

Theoretical Studies On Concerted versus Two Steps Hydrogen Atom Transfer Reaction by a non-heme Mn^{IV/III}=O complexes: How Important Is the Oxo Ligand Basicity in C-H Activation Step?

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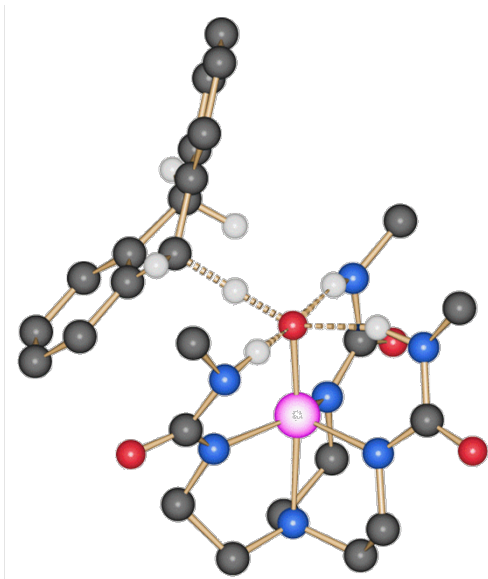
Table S1. Selected geometric parameters (bond distances in Å) and for the $[\text{Mn}^{\text{III}}\text{H}_3\text{buea}(\text{O})]^{2-}$ and $[\text{Mn}^{\text{IV}}\text{H}_3\text{buea}(\text{O})]^-$ complexes in their corresponding spin states with Int, ts1 and ts12.

	Mn-N1	Mn-N2	Mn-N3	Mn-N4	Mn-O	MnO-H1	Mn-OH2	MnO-H3	MnO-H4	C-H	N1-Mn-O	Mn-O-H4
$[\text{Mn}^{\text{III}}\text{H}_3\text{buea}(\text{O})]^{2-}$												
$S=2$	2.21	2.13	2.13	2.13	1.72	1.79	1.79	1.79	179.9			
$S=1$	2.20	2.14	2.09	2.06	1.72	1.77	1.77	1.78	176.3			
$S=0$	2.23	2.02	2.02	2.02	1.73	1.69	1.69	1.69	179.9			
ts1												
$S=2$	2.19	2.06	2.14	2.08	1.79	1.95	1.96	1.87	1.23	1.43	177.1	120.2
$S=1$	2.19	2.01	1.98	2.03	1.82	1.89	1.80	1.79	1.30	1.36	174.9	118.1
$S=0$	2.28	1.97	1.94	1.97	1.82	1.86	1.74	1.74	1.29	1.38	176.0	120.4
$[\text{Mn}^{\text{III}}(\text{H}_3\text{buea})\text{-OH}]^-$												
$S=2$	2.09	2.04	2.08	2.08	1.84	1.83	1.91	2.58	0.98		176.7	106.5
$S=1$	2.12	1.94	1.98	1.96	1.92	1.80	1.81	1.90	0.97		176.3	107.2
$S=0$	2.17	1.88	1.91	1.91	1.97	1.74	1.74	1.86	0.97		176.9	107.0
$[\text{Mn}^{\text{IV}}(\text{H}_3\text{buea})\text{-OH}]^{2-}$												
$S=5/2$	2.17	2.01	2.01	1.97	1.77	1.94	1.841	1.98	0.96		173.7	109.4
$S=3/2$	2.14	2.19	2.17	2.11	1.97	1.97	1.93	1.86	0.97		178.7	106.5
$S=1/2$	2.14	2.09	2.12	2.12	2.01	1.85	1.91	1.86	0.97		178.3	106.9
ts2												
$S=2$	2.21	2.11	2.13	2.08	1.78	1.98	1.89	1.87	1.35	1.31	178.1	127.6
$S=1$	2.19	2.09	2.14	2.07	1.77	1.94	1.92	1.87	1.36	1.30	178.3	120.6
$S=0$	2.22	2.04	2.01	2.01	1.79	1.87	1.77	1.79	1.41	1.27	177.2	121.7

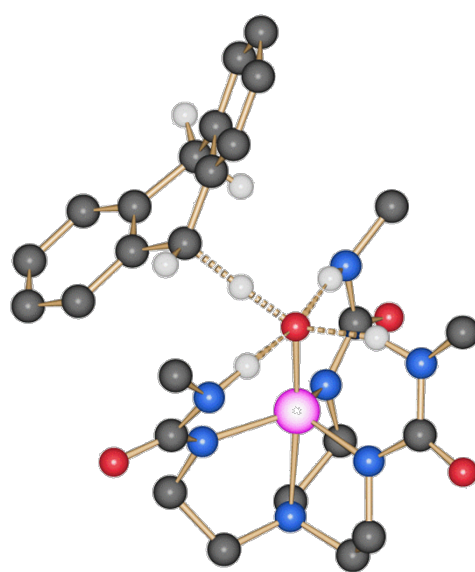
[Mn ^{IV} H ₃ buea(O)] ⁻												
S=3/2	2.22	1.99	1.97	1.92	1.68	1.76	1.83	1.82	175.7			
S=1/2	2.18	1.96	1.91	1.89	1.68	1.74	1.74	1.76	175.3			
ts1												
S=3/2	2.17	1.98	2.01	2.01	1.77	1.95	1.84	1.98	1.23	1.36	173.7	120.9
S=1/2	2.16	1.98	1.93	1.96	1.79	1.97	1.82	1.83	1.27	1.32	176.3	115.6
[Mn ^{IV} H ₃ buea(OH)]												
S=3/2	2.10	1.94	1.95	1.94	1.81	1.78	1.88	2.61	0.98		175.4	109.3
S=1/2	2.07	1.83	1.86	1.86	1.88	1.74	1.82	1.85	0.97		177.4	175.3
ts2												
S=3/2	2.18	1.99	2.01	2.01	1.75	1.94	1.91	1.83	1.43	1.25	174.2	121.6
S=1/2	2.19	1.96	1.92	1.96	1.75	1.93	1.81	1.83	1.44	1.24	175.5	117.3

Table S2. Spin densities (S) for the $[\text{Mn}^{\text{III}}\text{H}_3\text{buea}(\text{O})]^{2-}$ and $[\text{Mn}^{\text{IV}}\text{H}_3\text{buea}(\text{O})]^-$ complexes, with Int, ts1 and ts2 in their corresponding spin states.

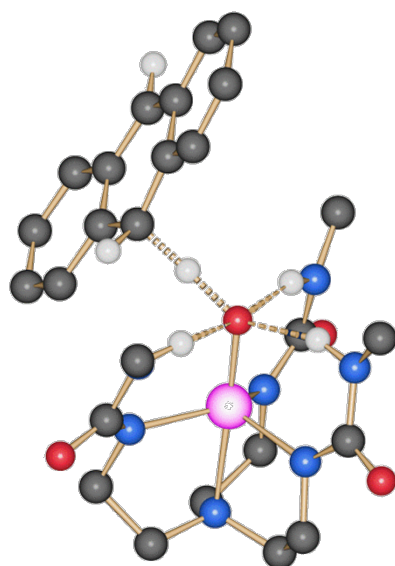
	S(Mn)	S(O)	S(C)
$[\text{Mn}^{\text{III}}\text{H}_3\text{buea}(\text{O})]^{2-}$			
$S=2$	3.70	0.13	
$S=1$	1.71	0.29	
$S=0$	0.0	0.0	
ts1			
$S=2$	3.80	0.05	0.01
$S=1$	1.93	0.00	0.00
$S=0$	0.00	0.00	0.00
$[\text{Mn}^{\text{III}}(\text{H}_3\text{buea})\text{-OH}]^-$			
$S=2$	3.80	0.02	
$S=1$	1.93	0.02	
$S=0$	0.00	0.00	
$[\text{Mn}^{\text{II}}(\text{H}_3\text{buea})\text{-OH}]^{2-}$			
$S=5/2$	4.78	0.06	
$S=3/2$	2.93	0.00	
$S=1/2$	0.99	0.004	
ts2			
$S=2$	3.80	0.06	0.61
$S=1$	1.91	0.01	0.61
$S=0$	0.00	0.00	0.00
$[\text{Mn}^{\text{IV}}\text{H}_3\text{buea}(\text{O})]^-$			
$S=3/2$	2.60	0.26	
$S=1/2$	0.84	0.15	
ts1			
$S=3/2$	3.40	-0.10	-0.25
$S=1/2$	1.62	-0.31	-0.31
$[\text{Mn}^{\text{IV}}\text{H}_3\text{buea}(\text{OH})]$			
$S=2$	3.20	0.07	
$S=1$	1.17	0.06	
ts2			
$S=3/2$	3.40	-0.02	0.44
$S=1/2$	1.45	-0.22	0.46



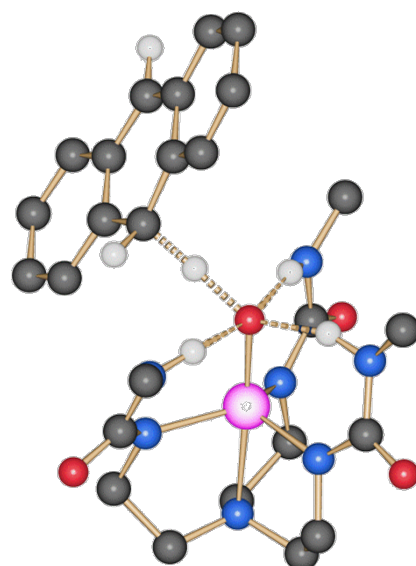
(a)



(b)



(c)



(d)

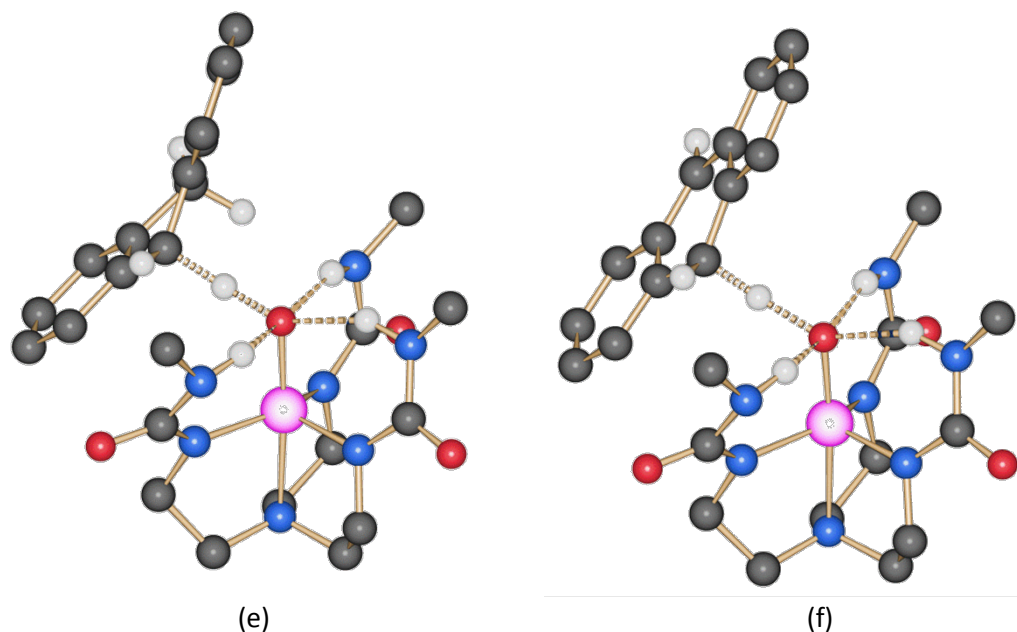


Figure S1. Optimized geometries of (a) $^3\mathbf{1}_{ts1}$, (b) $^1\mathbf{1}_{ts1}$, (c) $^3\mathbf{1}_{ts2}$, (d) $^1\mathbf{1}_{ts2}$, (e) $^2\mathbf{2}_{ts1}$ and (f) $^2\mathbf{2}_{ts2}$.

Computational methodology:

All calculations were performed using the Gaussian 09 suite of program. The geometry optimizations have been carried out using B3LYP functional and this has proven track record of yielding good numerical accuracy, particularly for transition metal complexes.¹⁸ In recent years the B3LYP-D3 functional incorporating the dispersion proposed by Grimme et al.⁹ is widely employed and is the state-of-the-art functional used to understand the mechanism of metal mediated catalytic reactions. Although dispersion is very important, our recent work on iron-oxo species reveals¹⁰ that the overall trend between B3LYP and the dispersion corrected functionals remains the same. Besides, particularly for H-abstraction reaction a method assessment with RCCSD(T) has been performed¹¹ and B3LYP and B3LYP-D along with TPSSh were found to predict energies of spin state energetics close to that of RCCSD(T) method. On this ground, we have not attempted to compute the transition states using dispersion as this is unlikely to affect the conclusion of our paper.

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