Supplementary Information

Structural Analysis of High-Spin States of S0-S4 at OEC Complex: A Theoretical Approach of Small Models

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Table S1. Relative percentage deviation for interatomic distances (in percentage). The High-Spin (HS), Experimental (Exp) and Reference (Ref) values have been compared one each other. The calculation has been done considering [(value in system A – value in system B) / (value in system B)] × 100%. Experimental (Exp) interatomic distance values come from X-ray crystal structure.[1] Reference interatomic distance values (Ref) come from theoretical data for a S2-state model.[2] Relative percentage deviations above 15.0% are assigned in bold

Parameter	S0 (%Δ)		S1 (%Δ)		S2 (%Δ)		S3 (%Δ)		S4 (%Δ)	
	HS/Exp	HS/Ref	HS/Exp	HS/Ref	HS/Exp	HS/Ref	HS/Exp	HS/Ref	HS/Exp	HS/Ref
MnD1–MnC2	–0.4	1.2	–3.4	–1.9	–2.4	–0.9	–3.1	–1.6	–3.3	–1.8
MnD1–MnB3	–1.3	–4.6	–0.2	–3.5	1.3	–2.1	1.3	–2.1	1.0	–2.4
MnD1–MnA4	–1.5	–	–5.6	–	–4.4	–	–4.4	–	2.9	–
MnC2–MnB3	–0.2	2.9	–3.3	–0.3	–3.5	–0.6	–3.6	–0.6	–2.9	0.1
MnC2–MnA4	–2.5	–	–7.4	–	–6.2	–	–6.5	–	–1.4	–
MnB3–MnA4	–2.7	4.7	–9.2	–2.3	–7.5	–0.4	–7.7	–0.7	0.9	8.6
MnD1–O1	–4.1	–4.0	–2.9	–2.8	–2.6	–2.6	–3.0	–2.9	–4.8	–4.7

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Parameter	S0 (%Δ)		S1 (%Δ)		S2 (%Δ)		S3 (%Δ)		S4 (%Δ)	
	HS/Exp	HS/Ref	HS/Exp	HS/Ref	HS/Exp	HS/Ref	HS/Exp	HS/Ref	HS/Exp	HS/Ref
MnD1–O3	3.9	–3.0	5.1	–2.0	7.8	0.6	6.6	–0.5	0.8	–6.0
MnD1–O5	11.9	–10.2	9.5	–12.0	**16.2**	–6.7	**16.6**	–6.3	9.6	–12.0
MnC2–O1	–8.1	1.8	–10.0	–0.3	–10.3	–0.6	–10.6	–0.9	–7.7	2.3
MnC2–O2	–10.6	4.1	**–15.3**	–1.4	–13.1	1.2	–13.5	0.7	**–16.0**	–2.2
MnC2–O3	9.9	**20.4**	–10.9	–2.4	–8.6	0.1	–8.5	0.2	–9.7	–1.1
MnB3–O2	–5.9	–4.3	–2.2	–0.5	–4.7	–3.0	–4.7	–3.0	–1.7	0.1
MnB3–O3	–14.4	–9.5	–5.7	–0.2	–10.2	–5.0	–9.7	–4.5	–1.5	4.2
MnB3–O4	–6.3	8.1	–13.5	–0.2	–7.6	6.6	–7.9	6.3	–8.6	5.4
MnB3–O5	**–15.6**	8.6	**–22.5**	–0.3	**–20.1**	2.8	**–20.5**	2.2	**–18.3**	5.0
MnA4–O4	**–17.5**	–8.6	–14.6	–5.3	**–18.0**	–9.1	**–17.8**	–8.9	**–17.0**	–7.9
MnA4–O5	**–17.9**	9.9	**–24.4**	1.3	**–28.8**	–4.7	**–29.4**	–5.5	–8.2	**22.9**
Ca–O1	5.2	–2.1	5.2	–2.1	6.1	–1.2	8.2	0.7	11.4	3.7
Ca–O2	–1.6	–6.0	–2.0	–6.3	0.7	–3.7	7.0	2.2	–0.4	–4.8
Ca–O5	5.1	–3.7	2.7	–5.9	10.4	1.2	14.4	4.8	**24.1**	13.8

The values showed in Table S2 have been calculated according equation S1:

$$\sigma = \sqrt{\frac{\sum(\%\Delta_i - \overline{\%\Delta})^2}{n-1}} \qquad \text{(S1)}$$

where %Δ is the percentage deviation for each interatomic distance for a specific model (as can be seen in Table S1), $\overline{\%\Delta}$ is the respective average value regarding the same model and n is the number of interatomic distances considered for each structure.

Table S2. Standard deviation (in percentage) for interatomic distances calculated by comparing all HS, Exp and Ref structures ones each other. Values in bold indicate standard deviations above 10.0%

	Standard deviation / %						
	S0-HS	S1-HS	S2-HS	S3-HS	S4-HS	Exp	Ref
	7.4	6.9	7.0	7.7	7.9	9.1	8.0
S0-HS	0	6.5	6.2	6.9	7.6	8.4	7.8
S1-HS	5.8	0	3.4	4.1	5.8	8.7	3.1
S2-HS	5.5	3.5	0	1.4	6.7	**10.4**	3.5
S3-HS	6.3	4.3	1.7	0	6.7	**11.2**	3.7
S4-HS	7.6	6.8	7.7	7.9	0	9.8	8.0
Exp	9.3	**10.5**	**12.3**	**13.1**	**10.0**	0	**12.9**
Ref	7.4	3.4	3.7	3.8	7.4	**11.7**	0

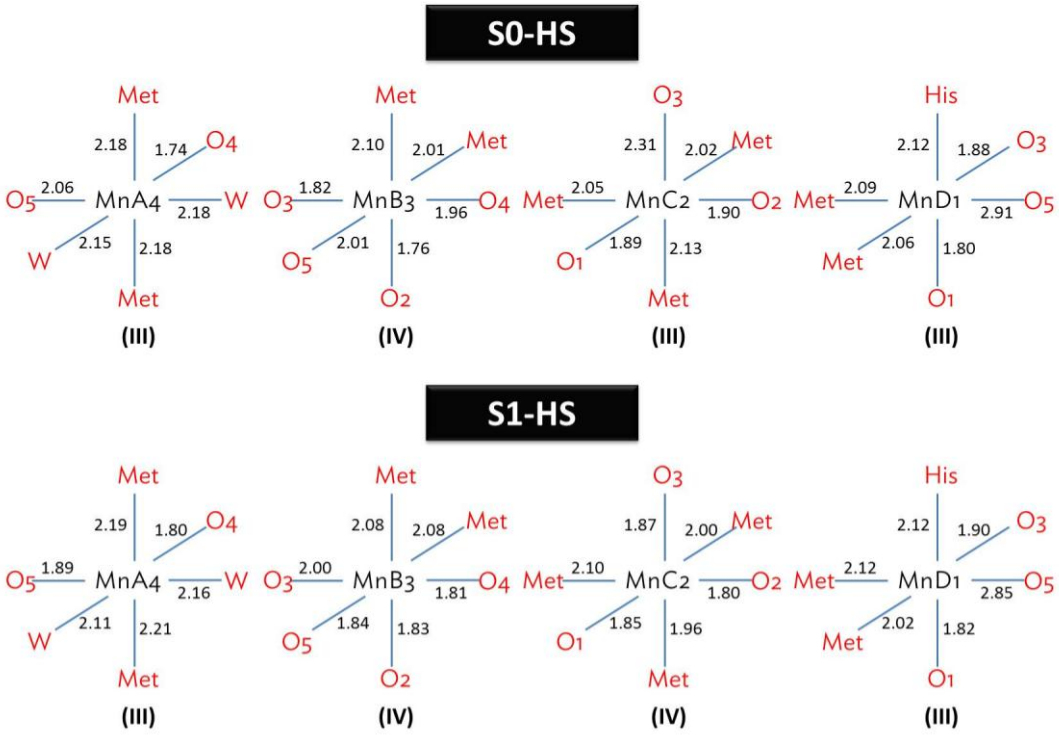

Figure S1. Interatomic distances involving the manganese centers in OEC calculated models. The manganese oxidation states are shown as well. All values displayed are in Angstrom (Å).

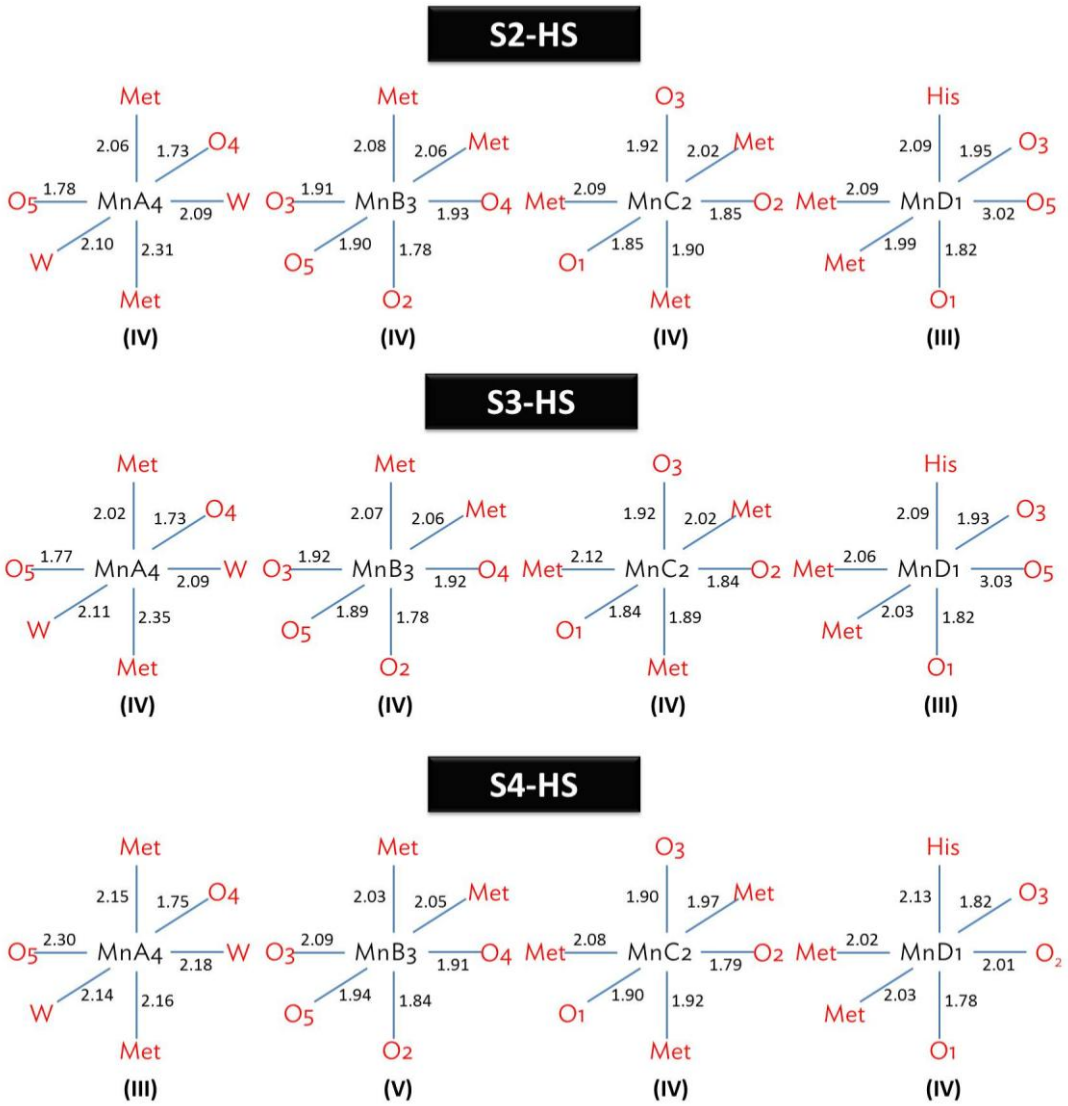

Figure S1. Interatomic distances involving the manganese centers in OEC calculated models. The manganese oxidation states are shown as well. All values displayed are in Angstrom (Å) (cont.).

References

1. Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N.; *Nature* **2011**, *473*, 55.

2. Lohmiller, T.; Krewald, V.; Navarro, M. P.; Retegan, M.; Rapatskiy, L.; Nowaczyk, M. M.; Boussac, A.; Neese, F.; Lubitz, W.; Pantazis, D.; Cox, N.; *Phys. Chem. Chem. Phys.* **2014**, *16*, 11877.