

## Electronic Supplementary Information

**Table S1.** Exchange interaction between manganese cations for complexes employed in the Magnetostructural Maps indicating the refcode in Cambridge Structural Database, the oxidation state, the bridging ligands, the intermetallic distance and the calculated J values.

Complex	Oxidation state	Bridging ligands	M···M (Å)	J B3LYP (cm <sup>-1</sup> )	J PBE (cm <sup>-1</sup> )	Reference
Mn4-TAVPAH	II II	OR-OR	3.220	-4.0	-9.1	1
Mn4-TAVNUZ	II II	OR-OR	3.227	-4.1	-9.3	1
Mn4-TAVNUZ	II II	OR-OR	3.227	-3.8	-9.0	1
Mn4-VAFBIO	II II	OR-OR	3.235	-7.0	-17.6	1
Mn4-TAVNUZ	II II	OR-OR	3.239	-3.5	-8.5	1
Mn4-TAVNUZ	II II	OR-OR	3.242	-3.4	-8.0	1
Mn4-TAVPAH	II II	OR-OR	3.246	-3.3	-8.0	1
Mn4-TAVPAH	II II	OR-OR	3.250	-3.3	-7.	1
Mn4-TAVPAH	II II	OR-OR	3.252	-3.0	-6.9	1
Mn2-BEQVAV	II II	OR-OR	3.262	-4.0	-8.2	2
Mn4-YAQXUK	II II	OR-OR	3.274	-3.2	-6.3	1
Mn4-TAVPAH	II II	OR-OR	3.284	-2.3	-8.4	1
Mn4-TAVNUZ	II II	OR-OR	3.297	-2.0	-7.0	1
Mn4-YAQXUK	II II	OR-OR	3.310	-2.5	-4.9	1
Mn4-TAVNUZ	II II	OR-OR	3.318	-2.0	-7.2	1
Mn4-MOFSAB	II II	OR-OR	3.342	+0.4	-0.6	1
Mn4-MOFSAB	II II	OR-OR	3.350	-1.5	-4.2	1
Mn4-TAVPAH	II II	OR-OR	3.352	-2.0	-8.6	1
Mn4-YAQXUK	II II	OR-OR	3.385	-0.3	-1.9	1
Mn4-VAFBIO	II II	OR-OR	3.408	-5.8	-13.6	1
Mn4-YAQXUK	II II	OR-OR	3.432	-1.0	-3.2	1
Mn2-DADQUV	II II	OR-OR	3.443	+0.9	+2.1	2
Mn4-YAQXUK	II II	OR-OR	3.447	-0.2	-1.6	1
Mn4-YAQXUK	II II	OR-OR	3.456	-1.3	-3.9	1
Mn2-QAPWOU	III III	O-O	2.658	-164.0	-200.0	2
Mn4-SAVRIR	III III	O-O	2.750	-118.0	-164.0	1
Mn4-SAVROX	III III	O-O	2.792	-112.0	-153.0	1
Mn4-SUXMIH	III III	O-O-C	2.841	-58.8	-	1

Mn4-VOFBEX	III III	O-O-C	2.843	-47.5	-	1
Mn4-FECFOI	III III	O-O-C	2.846	-37.5	-	1
Mn4-LAQYOS	III III	O-O-C	2.871	-39.7	-	1
Mn4-KIRNUU	III III	O-O-C	2.875	-59.7	-	1
Mn2-WEDPEB	III III	OR-OR	3.084	+19.1	+33.8	2
Mn4-VALRUV	III III	O-OH	3.103	+20.9	+32.0	1
Mn4-VALRUV	III III	O-OH	3.126	+22.3	+29.1	1
Mn4-VALRUV	III III	O-OH	3.137	+22.3	+32.8	1
Mn6-REJPEC	III III	O-ON-C	3.143	-21.0	-	3
Mn6-VIVFIQ	III III	ON-ON	3.154	+6.4	-	3
Mn6-VIVGEN	III III	O-ON	3.176	+5.0	-	<b>6, this work</b>
Mn19-XELCUN	III III	O-N <sub>3</sub>	3.185	+14.2	+22.2	4
Mn3-TAYCOM	III III	O-ON-C	3.188	+13.8	+40.8	5
Mn3-TAYCOM	III III	O-ON-C	3.191	+14.2	+45.4	5
Mn4-ZALSUA	III III	O-OR	3.195	+15.7	+27.3	1
Mn4-ZALSUA	III III	O-OR	3.196	+15.2	+26.9	1
Mn3-TAYCOM	III III	O-ON-C	3.201	+15.3	+43.8	5
Mn4-UFAMAP	III III	O-ONO <sub>2</sub>	3.201	+3.0	+8.9	1
Mn19-XELCUN	III III	O-N <sub>3</sub>	3.206	+11.3	+16.8	4
Mn4-ZALSUA	III III	O-OR	3.213	+17.4	+31.6	1
Mn19-XELCUN	III III	O-N <sub>3</sub>	3.219	+15.2	+15.7	4
Mn6-VIVGOX	III III	O-ON	3.224	+5.8	-	3
Mn4-UFAMAP	III III	O-ONO <sub>2</sub>	3.226	+5.0	+10.4	1
Mn6-VIVFOW	III III	ON-ON	3.231	+7.2	-	3
Mn6-VIVGEN	III III	O-ON	3.232	+2.4	-	<b>6, this work</b>
Mn6-VIVFOW	III III	O-ON	3.232	+1.6	-	3
Mn6-VIVGIR	III III	O-ON	3.234	-3.6	-	3
Mn6-VIVGIR	III III	O-ON	3.238	+4.6	-	3
Mn6-REJPEC	III III	O-ON	3.238	+2.6	-	3
Mn10-VEHQEF	III III	O-N <sub>3</sub>	3.239	+15.9	+23.2	4
Mn6	III III	O-ON	3.240	+4.2	-	<b>14, this work</b>
Mn6-VIVFIQ	III III	O-ON	3.241	-3.0	-	3
Mn6-CIFJUX	III III	O-ON	3.246	+8.0	-	<b>3, this work</b>
Mn6-CIFJUX	III III	O-ON	3.247	+1.8	-	<b>3, this work</b>
Mn6-CEYMAV	III III	O-ON	3.247	+5.2	-	3
Mn6-VIVFOW	III III	O-ON	3.248	+6.2	-	3
Mn6-VIVFOW	III III	O-ON	3.250	-6.8	-	3
Mn6-VIVFIQ	III III	O-ON	3.251	+2.4	-	3
Mn4-SUXMIH	III III	O-C2	3.255	-7.7	-	1
Mn6-CIFJUX	III III	O-ON	3.255	+4.0	-	<b>3, this work</b>
Mn6-CEYMAV	III III	ON-ON	3.255	+6.2	-	3

Mn6-CIFJUX	III III	O-ON	3.255	-1.4	-	<b>3</b> , this work
Mn6-CIFJUX	III III	O-ON	3.257	-5.6	-	<b>3</b> , this work
Mn6	III III	O-ON	3.257	-1.6	-	<b>14</b> , this work
Mn6-VIVGOX	III III	O-ON	3.258	-1.8	-	3
Mn6-REJPEC	III III	O-ON	3.258	-6.2	-	3
Mn4-UFAMAP	III III	O-ONO <sub>2</sub>	3.261	+7.5	+17.4	1
Mn6-VIVFIQ	III III	O-ON	3.263	-3.2	-	3
Mn6-CEYMAV	III III	O-ON	3.264	+3.2	-	3
Mn6-VIVGIR	III III	O-ON	3.269	-4.6	-	3
Mn6-CIFJUX	III III	O-ON	3.271	+0.4	-	<b>3</b> , this work
Mn6	III III	O-ON	3.273	+0.6	-	<b>14</b> , this work
Mn6	III III	ON-ON	3.280	+7.0	-	<b>14</b> , this work
Mn6-CEYMAV	III III	O-ON	3.282	+2.4	-	3
Mn6-VIVGOX	III III	O-ON	3.282	-0.04	-	3
Mn4-FECFOI	III III	O-C2	3.299	-15.1	-	1
Mn4-LAQYOS	III III	O-C2	3.299	-10.1	-	1
Mn4-KIRNUU	III III	O-C2	3.308	-12.9	-	1
Mn4-KIRNUU	III III	O-C2	3.308	-13.0	-	1
Mn4-VOFBEX	III III	O-C2	3.308	-14.0	-	1
Mn19-XELCUN	III III	O-N <sub>3</sub>	3.311	+3.0	+9.9	4
Mn4-FECFOI	III III	O-C2	3.311	-14.3	-	1
Mn4-VOFBEX	III III	O-C2	3.312	-13.8	-	1
Mn4-LAQYOS	III III	O-C2	3.314	-14.4	-	1
Mn6-VIVGOX	III III	ON-ON	3.322	+6.6	-	3
Mn6-VIVGIR	III III	ON-ON	3.328	+4.2	-	3
Mn6-REJPEC	III III	ON-ON	3.337	+5.8	-	3
Mn6-CIFJUX	III III	ON-ON	3.341	+4.2	-	<b>3</b> , this work
Mn4-SUXMIH	III III	O-C	3.362	-9.4	-	1
Mn4-FECFOI	III III	O-C	3.370	-15.2	-	1
Mn4-FECFOI	III III	O-C	3.384	-16.5	-	1
Mn4-VOFBEX	III III	O-C	3.387	-6.0	-	1
Mn4-KIRNUU	III III	O-C	3.398	-18.2	-	1
Mn4-KIRNUU	III III	O-C	3.398	-18.3	-	1
Mn4-VOFBEX	III III	O-C	3.407	-10.9	-	1
Mn6-VIVGEN	III III	O-ON	3.414	+1.4	-	<b>6</b> , this work
Mn4-LAQYOS	III III	O-C	3.437	-10.0	-	1
Mn4-LAQYOS	III III	O-C2	3.451	-12.9	-	1
Mn6-VIVGEN	III III	ON-ON	3.461	+1.6	-	<b>6</b> , this work
Mn6-VIVFOW	III III	OR-ON	3.635	-0.4	-	3
Mn6-VIVFIQ	III III	OR-ON	3.647	-1.6	-	3
Mn6-CIFJUX	III III	OR-ON	3.670	-0.4	-	<b>3</b> , this work

Mn6-CIFJUX	III III	OR-ON	3.728	+1.4	-	<b>3</b> , this work
Mn6	III III	OR-ON	3.779	-1.2	-	<b>14</b> , this work
Mn6-CEYMAV	III III	OR-ON	3.784	+1.0	-	3
Mn6-VIVGIR	III III	OR-ON	3.851	-1.4	-	3
Mn6-VIVGOX	III III	OR-ON	3.857	+0.2	-	3
Mn6-VIVGEN	III III	OR-ON	3.869	+3.4	-	<b>6</b> , this work
Mn6-REJPEC	III III	OR-ON	4.362	-1.0	-	3
Mn2-VOWCEP	IV IV	O-O-OH	2.265	-684.0	-998.0	2
Mn2-VADDAF	IV IV	O-O-O	2.307	-779.0	-1012.0	2
Mn2-HAJZOH01	IV IV	O-O-C	2.640	-29.0	-127.1	2
Mn3-IGOJET	IV IV	O-O-C	2.660	-22.4	-98.5	1
Mn3-IGOJET	IV IV	O-O-C	2.667	-22.4	-90.6	1
Mn3-JEBXUJ	IV IV	O-O	2.681	-107.5	-203.8	1
Mn2-BEPVIC	IV IV	O-O	2.701	-134.0	-258.0	2
Mn2-HISGOF	IV IV	O-O	2.722	-168.0	-322.0	2
Mn4-LIDVUP	IV IV	O-O	2.735	-141.0	-259.0	1
Mn4-LIDVUP	IV IV	O-O	2.746	-104.0	-210.0	1
Mn4-LIDVUP	IV IV	O-O	2.760	-111.0	-216.0	1
Mn12-RAHBIM	IV IV	O-O	2.820	+2.8	+5.4	6
Mn12-RAHBIM	IV IV	O-O	2.928	-10.0	-16.0	6
Mn3-JEBXUJ	IV IV	O	3.241	-56.8	-138.6	1
Mn3-JEBXUJ	IV IV	O	3.245	-55.3	-135.4	1
Mn12-RAHBIM	II III	OR-OR-C	3.149	-7.2	-16.3	6
Mn12-RAHBIM	II III	OR-OR-C	3.169	+4.5	+6.4	6
Mn2-GAVWOP	II III	OR-OR	3.181	+1.0	-8.5	2
Mn12-RAHBIM	II III	OR-OR-C	3.183	+5.1	+8.1	6
Mn12-RAHBIM	II III	OR-OR-C	3.183	+5.1	+8.1	6
Mn12-RAHBIM	II III	OR-OR-C	3.198	-2.8	-8.4	6
Mn12-RAHBIM	II III	OR-OR-C	3.206	-4.4	-12.1	6
Mn19-XELCUN	II III	O-OR	3.224	+1.6	+5.1	4
Mn10-VEHQEF	II III	O-OR	3.267	+1.6	+3.7	4
Mn19-XELCUN	II III	O-OR	3.298	+3.4	+7.2	4
Mn19-XELCUN	II III	O-OR	3.303	+5.4	+7.2	4
Mn19-XELCUN	II III	O-OR	3.436	+1.9	+3.6	4
Mn12-RAHBIM	II III	OR-C-C	3.473	-7.3	-1.8	6
Mn4-SAVRIR	II III	O	3.735	-10.7	-14.1	1
Mn4-SAVROX	II III	O	3.787	-8.6	-10.9	1
Mn2-QABHAC	III IV	O-O-C	2.553	-277.0	-517.0	2
Mn2-QABHAC	III IV	O-O-C	2.633	-197.0	-348.0	2
Mn12-RAHBIM	III IV	O-O-C	2.769	-53.9	-75.6	6
Mn4-UFAMAP	III IV	O-O-C	2.775	-38.7	-47.4	1

Mn4-VALRUV	III IV	O-O-C	2.787	-52.5	-74.3	1
Mn4-VALRUV	III IV	O-O-C	2.788	-51.8	-64.2	1
Mn4-UFAMAP	III IV	O-O-C	2.790	-39.5	-50.3	1
Mn4-ZALSUA	III IV	O-O-C	2.791	-45.9	-52.4	1
Mn4-VALRUV	III IV	O-O-C	2.792	-56.0	-69.2	1
Mn4-ZALSUA	III IV	O-O-C	2.794	-44.1	-52.3	1
Mn4-UFAMAP	III IV	O-O-C	2.798	-37.5	-44.8	1
Mn4-ZALSUA	III IV	O-O-C	2.812	-45.0	-62.9	1
Mn12-RAHBIM	III IV	O-C	3.328	-3.8	-2.7	6
Mn12-RAHBIM	III IV	O-C	3.417	-3.8	-2.7	6
Mn12-RAHBIM	III IV	O	3.450	-26.7	-49.8	6

C = carboxilate

1 To be submitted

2 To be submitted

3 E. Cremades, J. Cano, E. Ruiz, G. Rajaraman, C. J. Milios, E. K. Brechin, submitted to publication.

4 E. Ruiz, T. Cauchy, J. Cano, R. Costa, J. Tercero, and S. Alvarez, *J. Am. Chem. Soc.*, 2008, **130**, 7420.

5 J. Cano, T. Cauchy, E. Ruiz, C. J. Milios, C. C. Stoumpos, T. C. Stamatatos, S. P. Perlepes, G. Christou, and E. K. Brechin, *Dalton Trans.*, 2008, 234.

6 J. Cano, R. Costa, S. Alvarez, and E. Ruiz, *J. Chem. Theory Comput.*, 2007, **3**, 782.