 2.133(4)	O13, 2.028(3)	O18, 2.137(4)	O19, 2.136(4)	Cl2, 2.5214(15)	-	-
Mn8	O12, 1.821(3)	O13, 1.828(3)	O20, 1.917(4)	O21, 1.926(4)	O22, 1.924(4)	N7, 2.043(5)	-
Mn9	O20, 2.240(3)	O20', 2.255(3)	O21', 2.112(4)	O22, 2.110(4)	Cl2, 2.4971(15)	Cl3, 2.4908(14)	-
Mn10	O12', 2.029(3)	O23, 2.121(4)	O24, 2.127(4)	O25, 2.155(4)	Cl3, 2.5311(16)	-	-

Table S1. Bond lengths relating to the coordination spheres of crystallographically unique Mn ions in the crystal structure of **6**.

BVS

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	r(0)	beta
Mn1	1,942	1,927	1,89	1,967	2,143	2,24	1,76	0,37
	-0,182	-0,167	-0,13	-0,207	-0,383	-0,48		
	-0,49189	-0,45135	-0,35135	-0,559459	-1,03514	-1,2973		
	0,611468	0,636767	0,703736	0,5715179	0,355178	0,273269		
M(Ox.State)	3,151938							

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	r(0)	beta
Mn2	1,897	1,975	1,924	1,957	2,119	2,249	1,76	0,37
	-0,137	-0,215	-0,164	-0,197	-0,359	-0,489		
	-0,37027	-0,58108	-0,44324	-0,532432	-0,97027	-1,32162		
	0,690548	0,559293	0,641951	0,587175	0,378981	0,266702		
M(Ox.State)	3,12465							

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	d(M-L7)	r(0)	beta
Mn3	2,21	2,416	2,18	2,168	2,509	2,2	2,209	1,79	0,37
	-0,42	-0,626	-0,39	-0,378	-0,719	-0,41	-0,419		
	-1,13514	-1,69189	-1,05405	-1,021622	-1,94324	-1,10811	-1,13243		
	0,321379	0,184171	0,348522	0,3600107	0,143239	0,330183	0,322248		
M(Ox.State)	2,009752								

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	r(0)	beta
Mn4	1,894	1,885	1,866	1,865	2,281	1,76	0,37
	-0,134	-0,125	-0,106	-0,105	-0,521		
	-0,36216	-0,33784	-0,28649	-0,283784	-1,40811		
	0,696169	0,713311	0,750897	0,7529294	0,244606		
M(Ox.State)	3,157913						

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	r(0)	beta
Mn5	1,849	1,866	1,89	2,018	2,321	2,7804	1,76	0,37
	-0,089	-0,106	-0,13	-0,258	-0,561	-1,0204		
	-0,24054	-0,28649	-0,35135	-0,697297	-1,51622	-2,75784		
	0,786203	0,750897	0,703736	0,4979292	0,219541	0,063429		
M(Ox.State)	3,021735							

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	r(0)	beta
Mn6	1,859	1,871	1,891	2,021	2,295	2,8272	1,76	0,37
	-0,099	-0,111	-0,131	-0,261	-0,535	-1,0672		
	-0,26757	-0,3	-0,35405	-0,705405	-1,44595	-2,88432		
	0,765239	0,740818	0,701837	0,4939083	0,235523	0,055893		
M(Ox.State)	2,993218							

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	r(0)	beta
Mn7	2,133	2,137	2,136	2,028	2,5214	1,79	0,37
	-0,343	-0,347	-0,346	-0,238	-0,7314		
	-0,92703	-0,93784	-0,93514	-0,643243	-1,97676		
	0,395728	0,391473	0,392533	0,5255851	0,138518		
M(Ox.State)	1,843837						

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	r(0)	beta
Mn8	1,821	1,828	1,917	1,926	2,043	1,924	1,753	0,37
	-0,068	-0,075	-0,164	-0,173	-0,29	-0,171		
	-0,18378	-0,2027	-0,44324	-0,467568	-0,78378	-0,46216		
	0,832116	0,816521	0,641951	0,6265244	0,456675	0,62992		
M(Ox.State)	4,003707							

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	d(M-L6)	r(0)	beta
Mn9	2,254	2,24	2,112	2,11	2,4971	2,4908	1,79	0,37
	-0,464	-0,45	-0,322	-0,32	-0,7071	-0,7008		
	-1,25405	-1,21622	-0,87027	-0,864865	-1,91108	-1,89405		
	0,285346	0,296349	0,418838	0,4211085	0,14792	0,150461		
M(Ox.State)	1,720023							

metal VBS	d(M-L1)	d(M-L2)	d(M-L3)	d(M-L4)	d(M-L5)	r(0)	beta
Mn10	2,121	2,155	2,029	2,127	2,5311	1,79	0,37
	-0,331	-0,365	-0,239	-0,337	-0,7411		
	-0,89459	-0,98649	-0,64595	-0,910811	-2,00297		
	0,408773	0,372885	0,524166	0,402198	0,134934		
M(Ox.State)	1,842956						