Electronic Supplementary Information

Altering the nature of coupling by changing the oxidation state in a {Mn₆} cage

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S1. Experimental Characterisation

Elemental (C, H, N) analysis was performed using an Exeter Analytical CE 440 at the microanalytical laboratory at the School of Chemistry and Chemical Biology of University College Dublin, Belfield, Dublin, Ireland.

Powder X-ray diffraction data was collected on a Bruker D2 Phaser diffractometer at 25°C using Cu-K α radiation at 30 kV and 10 mA, with a step size of 0.02° (2 θ) between 5 and 25° (2 θ). The samples were grounded and loaded on a low-background silicon sample holder. The data obtained is presented in (**Fig. S1.1**) and can be seen to match the simulated data confirming the phase purity of the sample.



Fig. S1.1: Simulated and measure powder X-ray diffraction pattern for $[Cl \subset Mn^{III}_{6}(tert-butyl-PO_3)_{8}(4-picoline)_{6}]Cl.$

Infrared spectrum was obtained using a PerkinElmer Spectrum One FT-IR spectrometer with a universal Attenuated Total Reflectance (ATR) sampling accessory. The spectrum obtained is shown in **Fig. S1.2**.



Fig. S1.2: Infrared spectrum of [Cl⊂Mn^{III}₆(*tert*-butyl-PO₃)₈(4-picoline)₆]Cl.

S2. Fully reduced state

S2.1 Comparison of key bond lengths in the crystal structure and DFT model

Configuration\Parameter	Mn-Mn	Mn-Mn	Mn-Cl	Mn-N	Mn-O	P-O
	(trans)	(CIS)				
Experimental ¹	6.217	4.396	3.109	2.228	1.866	1.485
Ferromagnetic	6.192	4.378	3.096	2.279	1.896	1.543
Mn1	6.190	4.377	3.095	2.279	1.895	1.543
Mn12	6.189	4.376	3.095	2.279	1.893	1.543
Mn14	6.192	4.378	3.096	2.279	1.895	1.543
Mn123	6.188	4.376	3.094	2.279	1.895	1.543
Mn124	6.190	4.377	3.095	2.279	1.895	1.543

Table S2.1: Average of key bond lengths (Å) in the fully reduced state.

 Table S2.2: Mn-Mn distances (Å) in different charged states.

		Charged States							
	Fully			2 nd		3 rd		4 th	
	reduced	1 st	2 nd (Cis)	(Trans)	3 rd (Fac)	(Mer)	4 th (<i>Cis</i>)	(Trans)	
Mn1Mn2	4.386	4.328	4.455	4.325	4.488	4.156	4.374	4.162	
Mn1Mn3	4.386	4.473	4.532	5.506	4.539	4.405	4.503	4.425	
Mn1Mn5	4.406	4.487	4.488	5.482	4.539	4.389	4.334	4.411	
Mn1Mn6	4.406	4.482	4.534	4.509	4.462	4.415	4.215	4.434	
Mn2Mn3	4.386	4.322	4.387	4.324	4.462	4.409	4.514	4.425	
Mn2Mn4	4.406	4.328	4.107	4.325	4.228	4.461	4.513	4.415	
Mn2Mn6	4.406	4.322	4.382	4.320	4.228	4.413	4.384	4.427	
Mn3Mn4	4.406	4.482	4.407	4.509	4.487	4.566	4.575	4.542	
Mn3Mn5	4.406	4.493	4.534	4.480	4.539	4.512	4.505	4.545	
Mn4Mn5	4.386	4.487	4.441	4.482	4.462	4.485	4.524	4.470	
Mn4Mn6	4.386	4.473	4.379	4.504	4.229	4.568	4.487	4.549	
Mn5Mn6	4.386	4.493	4.549	4.478	4.488	4.505	4.334	4.538	
Mn1Mn4	6.217	6.332	6.183	6.377	6.262	6.223	6.286	6.177	
Mn2Mn5	6.217	6.130	6.182	6.072	6.262	6.140	6.259	6.165	
Mn3Mn6	6.217	3.332	6.436	6.369	6.262	6.468	6.281	6.510	

S2.2 Spin densities on the Mn centres in the fully reduced state

The spin densities calculated from Mulliken², Bader³ and Hirshfeld⁴ analysis are provided in **Table S2.4**, **Table S2.3** and **Table S2.5** respectively. As can be seen, the spin density values for all Mn³⁺ centres have been found to be greater than 3.9 in the different electronic states with Mulliken analysis which is slightly higher than the spin densities obtained using Bader and Hirshfeld analysis.

Table S2.3: Bader spin density on Mn centres in the different electronic configurations (the negativesign implies that the Mn centre has a beta spin). The states Mn16, Mn156 and Mn146 are symmetryequivalent to the Mn12, Mn123 and Mn124 states respectively.

Configuration\ Mn centre	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
Ferromagnetic	3.789072	3.789429	3.789459	3.789517	3.789554	3.789122
Mn1	-3.786139	3.788981	3.789256	3.787154	3.789234	3.789145
Mn16	-3.786148	3.788682	3.786628	3.786702	3.788807	-3.785996
Mn14	-3.788319	3.788483	3.788743	-3.788210	3.788925	3.789006
Mn156	-3.786332	3.786132	3.786311	3.786816	-3.786231	-3.786234
Mn146	-3.788598	3.788547	3.786669	-3.788525	3.788520	-3.786571

Table S2.4: Mulliken spin density on Mn centres in the different electronic configurations. The statesMn16, Mn156 and Mn146 are symmetry equivalent to the Mn12, Mn123 and Mn124 statesrespectively.

Configuration\ Mn centre	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
Ferromagnetic	3.945689	3.945697	3.945713	3.945697	3.945735	3.945724
Mn1	-3.917967	3.939913	3.941052	3.938917	3.939887	3.938917
Mn16	-3.923910	3.935124	3.934367	3.933188	3.935194	-3.922659
Mn14	-3.924529	3.933991	3.936438	-3.924586	3.934034	3.936377
Mn156	-3.928590	3.928520	3.928520	3.928556	-3.928570	-3.928545
Mn146	-3.930480	3.929221	3.929743	-3.930476	3.929271	-3.927297

Table S2.5: Hirshfield spin density on Mn centres in the different electronic configurations. Thestates Mn16, Mn156 and Mn146 are symmetry equivalent to the Mn12, Mn123 and Mn124 statesrespectively.

Configuration\ Mn centre	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
Ferromagnetic	3.744320	3.744325	3.744352	3.744344	3.744378	3.744361
Mn1	-3.728145	3.741182	3.741150	3.740853	3.741173	3.741185
Mn16	-3.731379	3.737919	3.737696	3.737706	3.737962	-3.731328
Mn14	-3.731633	3.738058	3.738109	-3.731674	3.738086	3.738064
Mn156	-3.734517	3.734491	3.734470	3.734499	-3.734523	-3.734498
Mn146	-3.734824	3.734790	3.734609	-3.734838	3.734810	-3.734575

Configuration	Energy (Hartrees)	Relative Energy (cm ⁻¹)
Ferromagnetic	-8605.80604922131	0.00
Mn1	-8605.80660988527	-123.05
Mn16	-8605.80700735046	-210.29
Mn14	-8605.80671484027	-146.09
Mn156	-8605.80722969148	-259.08
Mn146	-8605.80694625747	-196.88

Table S2.6: Energy of the various configurations modelled for the fully reduced state and their energy relative to the ferromagnetic state.

S2.3 $< S^2 >$ values for the different spin configurations of the {Mn₆} cage in the fully reduced state

The $\langle S^2 \rangle$ values (before annihilation of spin contamination), that are required for the generalized spin projection approach⁵ are presented in **Table S2.7**. The spin projection method for this complex leads to a spin polarisation value SP = 0.2574 indicating minimal polarisation.

Table S2.7: $< S^2 >$ values for the different spin configurations of the {Mn₆} cage in the fully reduced state.

State	Ferromagnetic	Mn1	Mn16	Mn14	Mn156	Mn146
$< S^2 >$	156.2574	76.2535	28.2534	28.2506	12.2515	12.2488

Table S2.8: Bader spin density on the coordinating atoms in the fully reduced state (ferromagnetic configuration). The number next to each N represents the Mn centre to which it is linked. For the O centres, the sum of spin density on the four oxygen centres linked to and residing in between the corresponding Mn centres is provided. The number next to O represents the Mn centres being taken into account.

	Bader		Bader		Bader		Bader
	Spin		Spin		Spin		Spin
012	0.085	O16	0.086	026	0.084	045	0.084
013	0.084	023	0.084	O34	0.084	O46	0.084
015	0.084	024	0.084	035	0.084	056	0.085
N1	0.056	N2	0.056	N3	0.056	N4	0.056
N5	0.056	N6	0.056				

Cl 0.116

S2.4 Calculation of J-values using different definitions of spin operator

In order to calculate the J-values, we used the formal spin values and the generalized spin projection approach⁵ to define the spin operator besides the charge analyses mentioned above. The J-values have been summarized in **Table S2.9**. The pair of coupling constants obtained by the spin projection approach is very close to that obtained by the formal spin approach which assumes that the unpaired electrons are strongly localised on the Mn centres. The J_{cis} value obtained by using Mulliken analysis to define the spin operators is very close to the J_{cis} value predicted by the experimental fit.

These J-values have been used to calculate the χT vs T plots for this state which are presented in **Fig. S2.1**. The plots obtained using Hirshfeld and Bader analyses seem to be closest to the experimental curve.

Approach\J value	J _{trans} (cm ⁻¹)	J _{cis} (cm ⁻¹)
Formal Spin	-3.12 ± 0.05	-1.15 ± 0.04
Spin Projection	-3.12 ± 0.05	-1.15 ± 0.04
Mulliken	-3.22 ± 0.05	-1.18 ± 0.04
Bader	-3.48 ± 0.05	-1.28 ± 0.04
Hirshfeld	-3.57 ± 0.05	-1.31 ± 0.04

 Table S2.9: J values obtained using different definitions of spin densities on the Mn centres.



Fig. S2.1: χ T vs T plots for the {Mn₆} cage using coupling constants obtained from different spin operator definitions.

S2.5 Possibility of 3 coupling constants in the fully reduced state

The Mn centres *cis*- to each other can also be divided into two groups based on the distance between them (4.41 and 4.39 Å). The reason for using Mn-Mn distance as a parameter to determine the number of coupling constants is because in this cage, if there is a difference in the Mn-Mn distance, it would imply different bond lengths between Mn and the atoms that form its coordinating environment (i.e O, N and Cl) which will ultimately affect the coupling between the two Mn-centres under consideration. Since Mn centres *cis*- to each other also can be divided into two groups based on the Mn-Mn distances, there is a possibility of having 3 coupling constants (using Bader spin densities) which was also investigated. In this case, the following Hamiltonian was employed:

$$H = -2J_1[\langle s_1 \cdot s_4 \rangle + \langle s_2 \cdot s_5 \rangle + \langle s_3 \cdot s_6 \rangle] - 2J_2[\langle s_1 \cdot s_2 \rangle + \langle s_1 \cdot s_3 \rangle + \langle s_2 \cdot s_3 \rangle + \langle s_4 \cdot s_5 \rangle + \langle s_5 \cdot s_5$$

The values for J_2 and J_3 obtained in this case (**Table S2.10**) are very close to the J_{cis} value. Thus, the former definition of the Hamiltonian with 2 J-values can be considered appropriate.

Table S2.10: J values for the fully reduced state of Mn₆ complex by dividing the *cis*- terms in two groups.

 J_1 J_2 J_3

 -3.46 ± 0.06
 -1.29 ± 0.06
 -1.26 ± 0.06

S2.6 Functional dependence of coupling constants

To look at the functional dependence of coupling constants, however, Mn123, Mn12 and Mn124 states were modelled with $B3LYP^6$ which has also been shown to give reasonable results for the calculation of exchange coupling constants.⁷ We used the same 2 J-value Hamiltonian as for PBE0 to calculate the value of J_{cis} and J_{trans} as shown below:

Η

$$= -2J_{trans}[\langle s_1.s_4 \rangle + \langle s_2.s_5 \rangle + \langle s_3.s_6 \rangle] - 2J_{cis}[\langle s_1.s_2 \rangle + \langle s_1.s_3 \rangle + \langle s_1.s_5 \rangle + \langle s_1.s_6 \rangle + \langle s_1.s_6 \rangle + \langle s_2.s_6 \rangle + \langle s_3.s_6 \rangle] - 2J_{cis}[\langle s_1.s_2 \rangle + \langle s_1.s_6 \rangle + \langle s_2.s_6 \rangle + \langle s_2.s_6 \rangle + \langle s_2.s_6 \rangle + \langle s_3.s_6 \rangle + \langle s_3.s_6 \rangle + \langle s_3.s_6 \rangle + \langle s_4.s_6 \rangle + \langle s_4.s_$$

The values obtained are quite similar to those obtained using PBEO as can be seen from **Table S2.12**. The comparison of susceptibility plot obtained with B3LYP with the other plots is given in **Fig. S2.2**.

Table S2.11: Bader spin density on Mn centres in the different electronic configurations using B3LYPfunctional. The states Mn126 is symmetry equivalent to the Mn123 state.

Configuration \	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
Mn centre						
Mn12	-3.740069	-3.739850	3.743009	3.742947	3.740875	3.740913
Mn126	-3.742518	-3.740869	3.742687	3.742613	3.740886	-3.742654
Mn124	-3.740720	-3.740373	3.740439	-3.740302	3.740463	3.740489

Table S2.12: Calculated J values (using Bader charge densities) with both PBEO and B3LYP, and fittedJ-values for the Mn_6 cage.

Approach\J value	J _{trans} (cm ⁻¹)	J _{cis} (cm ⁻¹)
Calculated (PBE0)	-3.48 ± 0.05	-1.28 ± 0.04
Calculated (B3LYP)	-3.86	-1.48
Fit to Experiment (2 J-values)	-2.53	-1.28
Fit to Experiment (1 J-value)	-	-1.88



Fig. S2.2: Experimental χ T vs T plot for {Mn₆} cage and the same plot obtained using the calculated (PBEO and B3LYP) and fitted coupling constants.

S2.7 Overlap Analysis

Cl\Mn	D	D+1	D-1	D+2	D-2
			Mn1		
Px	0.00	0.04	0.00	0.00	0.00
P _Y	0.00	0.00	0.04	0.00	0.00
Pz	1.40	0.00	0.00	0.00	0.00
			Mn2		
Px	0.36	0.00	0.00	1.04	0.00
Py	0.00	0.00	0.00	0.00	0.04
Pz	0.00	0.04	0.00	0.00	0.00
			Mn3		
Px	0.00	0.00	0.00	0.00	0.04
P _Y	0.34	0.00	0.00	1.06	0.00
Pz	0.00	0.00	0.04	0.00	0.00
			Mn4		
Px	0.00	0.04	0.00	0.00	0.00
P _Y	0.00	0.00	0.04	0.00	0.00
Pz	1.40	0.00	0.00	0.00	0.00
			Mn5		
Px	0.36	0.00	0.00	1.04	0.00
Py	0.00	0.00	0.00	0.00	0.04
Pz	0.00	0.04	0.00	0.00	0.00
			Mn6		
Px	0.00	0.00	0.00	0.00	0.04
Py	0.34	0.00	0.00	1.06	0.00
Pz	0.00	0.00	0.04	0.00	0.00

Table S2.13: Overlap matrix (imes 100) for the d-orbitals of the Mn centres and the p-orbitals of Cl.

S3. Comparison of The Geometric and The Electronic Structure in Various Charged States

Charged state	g-tensor
Fully reduced	1.998
1 st	1.998
2 nd (Cis)	1.997
2 nd (Trans)	1.997
3 rd (Fac)	1.997
3 rd (Mer)	1.997
4 th (<i>Cis</i>)	1.996
4 th (Trans)	1.996

Table S3.1: g-tensor for the {Mn₆} cage in the different oxidation states calculated using ORCA.

	Charged State							
	Fully			2 nd		3 rd		4 th
	reduced	1 st	2 nd (<i>Cis</i>)	(Trans)	3 rd (Fac)	(Mer)	4 th (<i>Cis</i>)	(Trans)
Mn1								
Cl	3.096	3.219	3.692	3.227	3.626	2.506	2.661	2.648
Ν	2.279	2.242	2.213	2.226	2.196	1.997	1.979	1.982
0126	1.892	1.895	1.895	1.881	1.922	1.851	1.864	1.845
0123	1.899	1.906	1.909	1.890	1.897	1.849	1.846	1.844
0135	1.892	1.882	1.875	1.896	1.864	1.864	1.842	1.861
0156	1.899	1.889	1.880	1.909	1.894	1.866	1.864	1.863
Mn2								
Cl	3.096	2.369	2.551	2.425	2.712	2.742	3.245	2.652
Ν	2.279	2.027	1.991	2.012	1.971	1.970	1.942	1.980
0126	1.892	1.865	1.846	1.862	1.847	1.862	1.873	1.849
0123	1.899	1.862	1.844	1.859	1.826	1.859	1.839	1.847
0234	1.892	1.865	1.868	1.862	1.852	1.839	1.812	1.868
O246	1.899	1.862	1.865	1.859	1.880	1.837	1.842	1.859
Mn3								
Cl	3.095	3.218	3.299	3.225	3.624	3.279	3.665	3.292
Ν	2.279	2.240	2.218	2.223	2.196	2.201	2.179	2.186
0123	1.899	1.906	1.892	1.892	1.894	1.914	1.910	1.902
0234	1.892	1.902	1.925	1.887	1.922	1.880	1.888	1.890
0135	1.892	1.881	1.872	1.905	1.864	1.900	1.904	1.892
0345	1.899	1.889	1.893	1.906	1.897	1.897	1.886	1.913
Mn4								
Cl	3.095	3.219	2.552	3.227	2.712	3.741	3.669	3.566
Ν	2.279	2.242	1.990	2.226	1.971	2.196	2.180	1.936
0234	1.892	1.895	1.864	1.881	1.847	1.882	1.879	1.827
0345	1.899	1.888	1.843	1.909	1.826	1.901	1.889	1.846
O456	1.892	1.882	1.847	1.896	1.852	1.888	1.904	1.837
O246	1.899	1.907	1.862	1.890	1.880	3.578	1.911	1.836
Mn5								
Cl	3.096	3.760	3.689	3.648	3.626	3.472	3.111	3.552
Ν	2.279	2.228	2.210	1.932	2.196	1.934	1.946	1.933
0135	1.892	1.885	1.874	1.831	1.864	1.851	1.843	1.835
0345	1.899	1.893	1.908	1.834	1.894	1.824	1.816	1.842
O456	1.892	1.885	1.906	1.831	1.922	1.821	1.837	1.846
0156	1.899	1.893	1.882	1.834	1.897	1.850	1.877	1.834
Mn6								
Cl	3.097	3.217	3.268	3.225	2.713	3.293	2.663	3.302
Ν	2.279	2.240	2.217	2.223	1.971	2.201	1.978	2.186
O126	1.892	1.902	1.890	1.887	1.852	1.908	1.866	1.897
O456	1.892	1.881	1.881	1.905	1.847	1.896	1.848	1.907
0156	1.899	1.889	1.879	1.906	1.826	1.905	1.862	1.895
O246	1.899	1.906	1.933	1.892	1.880	1.883	1.843	1.899

Table S3.2: Mn-ligand bond distances (Å) for all their coordinating atoms in all oxidation states (ferromagnetic configuration). The number next to each O represents the Mn centres which are linked together by the corresponding phosphonate group. For example, O123 denotes that this oxygen belongs to a phosphonate that links Mn1, Mn2 and Mn3.

Table S3.3: Bader spin density on the coordinating atoms in all oxidation states (ferromagnetic configuration). The number next to each N represents the Mn centre to which it is linked. For the O centres, the sum of spin density on the four oxygen centres linked to and residing in between the corresponding Mn centres is provided. The number next to O represents the Mn centres being taken into account.

	Charged States							
	Fully			2 nd		3 rd		4 th
_	reduced	1 st	2 nd (<i>Cis</i>)	(Trans)	3 rd (Fac)	(Mer)	4 th (<i>Cis</i>)	(Trans)
Cl	0.116	0.012	-0.022	0.016	-0.027	-0.019	-0.019	-0.014
N1	0.056	0.062	0.068	0.067	0.072	-0.117	-0.150	-0.149
N2	0.056	-0.075	-0.112	-0.095	-0.139	-0.142	-0.165	-0.150
N3	0.056	0.062	0.067	0.067	0.072	0.072	0.078	0.077
N4	0.056	0.062	-0.112	0.067	-0.139	0.073	0.078	-0.163
N5	0.056	0.063	0.068	-0.134	0.072	-0.147	-0.165	-0.164
N6	0.056	0.062	0.067	0.067	-0.139	0.072	-0.150	0.077
012	0.085	0.091	0.130	0.102	0.137	0.105	0.137	0.118
013	0.084	0.100	0.111	0.096	0.117	0.100	0.123	0.112
015	0.084	0.107	0.119	0.135	0.116	0.139	0.132	0.152
016	0.086	0.100	0.110	0.096	0.127	0.102	0.100	0.113
023	0.084	0.089	0.106	0.100	0.127	0.123	0.144	0.109
024	0.084	0.091	0.087	0.102	0.113	0.140	0.136	0.151
026	0.084	0.089	0.111	0.100	0.113	0.118	0.140	0.111
034	0.084	0.100	0.113	0.096	0.137	0.104	0.107	0.129
035	0.084	0.107	0.108	0.134	0.116	0.133	0.135	0.134
O45	0.084	0.107	0.128	0.136	0.126	0.147	0.148	0.164
O46	0.084	0.099	0.106	0.096	0.112	0.104	0.121	0.134
O56	0.085	0.106	0.111	0.133	0.135	0.137	0.133	0.127

Table S3.4: Sum of overlaps (\times 100) between the d-orbitals of Mn and p-orbitals of Cl in the various
charged states.

	Charged State							
	Fully			2 nd				4 th
	reduced	1 st	2 nd (<i>Cis</i>)	(Trans)	3 rd (Fac)	3 rd (Mer)	4 th (<i>Cis</i>)	(Trans)
Mn1-Cl	1.4800	1.0630	0.2960	1.1890	0.3970	5.9630	3.9200	4.7310
Mn2-Cl	1.4800	6.7060	4.9670	5.9670	3.9230	3.6810	1.5120	4.3330
Mn3-Cl	1.4800	0.8340	0.8310	1.0260	0.4440	0.9610	0.3120	1.0500
Mn4-Cl	1.4800	1.0640	5.8710	1.1960	4.0150	0.3650	0.2360	1.0630
Mn5-Cl	1.4800	0.6040	0.2590	1.0800	0.3840	1.0180	2.0060	0.9760
Mn6-Cl	1.4800	0.8310	0.9190	1.0300	3.8310	0.9310	4.1890	1.0250

S4.1st charged state

The Hamiltonian used for the first charged state is the following:

$$\begin{split} H &= -2J_1[\langle s_2.s_5 \rangle] - 2J_2[\langle s_1.s_4 \rangle + \langle s_3.s_6 \rangle] \\ &- 2J_3[\langle s_1.s_2 \rangle + \langle s_2.s_3 \rangle + \langle s_2.s_4 \rangle + \langle s_2.s_6 \rangle] \\ &- 2J_4[\langle s_1.s_3 \rangle + \langle s_1.s_6 \rangle + \langle s_3.s_4 \rangle + \langle s_4.s_6 \rangle] \\ &- 2J_5[\langle s_1.s_5 \rangle + \langle s_3.s_5 \rangle + \langle s_4.s_5 \rangle + \langle s_5.s_6 \rangle] \end{split}$$

When this state is modelled without the Cl in the centre, using the same Hamiltonian, the J-values obtained are provided in **Table S4.3**. It can be seen that the value of J_1 has a high standard deviation and its sign cannot be determined. The magnitude of J_1 however, is smaller compared to the value of J_1 obtained with Cl in the centre (1.94 ± 0.10 cm⁻¹). This confirms that the coupling between Mn2 and Mn5 is via the Cl bridge.

Table S4.1: Bader spin density on each Mn centre and the relative energy of each spin state withrespect to the ferromagnetic state for the 1st charged state.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.772989	3.036106	3.774843	3.773106	3.765234	3.774816	0.00
3.772606	3.032264	3.774363	3.772663	-3.764590	3.774473	-60.69
3.772342	3.035917	3.773937	3.772403	3.764727	-3.772274	-109.21
-3.770390	3.036010	3.774451	3.772266	3.764882	3.774544	-109.34
3.772320	-3.030300	3.774149	3.772276	3.765653	3.774120	-132.38
3.771868	-3.033934	3.773516	3.771797	-3.763956	3.773650	-237.25
-3.770947	3.035714	3.773652	3.771791	3.764617	-3.772572	-183.72
3.771560	-3.030718	3.773239	3.771519	3.765353	-3.772947	-165.47
3.771922	3.035124	-3.772900	3.771891	3.764410	-3.772967	-189.45
3.771884	3.031591	3.773541	3.771928	-3.764702	-3.772766	-128.00
3.771241	-3.034336	-3.773242	3.771225	-3.764161	3.772867	-228.74
3.771229	-3.030651	-3.773210	-3.771435	3.765263	3.772841	-161.38
3.771142	-3.034874	3.772847	3.771359	-3.764165	-3.773274	-228.72
-3.771634	-3.030806	3.773250	-3.771561	3.764925	3.773246	-166.63
-3.771399	-3.030335	3.772783	3.771094	3.765296	-3.773199	-161.39
3.770957	-3.031359	-3.773861	3.771139	3.765228	-3.773893	-169.45

Table S4.2: Bader spin density on each Mn centre and the relative energy of each spin state with respect to the ferromagnetic state for the 1st charged state without the central Cl.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.750293	2.926209	3.751704	3.750369	3.749062	3.751713	0.00
-3.747820	2.925458	3.751137	3.750005	3.748505	3.750845	-79.18
3.749772	-2.920550	3.751099	3.749796	3.748566	3.751092	-70.55
3.749575	2.925790	3.750952	3.749674	-3.747527	3.750924	-93.42
3.749599	2.925277	3.751467	3.749379	3.748545	-3.749411	-78.40
-3.748300	2.924016	3.751063	3.749479	3.748093	-3.749897	-121.21
3.748871	2.924672	-3.749575	3.748858	3.748181	-3.749579	-154.39
3.748996	2.924675	3.750707	3.748753	-3.747409	-3.749884	-125.34
-3.748655	-2.923687	3.750551	3.748877	3.747922	-3.750298	-120.89

3.748331 -2.922017 3.750299 3.748356 -3.747834 -3.750251 -161.63

J-value	Interacting Mn centres	Magnitude (cm ⁻¹)
J_1	Trans-Mn2(IV)-Mn5(III)	0.04 ± 0.05
	Trans-Mn1(III)-Mn4(III)	
J ₂	Trans-Mn3(III)-Mn6(III)	-0.09 ± 0.02
	cis-Mn1(III)-Mn2(IV)	
.	cis-Mn2(IV)-Mn3(III)	1 62 + 0.02
J ₃	cis-Mn2(IV) –Mn4(III)	-1.03 ± 0.02
	cis-Mn2(IV) –Mn6(III)	
	cis-Mn1(III)-Mn3(III)	
.	cis-Mn1(III)-Mn6(III)	1.20 . 0.02
J ₄	cis-Mn3(III)-Mn4(III)	-1.28 ± 0.02
	cis-Mn4(III)-Mn6(III)	
	cis-Mn1(III)-Mn5(III)	
J ₅	cis-Mn3(III)-Mn5(III)	1 67 1 0 02
	cis-Mn4(III)-Mn5(III)	-1.07 ± 0.02
	cis-Mn5(III)-Mn6(III)	

Table S4.3: Magnitude of J-values (cm⁻¹) and the Mn-Mn interactions that constitute each J-value forthe 1st charged state without the central Cl.



Fig. S4.1: (a) Optimised model of the 1st charged state for the {Mn₆} cage. Colour scheme: Mn^{III} (dark blue), Mn^{IV} (light blue), P(pink), Cl (green), C (black) O (red). Hydrogens have been removed for clarity. (b) The distribution of the spin density in this state. Blue and green regions in the spin density plots represent the spin density associated with up and down spin respectively. Spin density associated with Mn3 and the ligands coordinated to it has been removed for clarity. Cl can be clearly seen to be accommodating both up and down spin density confirming the presence of spin delocalisation and polarisation.

S5. 2nd charged state

S5.1 Cis-isomer

The Hamiltonian used for this charged state is the following:

Η

$$= -2J_1[\langle s_1.s_4 \rangle + \langle s_2.s_5 \rangle] - 2J_2[\langle s_3.s_6 \rangle] - 2J_3[\langle s_2.s_4 \rangle] - 2J_4[\langle s_1.s_2 \rangle] - 2J_5[\langle s_2.s_3 \rangle] - 2J_8[\langle s_4.s_5 \rangle] - 2J_9[\langle s_4.s_6 \rangle] - 2J_{10}[\langle s_1.s_5 \rangle] - 2J_{11}[\langle s_1.s_3 \rangle + \langle s_5.s_6 \rangle] - 2J_{12}[\langle s_1.s_6 \rangle + 2$$

Table S5.1: Bader spin density on each Mn centre and the relative energy of each spin state with respect to the ferromagnetic state for the *cis*-isomer of the 2nd charged state.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.755435	3.030663	3.764444	3.026284	3.758744	3.763959	0.00
3.755132	3.027213	3.763860	3.024670	-3.757984	3.763174	-76.69
3.755026	3.029599	3.763676	3.025193	3.758392	-3.761421	-106.06
3.754907	-3.019001	3.764063	3.022230	3.759383	3.763497	-87.38
-3.754705	3.025811	3.763586	3.021522	-3.758129	3.762890	-107.23
3.755455	-3.023038	3.763424	-3.018988	3.758870	3.762636	-136.81
3.754773	-3.022077	3.763580	3.020643	-3.757366	3.762866	-191.56
3.754766	-3.020083	3.763484	3.021008	3.758983	-3.761699	-133.51
3.754665	3.028037	-3.762649	3.024016	3.757949	-3.761989	-195.24
3.755661	3.023022	3.763538	-3.017179	-3.758406	3.762855	-117.78
3.754750	3.026328	3.763302	3.023248	-3.758199	-3.761821	-140.06
-3.754231	3.021259	3.763206	-3.020216	-3.758650	3.762282	-175.60
3.755228	-3.024699	-3.762800	-3.020193	3.758612	3.762295	-131.37
3.755157	-3.026141	3.762919	-3.020999	-3.757678	3.762332	-193.94
3.755198	-3.024009	3.762824	-3.020368	3.758534	-3.762211	-128.31
3.754503	-3.022933	3.762915	3.019172	-3.757665	-3.762388	-195.00
3.755222	3.024054	-3.763250	-3.017435	3.757663	-3.762630	-165.84
-3.754530	-3.024825	3.763117	-3.022129	3.758452	3.762275	-188.72
3.755534	3.022268	3.762905	-3.018259	-3.758802	-3.762167	-126.40

The comparison of coupling strength between Mn centres calculated using 12 and 15 J-value Hamiltonians is given in **Table S5.2** below.

Interaction	J-value(15 J-values)	J-value(10 J-values)
Mn1Mn2	-2.48 ± 0.01	-2.50 ± 0.03
Mn1Mn3	-1.53 ± 0.00	-1.51 ± 0.02
Mn1Mn4	1.20 ± 0.01	1.20 ± 0.02
Mn1Mn5	-1.79 ± 0.01	-1.79 ± 0.02
Mn1Mn6	-1.39 ± 0.00	-1.42 ± 0.02
Mn2Mn3	-2.07 ± 0.01	-2.04 ± 0.04
Mn2Mn4	-2.12 ± 0.01	-2.13 ± 0.04
Mn2Mn5	1.21 ± 0.00	1.20 ± 0.02
Mn2Mn6	-2.63 ± 0.00	-2.64 ± 0.02
Mn3Mn4	-2.77 ± 0.01	-2.76 ± 0.03
Mn3Mn5	-1.43 ± 0.00	-1.42 ± 0.02
Mn3Mn6	-0.55 ± 0.00	-0.52 ± 0.03
Mn4Mn5	-2.08 ± 0.01	-2.07 ± 0.04
Mn4Mn6	-2.40 ± 0.00	-2.40 ± 0.02
Mn5Mn6	-1.50 ± 0.00	-1.51 ± 0.02

Table S5.2: J-values (cm⁻¹) for the *cis*-isomer of the 2nd oxidised state obtained with the 15 J-valueand 12 J-value Hamiltonians.



Fig. S5.1: (a) Optimised model of the *cis*-isomer of the 2nd charged state for the {Mn₆} cage. Colour scheme: Mn^{III} (dark blue), Mn^{IV} (light blue), P(pink), Cl (green), C (black) O (red). Hydrogens have been removed for clarity. **(b)** The distribution of the spin density in this state. Blue and green regions in the spin density plots represent the spin density associated with up and down spin respectively. Spin density associated with Mn3 and the ligands coordinated to it has been removed for clarity. Cl can be clearly seen to be accommodating both up and down spin density confirming the presence of spin delocalisation and polarisation with the latter being dominant.

S5.2 Trans-isomer

The Hamiltonian used for this charged state is the following:

$$\begin{split} H &= -2J_1[\langle s_2.s_5 \rangle] - 2J_2[\langle s_1.s_4 \rangle + \langle s_3.s_6 \rangle] - 2J_3[\langle s_1.s_2 \rangle + \langle s_2.s_4 \rangle] \\ &- 2J_4[\langle s_2.s_3 \rangle + \langle s_2.s_6 \rangle] - 2J_5[\langle s_1.s_5 \rangle + \langle s_4.s_5 \rangle] - 2J_6[\langle s_3.s_5 \rangle + \langle s_5.s_6 \rangle] \\ &- 2J_7[\langle s_1.s_3 \rangle + \langle s_1.s_6 \rangle] - 2J_8[\langle s_3.s_4 \rangle + \langle s_4.s_6 \rangle] \end{split}$$

Table S5.3: Bader spin density on each Mn centre and the relative energy of each spin state with respect to the ferromagnetic state for the trans-isomer of the 2nd charged state.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.765050	3.036189	3.769443	3.765131	2.943885	3.769401	0.00
3.764377	3.035988	3.768427	3.764850	2.941865	-3.766506	-109.57
3.764370	-3.034544	3.768473	3.764037	2.941616	3.768435	-158.35
-3.762518	3.035553	3.767701	3.763864	2.939555	-3.766677	-187.77
3.763872	-3.034913	3.768036	3.763587	-2.934085	3.767952	-241.84
3.763639	-3.034762	3.767729	3.764219	2.939772	-3.767134	-190.25
3.764402	3.035690	-3.767358	3.764304	2.939783	-3.767399	-188.62
-3.763227	-3.035018	3.766986	3.763226	2.937657	-3.767251	-186.61
3.762853	-3.035462	3.767892	-3.763348	-2.937061	3.767531	-231.06
3.763624	-3.035015	-3.768067	3.763504	2.937913	-3.767994	-191.29
3.763598	-3.035388	3.766877	3.763825	-2.937250	-3.767692	-234.93



Fig. S5.2: (a) Optimised model of the *trans*-isomer of the 2nd charged state for the {Mn₆} cage. Colour scheme: Mn^{III} (dark blue), Mn^{IV} (light blue), P(pink), Cl (green), C (black) O (red). Hydrogens have been removed for clarity. (b) The distribution of the spin density in this state. Blue and green regions in the spin density plots represent the spin density associated with up and down spin respectively. Spin density associated with Mn3 and the ligands coordinated to it has been removed for clarity. Cl can be clearly seen to be accommodating both up and down spin density confirming the presence of spin delocalisation and polarisation.

S6. 3rd charged state

To look at whether the tendency to switch the ground state can be retained in even higher oxidation states, the 3rd charged state was modelled. In this state, the Mn(IV) centres can be arranged to form the *fac*- and *mer*- isomer and both these configurations were modelled.

S6.1 Fac-isomer

In this state, Mn2, Mn4 and Mn6 are in oxidation state IV (Fig. 2e) and Cl is shifted towards the Mn(IV) centres. A proper description of the electronic picture requires the use of only 5 J-values. The Hamiltonian thus used for this charged state is the following:

$$\begin{aligned} H &= -2J_1[\langle s_1.s_4 \rangle + \langle s_2.s_5 \rangle + \langle s_3.s_6 \rangle] - 2J_2[\langle s_2.s_4 \rangle + \langle s_2.s_6 \rangle + \langle s_4.s_6 \rangle] \\ &- 2J_3[\langle s_1.s_2 \rangle + \langle s_3.s_4 \rangle + \langle s_5.s_6 \rangle] - 2J_4[\langle s_1.s_6 \rangle + \langle s_2.s_3 \rangle + \langle s_4.s_5 \rangle] \\ &- 2J_6[\langle s_1.s_3 \rangle + \langle s_1.s_5 \rangle + \langle s_3.s_5 \rangle] \end{aligned}$$

14 electronic configurations were modelled for this state (**Table S6.1**) and the J-values obtained are given in **Table S6.2**. The J₁ term corresponding to the coupling between the trans-Mn centres is ferromagnetic although weaker compared to the lower charged states owing to the relatively smaller Mn(IV)-Cl overlaps. The coupling between the Mn(IV) centres *cis*- to each other (J₂) is stronger compared to that in the *cis*- isomer of the +2 charged state. This is due to higher delocalisation of spin density (**Table S3.3**). Each Mn(IV) centre has two *cis*-Mn(III) neighbours out of which one is closer than the other by ~0.03 Å and the impact of this difference seems to be quite large if one compares J₃ and J₄. This is again due to differences in the spin density of the oxygens attached to the Mn centres.

For this configuration, the S = 1/2 state (**Fac - 246 - Mn236**) has been found to be the lowest in energy which shows its similarity with the fully reduced state. The ferromagnetic state is the highest in energy.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.750115	3.034038	3.750301	3.034435	3.750404	3.034396	0.00
3.749583	-3.022536	3.750147	3.032145	3.750796	3.032462	-96.22
3.749858	3.031536	-3.749374	3.032493	3.749872	3.031483	-86.23
3.749356	-3.025749	-3.749639	3.030358	3.750376	3.029723	-150.43
3.749830	-3.024557	3.750624	3.030178	3.750306	-3.024400	-132.20
3.749347	3.028724	-3.749928	3.029361	-3.749958	3.029661	-121.30
3.749788	3.029066	-3.749087	3.030610	3.749319	-3.024548	-203.23
3.750129	3.027831	3.750003	-3.027488	-3.749698	-3.026912	-126.31
-3.749864	-3.026935	3.750394	3.027455	3.749952	-3.027418	-125.25
3.749723	-3.027420	-3.749990	-3.026755	3.750256	3.027728	-124.93
-3.749176	3.028111	3.749938	-3.026940	3.749266	-3.028078	-208.14
3.748965	-3.028186	-3.749166	3.028216	3.749924	-3.027071	-208.09
3.750033	-3.026693	3.750298	-3.026559	3.750103	-3.026645	-106.43

Table S6.1: Bader spin density on each Mn centre and the relative energy of each spin state with respect to the ferromagnetic state for the *fac*-isomer of the 3rd charged state.

J-value	Interacting Mn centres	Magnitude (cm ⁻¹)
J ₁	trans-Mn1(III)-Mn4(IV)	
	trans-Mn2(IV)-Mn5(III)	0.95 ± 0.04
	trans-Mn3(III)-Mn6(IV)	
	cis-Mn2(IV)-Mn4(IV)	
J ₂	cis-Mn2(IV)-Mn6(IV)	-3.32 ± 0.04
	cis-Mn4(IV)-Mn6(IV)	
J ₃	cis-Mn1(III)-Mn2(IV)	
	cis-Mn3(III)-Mn4(IV)	-2.69 ± 0.04
	cis-Mn5(III)-Mn6(IV)	
	cis-Mn1(III)-Mn6(IV)	
J_4	cis-Mn2(IV)-Mn3(III)	-1.39 ± 0.05
	cis-Mn4(IV)-Mn5(III)	
J ₅	cis-Mn1(III)-Mn3(III)	
	cis-Mn1(III)-Mn5(III)	-1.79 ± 0.03
	cis-Mn3(III)-Mn5(III)	

Table S6.2: Magnitude of J-values (cm⁻¹) and the Mn-Mn interactions that constitute each J-value for
the *fac*-isomer of the 3rd charged state.



Fig. S6.1: (a) Optimised model of the *fac*-isomer of the 3rd charged state for the {Mn₆} cage. Colour scheme: Mn^{III} (dark blue), Mn^{IV} (light blue), P(pink), Cl (green), C (black) O (red). Hydrogens have been removed for clarity. (b) The distribution of the spin density in this state. Blue and green regions in the spin density plots represent the spin density associated with up and down spin respectively. Spin density associated with Mn3 and the ligands coordinated to it has been removed for clarity.

S6.2 Mer-isomer

For this isomer, Mn1, Mn2 and Mn5 are in oxidation state IV (Fig. 2f). The Mn1-Mn4, Mn2-Mn5 and Mn3-Mn6 distances are 6.223, 6.141 and 6.468 Å respectively. This configuration is the least symmetric configuration studied. The Mn(IV)-Cl distance follows the order Mn1-Cl (2.506 Å) < Mn2-Cl (2.74 Å) < Mn5-Cl (3.47 Å) which suggests that each Mn(IV) resides in a unique environment. The Hamiltonian used for this charged state is the following:

$$\begin{split} H &= -2J_1 \big[< s_2 \cdot s_5 > \big] - 2J_2 \big[< s_1 \cdot s_4 > \big] - 2J_3 \big[< s_3 \cdot s_6 > \big] - 2J_4 \big[< s_1 \cdot s_2 > \big] \\ &- 2J_5 \big[< s_1 \cdot s_5 > \big] - 2J_6 \big[< s_1 \cdot s_3 > \big] - 2J_7 \big[< s_1 \cdot s_6 > \big] - 2J_8 \big[< s_2 \cdot s_3 > \big] \\ &- 2J_9 \big[< s_2 \cdot s_4 > \big] - 2J_{10} \big[< s_2 \cdot s_6 > \big] - 2J_{11} \big[< s_3 \cdot s_5 > \big] - 2J_{12} \big[< s_4 \cdot s_5 > \big] \\ &- 2J_{13} \big[< s_5 \cdot s_6 > \big] - 2J_{14} \big[< s_3 \cdot s_4 > \big] - 2J_{15} \big[< s_4 \cdot s_6 > \big] \end{split}$$

21 electronic configurations were modelled (**Table S6.3**) and the J-values obtained are given in **Table S6.4**. The coupling strengths between Mn centres are in line with what is expected from the spin density on the phosphonate oxygens. The interaction between Mn2(IV) and Mn5(IV) (J₁) is ferromagnetic but weaker than that between the Mn1(IV) and its *trans*-Mn4(III) (J₂). The ferromagnetic interaction between Mn1(IV) and Mn4(III) is stronger compared to that in the *cis*-isomer of this charged state because of the larger Mn-Cl overlaps (**Table S3.4**). The spin density on Cl and the N of the 4-picoline ligands attached to the Mn(IV) centres is opposite to that on the Mn centres indicating the presence of spin polarisation mechanism. Mn3 and Mn6 (J₃), both being in oxidation state III, couple antiferromagnetically. The coupling between *cis*-Mn(IV) centres (J₄ and J₅) is quite strong as can be expected due to higher oxidation states of the interacting Mn centres. The similarity in the coupling Mn3 and Mn6 with their *cis*-neighbours suggests that these Mn centres reside in similar electronic environments.

For this configuration, unlike the *trans*-isomer of the 2^{nd} oxidised state, the S = 1/2 state (**Mer - 125 - Mn256**) has been found to be the lowest in energy which indicates that the stability to stabilise intermediate states is lost. The ferromagnetic state is the highest in energy.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.049052	3.032645	3.757953	3.746980	2.970550	3.758331	0.00
3.045647	3.030977	3.757581	-3.745308	2.968151	3.757798	-83.33
3.047301	3.031570	3.757642	3.746394	-2.960381	3.757779	-89.31
3.048042	3.030586	3.757113	3.746461	2.968495	-3.755838	-103.45
-3.038942	3.029362	3.757413	3.747227	2.970480	3.757860	-100.60
-3.042022	3.027337	3.757022	-3.745153	2.968387	3.757421	-212.33
-3.040848	3.028378	3.756972	3.746583	-2.961278	3.757457	-136.01
-3.039673	3.027413	3.756735	3.746865	2.968396	-3.756201	-142.84
3.043728	-3.024352	3.756994	3.746015	-2.961361	3.757368	-201.74
3.047461	3.029257	-3.756148	3.745887	2.965141	-3.756524	-187.46
3.044138	3.029943	3.757198	-3.745815	-2.963283	3.757244	-120.86
3.044797	3.028520	3.756822	-3.745827	2.965824	-3.756346	-145.59
3.046407	3.029647	3.756882	3.745941	-2.962673	-3.756449	-147.95
-3.044340	-3.027316	3.756489	3.746378	-2.961842	3.756955	-190.04
-3.044036	3.026693	3.756717	-3.745711	-2.964384	3.756980	-195.42
-3.041685	3.026757	3.756310	3.746312	-2.963292	-3.756755	-133.24
3.042903	-3.025249	-3.756501	3.745581	-2.965935	3.756714	-213.25
3.040578	-3.026480	3.756707	-3.746315	-2.964456	3.756928	-171.40
3.042805	-3.026139	3.756345	3.745673	-2.964289	-3.756850	-218.93
-3.045549	-3.028496	3.756564	-3.745566	2.966547	3.757115	-202.44
-3.043283	-3.027886	-3.756529	3.746248	2.965181	3.756877	-138.30

Table S6.3: Bader spin density on each Mn centre and the relative energy of each spin state with respect to the ferromagnetic state for the *mer*-isomer of the 3rd charged state.

Table S6.4: Magnitude of J-values (cm⁻¹) and the Mn-Mn interactions that constitute each J-value forthe *mer*-isomer of the 3rd charged state.

J-value	Interacting Mn centres	Magnitude (cm ⁻¹)
J ₁	trans-Mn2(IV)-Mn5(IV)	0.11 ± 0.01
J ₂	trans-Mn1(IV)-Mn4(III)	1.23 ± 0.01
J ₃	trans-Mn3(III)-Mn6(III)	-0.64 ± 0.00
J ₄	cis-Mn1(IV)-Mn2(IV)	-3.17 ± 0.01
J ₅	cis-Mn1(IV)-Mn5(IV)	-3.00 ± 0.01
J ₆	cis-Mn1(IV)-Mn3(III)	-2.43 ± 0.01
J ₇	cis-Mn1(IV)-Mn6(III)	-2.68 ± 0.00
J ₈	cis-Mn2(IV)-Mn3(III)	-2.69 ± 0.01
J ₉	cis-Mn2(IV)-Mn4(III)	-2.73 ± 0.01
J ₁₀	cis-Mn2(IV)-Mn6(III)	-1.82 ± 0.00
J ₁₁	cis-Mn3(III)-Mn5(IV)	-1.33 ± 0.01
J ₁₂	cis-Mn4(III)-Mn5(IV)	-2.34 ± 0.01
J ₁₃	cis-Mn5(IV)-Mn6(III)	-2.01 ± 0.00
J ₁₄	cis-Mn3(III)-Mn4(III)	-1.41 ± 0.01
J ₁₅	cis-Mn4(III)-Mn6(III)	-1.46 ± 0.00



Fig. S6.2: (a) Optimised model of the *mer*-isomer of the 3rd charged state for the {Mn₆} cage. Colour scheme: Mn^{III} (dark blue), Mn^{IV} (light blue), P(pink), Cl (green), C (black) O (red). Hydrogens have been removed for clarity. (b) The distribution of the spin density in this state. Blue and green regions in the spin density plots represent the spin density associated with up and down spin respectively. Spin density associated with Mn3 and the ligands coordinated to it has been removed for clarity. Cl can be clearly seen to be accommodating both up and down spin density confirming the presence of spin delocalisation and polarisation with the latter being dominant.

S7.4th charged state

To ensure that further oxidation does not stabilise the intermediate spin states either, the 4th charged state was modelled. This charged state is very similar to the 2nd charged state although the symmetry in this state is lower. Just like the 2nd charged state, there are two possible configurations depending upon whether the Mn(III) centres are *cis*- to each other or *trans*- to each other both of which were modelled.

S7.1 Cis-isomer

For this isomer, Mn3 and Mn4 are in oxidation state III while the others are in oxidation state IV (Fig. 2g). The *trans*-Mn(IV)-Mn(IV) and Mn(IV)-Mn(III) distances are 6.259 and 6.286 Å respectively. The cage has expanded even further which implies that Cl⁻ ion can move more freely within the void. The Mn-Cl distance follows the order Mn1(IV)-Cl ~ Mn6(IV)-Cl (2.66Å) < Mn5(IV)-Cl (3.11Å) < Mn2(IV)-Cl (3.24.Å) < Mn3(III)-Cl ~ Mn4(III)-Cl (3.66Å). Like the *cis*-isomer of the 2nd charged state, 12 coupling constants are needed to fully describe the spin environment of the system. The Hamiltonian thus used for this charged state is the following:

$$\begin{split} H &= -2J_1[\langle s_2 \cdot s_5 \rangle] - 2J_2[\langle s_1 \cdot s_4 \rangle + \langle s_3 \cdot s_6 \rangle] - 2J_3[\langle s_1 \cdot s_2 \rangle + \langle s_2 \cdot s_6 \rangle] \\ &- 2J_4[\langle s_1 \cdot s_5 \rangle + \langle s_5 \cdot s_6 \rangle] - 2J_5[\langle s_1 \cdot s_6 \rangle] - 2J_6[\langle s_1 \cdot s_3 \rangle] - 2J_7[\langle s_2 \cdot s_3 \rangle] \\ &- 2J_8[\langle s_2 \cdot s_4 \rangle] - 2J_9[\langle s_3 \cdot s_5 \rangle] - 2J_{10}[\langle s_4 \cdot s_5 \rangle] - 2J_{11}[\langle s_4 \cdot s_6 \rangle] - 2J_{12}[\langle s_3 \cdot s_4 \rangle] \end{split}$$

18 electronic configurations were modelled for this state (**Table S7.1**) and the J-values obtained are given in **Table S7.2**. The coupling strengths are in line with the observed trend. The difference in J_7 and J_8 , and J_9 and J_{10} is due to differences in the spin density of the oxygens joining Mn2 and Mn5 to Mn3 and Mn4 respectively (**Table S3.3**). The large spin densities on the phosphonate oxygens joining Mn3 and Mn4 make them strongly coupled.

The coupling between Mn2 and Mn5 (J₁) is greater in this state compared to the same in the *trans*- isomer of the 3rd charged state. At the same time however, the standard deviation is also quite high. To check the reliability of these values, all 15 coupling constants were also calculated which gives a value of 0.02 \pm 0.02 for J₁ (**Table S7.3**). The coupling strength between Mn2 and Mn5 is thus in line with the observed trend (i.e. decreasing with increasing Mn-Mn distance).

For this configuration again the antiferromagnetic coupling dominates and like the *cis*-configuration of the 2^{nd} oxidised state, the S = 0 state (*Cis* - **1256 – Mn356**) has been found to be the lowest in energy while the ferromagnetic state is the highest in energy.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.064250	3.011474	3.742397	3.740791	3.020299	3.065639	0.00
3.061218	3.008064	3.742149	-3.739551	3.018476	3.063512	-83.10
3.061862	3.011037	3.742920	3.740511	3.020108	-3.054765	-98.54
3.062028	-3.003563	3.741741	3.740540	3.018717	3.064082	-101.62
-3.054956	3.011193	3.742676	3.740962	3.019267	-3.056904	-144.03
3.059102	-3.007727	3.741465	-3.739677	3.017169	3.061433	-149.68
3.059934	-3.003526	3.741643	3.740066	-3.012468	3.062415	-210.51
3.059630	-3.004178	3.742366	3.740087	3.019174	-3.056413	-140.54
3.059581	3.004969	-3.741719	-3.740106	3.014162	3.060618	-115.99
3.060004	3.008251	-3.740882	3.739975	3.016097	-3.057119	-201.69
3.058962	3.006130	3.742653	-3.739675	3.018509	-3.057295	-139.74
-3.057423	-3.004058	3.742110	3.740550	3.018818	-3.058701	-132.83
-3.057573	3.006104	3.742378	-3.739400	3.017640	-3.059594	-206.73
3.057640	-3.006869	-3.741487	3.739557	3.015391	-3.059201	-188.03
3.057193	-3.008803	3.741297	-3.740442	-3.014690	3.059412	-195.44
3.056835	-3.007922	3.742096	-3.740145	3.017568	-3.058556	-146.66
3.057621	-3.004565	3.742239	3.739555	-3.013154	-3.058308	-187.31
3.057836	3.009146	-3.741475	3.739251	-3.017959	-3.059602	-219.03

Table S7.1: Bader spin density on each Mn centre and the relative energy of each spin state with respect to the ferromagnetic state for the *cis*-isomer of the 4th charged state.

Table S7.2: Magnitude of J-values (cm⁻¹) and the Mn-Mn interactions that constitute each J-value for
the *cis*-isomer of the 4th charged state.

J-value	Interacting Mn centres	Magnitude (cm ⁻¹)	
J_1	<i>trans</i> -Mn2(IV)-Mn5(IV)	0.23 ± 0.18	
I	trans-Mn1(IV)-Mn4(III)	1 01 + 0 08	
J 2	trans-Mn3(III)-Mn6(IV)	1.01 ± 0.08	
	cis-Mn1(IV)-Mn2(IV)	2.06 + 0.14	
J 3	cis-Mn2(IV)-Mn6(IV)	-3.00 ± 0.14	
1	cis-Mn1(IV)-Mn5(IV)	2 20 ± 0 12	
J ₄	cis-Mn5(IV)-Mn6(IV)	-5.59 ± 0.12	
J_5	cis-Mn1(IV)-Mn6(IV)	-2.99 ± 0.15	
J ₆	cis-Mn1(IV)-Mn3(III)	-2.31 ± 0.13	
J ₇	cis-Mn2(IV)-Mn3(III)	-2.54 ± 0.11	
J ₈	cis-Mn2(IV)-Mn4(III)	-1.50 ± 0.16	
J ₉	<i>cis</i> -Mn3(III)-Mn5(IV)	-1.14 ± 0.15	
J_{10}	<i>cis</i> -Mn4(III)-Mn5(IV)	-2.80 ± 0.11	
J ₁₁	cis-Mn4(III)-Mn6(IV)	-1.83 ± 0.16	
J ₁₂	cis-Mn3(III)-Mn4(III)	-1.74 ± 0.10	

Interaction	J-values (15 J values)	J-values (12 J values)
Mn1Mn2	-2.89 ± 0.01	-3.06 ± 0.14
Mn1Mn3	-2.25 ± 0.01	-2.31 ± 0.13
Mn1Mn4	0.95 ± 0.00	1.01 ± 0.08
Mn1Mn5	-3.43 ± 0.01	-3.39 ± 0.12
Mn1Mn6	-2.98 ± 0.01	-2.99 ± 0.15
Mn2Mn3	-2.47 ± 0.01	-2.54 ± 0.11
Mn2Mn4	-1.56 ± 0.00	-1.50 ± 0.16
Mn2Mn5	0.02 ± 0.02	0.23 ± 0.18
Mn2Mn6	-3.24 ± 0.00	-3.06 ± 0.14
Mn3Mn4	-1.70 ± 0.01	-1.74 ± 0.10
Mn3Mn5	-1.28 ± 0.01	-1.14 ± 0.15
Mn3Mn6	0.98 ± 0.01	1.01 ± 0.08
Mn4Mn5	-2.79 ± 0.01	-2.80 ± 0.11
Mn4Mn6	-1.83 ± 0.00	-1.83 ± 0.16
Mn5Mn6	-3.37 ± 0.01	-3.39 ± 0.12

Table S7.3: A comparison of the J-values (cm⁻¹) for the *cis*-isomer of the 4th oxidised state obtainedwith the 15 J-value and 12 J-value Hamiltonians.



Fig. S7.1: (a) Optimised model of the *cis*-isomer of the 4th charged state for the {Mn₆} cage. Colour scheme: Mn^{III} (dark blue), Mn^{IV} (light blue), P(pink), Cl (green), C (black) O (red). Hydrogens have been removed for clarity. (b) The distribution of the spin density in this state. Blue and green regions in the spin density plots represent the spin density associated with up and down spin respectively. Spin density associated with Mn3 and the ligands coordinated to it has been removed for clarity.

S7.2 Trans-isomer

In this state, Mn3 and Mn6 are in oxidation state III while the others are in oxidation state IV (Fig. 2h). The *trans*- Mn(IV)-Mn(IV) and Mn(III)-Mn(III) distances are ~6.170 and 6.510 Å respectively. The Mn(IV)-Mn(IV) distance between the *trans*-Mn centres is close to the Mn-Mn distance between the *trans*-Mn centres in the fully reduced state. The Mn-Cl distance follows the order Mn1(IV)-Cl ~ Mn2(IV)-Cl (2.65Å) < Mn3(III)-Cl (3.29Å) ~ Mn6(III)-Cl (3.30.Å) < Mn5(IV)-Cl ((3.55Å)) < Mn4(IV)-Cl (3.57Å). Cl is shifted towards Mn1(IV) and Mn2(IV) just like the *trans*-configuration of the second oxidised state. Surprisingly, the Mn(III)-Cl distance is smaller than Mn-Cl distance for Mn4 and Mn5 which are in oxidation state IV. The Hamiltonian used for this charged state is the following:

$$H = -2J_1[\langle s_1.s_4 \rangle + \langle s_2.s_5 \rangle] - 2J_2[\langle s_3.s_6 \rangle] - 2J_3[\langle s_1.s_2 \rangle] - 2J_4[\langle s_4.s_5 \rangle] - 2J_5[\langle s_1.s_5 \rangle + 2J_7[\langle s_1.s_6 \rangle] - 2J_8[\langle s_2.s_6 \rangle] - 2J_9[\langle s_3.s_4 \rangle + \langle s_3.s_5 \rangle] - 2J_{10}[\langle s_4.s_6 \rangle + \langle s_5.s_6 \rangle]$$

19 electronic configurations were modelled for this state (**Table S7.4**) and the 10 J-values obtained are given in **Table S7.5**. The coupling between *cis*-Mn(IV) centres with each other can be correlated to the Mn-Cl distances and hence the Mn-Cl overlaps. Mn1 and Mn2 also couple strongly to Mn(III) centres compared to the coupling of Mn(III) centres with Mn4 and Mn5. This is due to relatively stronger coupling of Mn1 and Mn2 with the Mn(III) centres via the Cl bridge. The coupling strength between Mn(III) centres is antiferromagnetic and is in line with the observed trends.

As J₁ has a standard deviation larger than its value, a set of 14 coupling constants was also determined (**Table S7.6**) using a Hamiltonian in which the only terms that were kept coupled were $\langle s_1 \cdot s_4 \rangle$ and $\langle s_2 \cdot s_5 \rangle$ (since these are the only two terms that should be identical based on the Mn-Mn distances) and J₇ was found to be 0.10 ± 0.01 cm⁻¹ which implies that it follows the observed trend.

In this configuration unlike the *trans*-configuration of the 2^{nd} oxidised state, the S = 0 state (*Trans* - **1245** – **Mn256**) has been found to be the lowest in energy while the ferromagnetic state is the highest in energy. This indicates that the ability to stabilise intermediate spin states is lost.

Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Energy (cm ⁻¹)
3.063026	3.069503	3.748202	2.989588	2.996799	3.749655	0.00
3.059819	-3.062507	3.747905	2.989417	2.995261	3.749093	-125.65
3.061978	3.068299	-3.745651	2.986853	2.994633	3.748734	-100.71
-3.058474	-3.065467	3.746986	2.987637	2.994925	3.748819	-174.33
3.058975	-3.063663	-3.746192	2.986406	2.993431	3.748414	-168.38
3.058656	-3.062724	3.747579	2.988856	-2.989737	3.748922	-219.73
3.060817	3.067185	-3.746317	2.984558	2.991729	-3.747954	-183.35
-3.059746	-3.066361	-3.746940	2.985113	2.992625	3.748111	-163.92
-3.060039	-3.065964	3.746939	2.987368	-2.990748	3.748445	-205.62
3.057204	-3.064037	-3.746401	2.985588	-2.993079	3.748200	-225.95
-3.057777	3.065170	3.746901	-2.983664	-2.990728	3.748465	-203.40
3.062211	3.068440	3.747838	-2.981189	2.996625	3.749184	-97.57
3.061674	3.068220	3.747184	2.987462	2.994097	-3.747344	-100.46
3.059590	-3.063630	3.747530	-2.982525	2.995188	3.748682	-156.41
3.058878	-3.064056	3.747015	2.986950	2.992668	-3.747758	-178.69
-3.059664	-3.066874	3.746481	2.985369	2.991955	-3.748001	-164.60
3.058434	-3.064750	-3.746577	-2.985429	2.992835	3.747853	-164.28
3.057160	-3.063947	-3.746494	2.985595	-2.993209	3.748216	-226.21
3.057291	-3.064291	3.746673	2.985926	-2.993381	-3.748157	-241.01

Table S7.4: Bader spin density on each Mn centre and the relative energy of each spin state with respect to the ferromagnetic state for the trans-isomer of the 4th charged state.

Table S7.5: Magnitude of J-values (cm⁻¹) and the Mn-Mn interactions that constitute each J-value forthe *trans*-isomer of the 4th charged state.

J-value	Interacting Mn centres	Magnitude (cm ⁻¹)
J_1	trans-Mn1(IV)-Mn4(IV)	0.02 + 0.45
	trans-Mn2(IV)-Mn5(IV)	0.02 ± 0.15
J ₂	trans-Mn3(III)-Mn6(III)	-0.55 ± 0.12
J_3	cis-Mn1(IV)-Mn2(IV)	-4.44 ± 0.27
J_4	cis-Mn4(IV)-Mn5(IV)	-3.13 ± 0.26
	cis-Mn1(IV)-Mn5(IV)	2 46 + 0 15
J 5	cis-Mn2(IV)-Mn4(IV)	-3.40 ± 0.15
	cis-Mn1(IV)-Mn3(III)	2 40 + 0 14
J ₆	cis-Mn2(IV)-Mn3(III)	-2.40 ± 0.14
J_7	cis-Mn1(IV)-Mn6(III)	-2.86 ± 0.27
J ₈	cis-Mn2(IV)-Mn6(III)	-1.88 ± 0.24
J ₉	cis-Mn3(III)-Mn4(IV)	1 57 4 0 11
	cis-Mn3(III)-Mn5(IV)	-1.57 ± 0.11
J ₁₀	cis-Mn4(IV)-Mn6 (III)	1 54 4 0 19
	cis-Mn5(IV)-Mn6(III)	-1.54 ± 0.18

Interaction	J-values (14 J values)	J-values (10 J values)
Mn1Mn2	-4.29 ± 0.02	-4.44 ± 0.27
Mn1Mn3	-2.34 ± 0.03	-2.40 ± 0.14
Mn1Mn4	0.10 ± 0.01	0.02 ± 0.15
Mn1Mn5	-3.46 ± 0.03	-3.46 ± 0.15
Mn1Mn6	-2.75 ± 0.02	-2.86 ± 0.27
Mn2Mn3	-2.52 ± 0.01	-2.40 ± 0.14
Mn2Mn4	-3.65 ± 0.02	-3.46 ± 0.15
Mn2Mn5	0.10 ± 0.01	0.02 ± 0.15
Mn2Mn6	-2.06 ± 0.01	-1.88 ± 0.24
Mn3Mn4	-1.56 ± 0.02	-1.57 ± 0.11
Mn3Mn5	-1.64 ± 0.02	-1.57 ± 0.11
Mn3Mn6	-0.64 ± 0.01	-0.55 ± 0.12
Mn4Mn5	-3.07 ± 0.02	-3.13 ± 0.26
Mn4Mn6	-1.80 ± 0.02	-1.54 ± 0.18
Mn5Mn6	-1.43 ± 0.02	-1.54 ± 0.18

Table S7.6: A comparison of the J-values (cm⁻¹) for the *trans*-isomer of the 4th oxidised stateobtained with the 14 J-value and 12 J-value Hamiltonians.



Fig. S7.2: (a) Optimised model of the *trans*-isomer of the 4th charged state for the {Mn₆} cage. Colour scheme: Mn^{III} (dark blue), Mn^{IV} (light blue), P(pink), Cl (green), C (black) O (red). Hydrogens have been removed for clarity. (b) The distribution of the spin density in this state. Blue and green regions in the spin density plots represent the spin density associated with up and down spin respectively. Spin density associated with Mn3 and the ligands coordinated to it has been removed for clarity.

S8. χT vs T plots for the different charged states

Table S8.1: Total possible sets of solutions, total non-singular solutions and the number of solutionsthat were found to be within three standard deviations for each charged state.

Oxidation State	Possible solutions	Non-singular solutions	Solutions considered
Fully reduced	60	60	60
1 st charged state	48032	20916	19254
1 st charged state no Cl	1260	756	678
Cis - 2 nd charged state	352716	152750	121368
trans - 2 nd charged state	495	207	207
Fac – 3 rd charged state	18018	4380	4044
Mer – 3 rd charged state	325563	81261	42624
Cis – 4 th charged state	111384	45786	32890
trans – 4 th charged state	831402	335819	248985



Fig. S8.1: χ T vs T plots for the different charged states of the {Mn₆} complex.

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