Supporting Information for:

Introducing a closed system approach for the investigation of chemical steps involving proton and electron transfer; as illustrated by a copper-based water oxidation catalyst

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Table S1 Comparison between geometrical parameters of the metal centre of [*Cu*(OH)$_2$] as calculated with OPBE and B3LYP using two different basis sets. Percentages indicate relative error with respect to experimental data of the Cu(bpy)(O$_2$CMe)$_2$ crystal structure.[1]

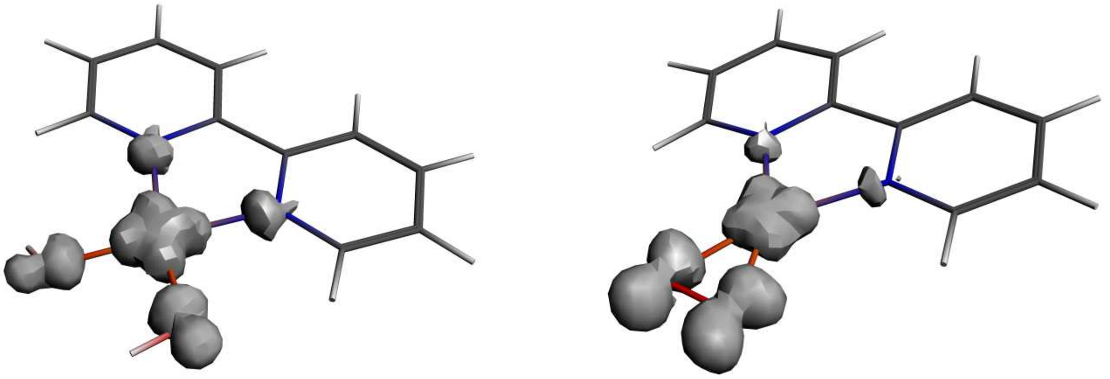
	Cu(bpy)(O$_2$CMe)$_2$	**OPBE/TZP**		**OPBE/pVQZ**		**B3LYP/TZP**		**B3LYP/pVQZ**	
Cu – N$_1$ (Å)	2.020	2.068	2.4%	2.000	1.0%	2.097	3.8%	2.043	1.1%
Cu – N$_2$ (Å)	2.015	2.048	1.6%	2.040	1.2%	2.072	2.8%	2.047	1.6%
Cu – O$_1$ (Å)	1.952	1.929	1.2%	1.924	1.4%	1.916	1.8%	1.913	2.0%
Cu – O$_2$ (Å)	1.927	1.922	0.3%	1.909	0.9%	1.915	0.6%	1.922	0.3%
O$_1$ – Cu – O$_2$ (˚)	90.5	90.7	0.2%	90.9	0.4%	93.0	2.8%	92.7	2.4%
N$_1$ – Cu – N$_2$ (˚)	79.8	78.7	1.4%	80.2	0.5%	78.3	1.9%	79.3	0.6%
O$_1$ – Cu – N$_2$ (˚)	172.9	170	1.7%	160.5	7.2%	172	0.5%	165.9	4.0%
O$_2$ – Cu – N$_1$ (˚)	173.0	166.6	3.7%	165.4	4.4%	167.5	3.2%	159.2	8.0%

Table S2 Investigated multiplicities and geometries of possible intermediates as calculated using ADF. ΔE is the energy relative to the lowest energy multiplicity for that intermediate (indicated by asterisks). ΔS^2 is here defined as the difference between the exact and expected value for S^2, which can be considered an indication of the level of spin contamination for that multiplicity.[2]

Intermediate	**Charge**	**Multiplicity**	**ΔE (eV)**	**ΔS^2**	**ΔE (eV)**	**ΔS^2**	**Copper conformation**
			B3LYP		OPBE		
[*Cu*(OH)$_2$]	0	*doublet*	0.00	0.00	0.00	0.00	planar
	0	quartet	2.85	0.02	2.48	0.01	distorted tetrahedral
[*Cu*(OH)(O)]	0	*singlet*	0.00	0.00	0.00	0.00	planar
	0	triplet	0.03	0.01	0.45	0.01	distorted tetrahedral
[*Cu*(OH)(O)]$^-$	-1	*doublet*	0.00	0.00	0.00	0.01	distorted planar
	-1	quartet	1.03	0.02	0.90	0.01	planar
[*Cu*(O)(O)]	0	*doublet*	0.00	0.01	0.00	0.00	planar
	0	quartet	1.16	0.01	1.70	0.02	distorted tetrahedral
[Cu(O)(O)]$^+$	+1	singlet	0.33	0.00	0.19	0.00	planar
	+1	*triplet*	0.00	0.01	0.00	0.01	planar
[*Cu*(OH)(OOH)]	0	doublet	0.00	0.00	0.00	0.00	distorted planar
	0	*quartet*	3.30	0.02	1.90	0.01	distorted tetrahedral
[*Cu*(OH)(OO)]	0	singlet	0.76	0.00	0.21	0.89	distorted planar
	0	*triplet*	0.00	0.01	0.00	0.01	distorted planar
[*Cu*(OH)(OH$_2$)]	0	singlet	*unstable*				*H$_2$O dissociates*
	0	*triplet*	0.00	0.01	0.00	0.00	*d(Cu – OH$_2$) = 2.25, planar*

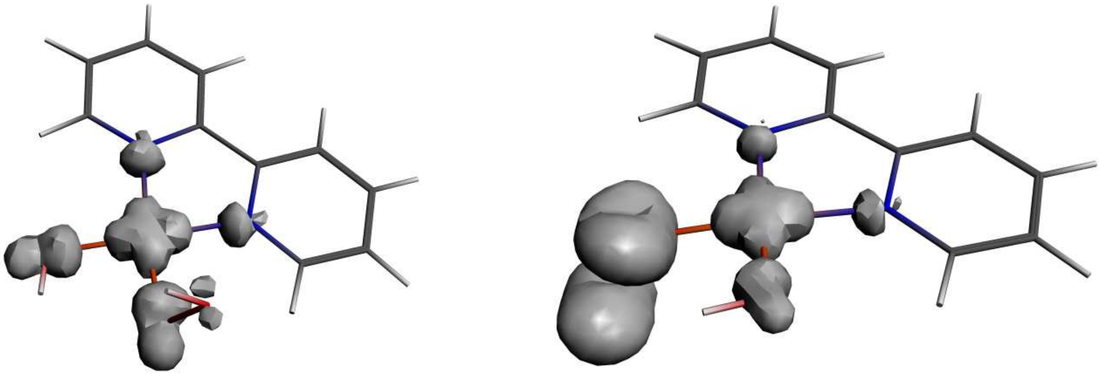
Table S3 Geometrical details of possible intermediates as calculated using ADF (OPBE/TZP). The atomic charge of Cu calculated using the Hirshfeld and Voronoi deformation density methods is also reported (B3LYP/TZP, using the geometry optimized with OPBE/TZP).

Intermediate	Charge	Multiplicity	Hirschfeld	Voronoi	Cu - O1	Cu - O2	Cu - N1	Cu - N2	O - Cu - O	O1 - O2	O1 - O3
[*Cu*(OH)$_2$]	0	doublet	0.467	0.484	1.916	1.915	2.097	2.072	93.0	2.778	
	0	quartet	0.528	0.500	1.974	1.977	0.961	1.961	67.8	2.202	
[*Cu*(OH)(O)]	0	singlet	0.467	0.510	1.765	1.813	1.952	1.979	85.8	2.435	
	0	triplet	0.433	0.467	1.805	1.943	2.051	2.091	94.6	2.756	
[*Cu*(OH)(O)]$^-$	-1	doublet	0.295	0.380	1.844	1.964	2.101	2.114	88.9	2.669	
	-1	quartet	0.392	0.439	1.819	1.98	2.026	2.045	91.7	2.729	
[*Cu*(O)(O)]	0	doublet	0.384	0.402	1.926	1.923	2.011	2.014	44.4	1.453	
	0	quartet	0.412	0.457	1.854	1.855	2.089	2.097	95.3	2.741	
[Cu(O)(O)]$^+$	+1	singlet	0.572	0.552	1.837	1.838	1.927	1.928	44.0	1.375	
	+1	triplet	0.534	0.498	1.986	1.984	1.981	1.982	38.6	1.313	
[*Cu*(OH)(OOH)]	0	doublet	0.462	0.469	1.966	1.919	2.064	2.064	89.7	2.74	1.444
	0	quartet	0.458	0.455	2.029	1.895	1.980	1.991	93.0	2.849	1.343
[*Cu*(OH)(OO)]	0	singlet	0.434	0.429	1.999	1.900	2.047	2.051	89.8	2.751	1.307
	0	triplet	0.431	0.430	2.105	1.909	2.049	2.076	90.7	2.858	1.484
[*Cu*(OH)(OH$_2$)]	0	triplet	0.520	0.507	2.253	1.895	1.971	1.965	86.8	2.861	



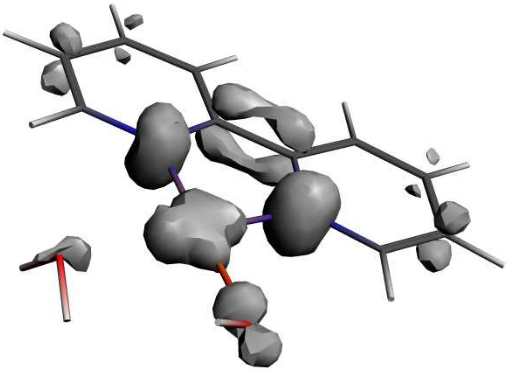
[*Cu*(OH)$_2$] (doublet)

[*Cu*(O)(O)] (doublet)



[*Cu*(OH)(OOH)] (doublet)

[*Cu*(OH)(OO)] (triplet)



[*Cu*(OH)(OH$_2$)] (triplet)

Figure S1 The localisation of the spin density of the relevant intermediates as calculated in ADF (B3LYP/TZP).

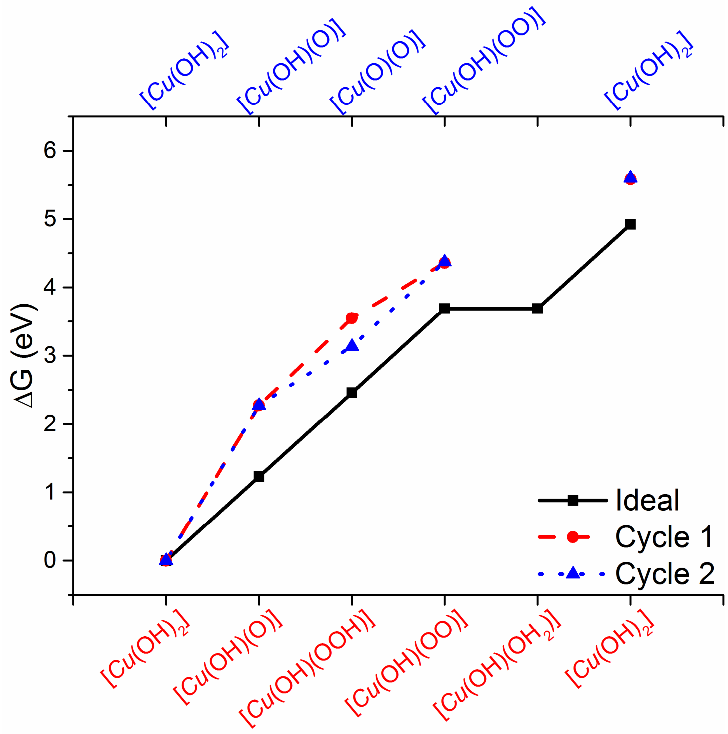


Figure S2 Cumulative free energy of the two proposed mechanisms for [Cu(bpy)(OH)$_2$] ([*Cu*(OH)$_2$]) as compared to the ideal case for water splitting as calculated by ADF (B3LYP/TZP/COSMO).

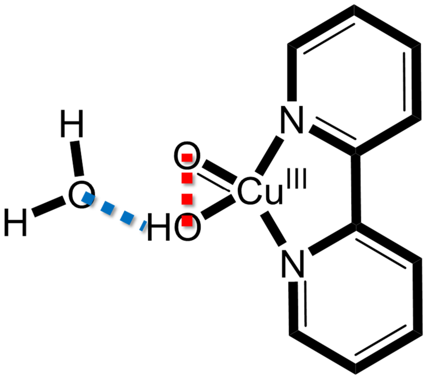


Figure S3 The two constraints examined in the investigation of the [*Cu*(OH)(O)] → [*Cu*(O)(O)] step: (1) the distance between the oxygen of a solvent water molecule and the H atom of the hydroxyl ligand (blue line) and (2) the distance between the oxygen atoms of the two oxo ligands (red line).

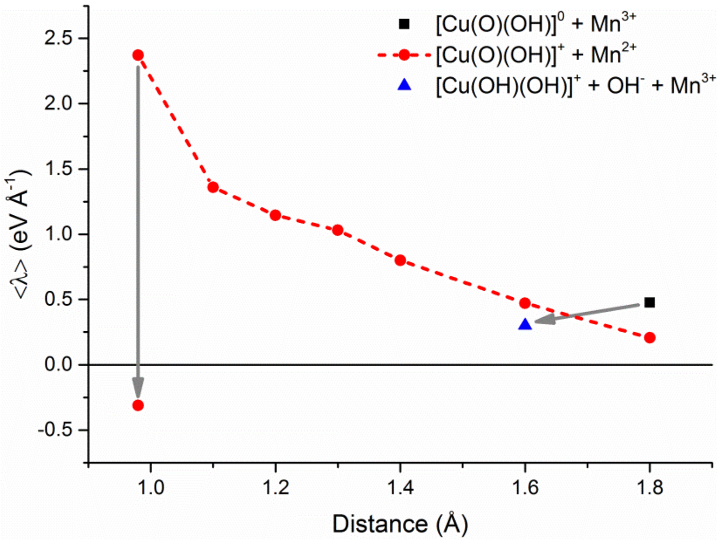


Figure S4 **The time-averaged constraint force (<λ>) as a function of the O – H distance between the oxygen of a solvent water molecule and the H atom of the hydroxyl ligand (blue line in Figure S3). The black square indicates <λ> for the initial [*Cu*(OH)(O)] intermediate as calculated in the closed system approach. The initial [*Cu*(OH)(O)] intermediate accepts a proton to form the [*Cu*(OH)(OH)] intermediate (blue triangle) in order to relieve λ. The red circles show the process for the ionised intermediate ([*Cu*(OH)(O)]$^+$ + Mn^{2+}). The proton does not dissociate from the OH ligand , even when an electron has been removed: see the high value of <λ> corresponding to a distance of 1.0 Å where we are forcing the H_3O^+ formation. After a further 1.21 ps of dynamics a proton shuttle occurs in which a proton is accepted by the other oxo group, thus leading back to the initial complex with a very small <λ> (as shown by a grey arrow). The [*Cu*(OH)(O)] → [*Cu*(O)(O)] step would therefore be very unlikely via this pathway.**

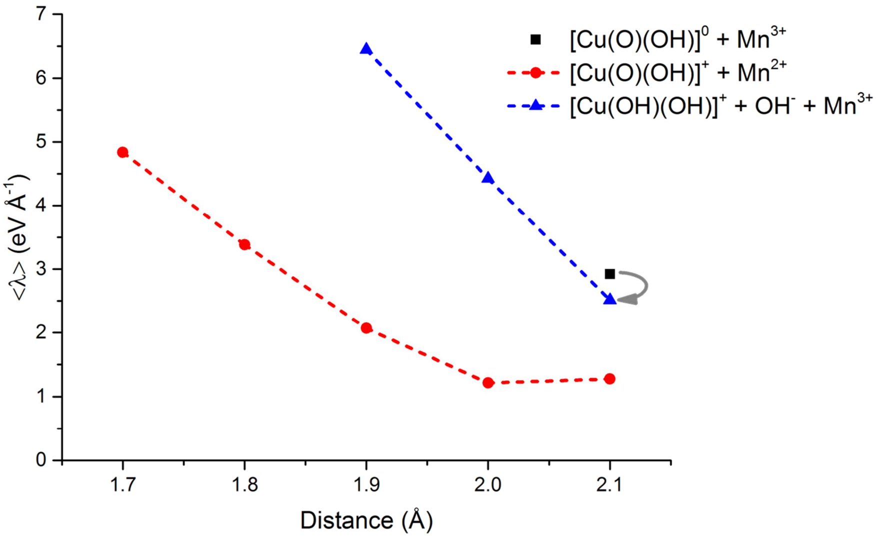


Figure S5 **The time-averaged constraint force (<λ>) as a function of the O – O distance between the oxygen atoms ligated to the copper centre (red line in Figure S3). The black square indicates <λ> for the initial [*Cu*(OH)(O)] intermediate as calculated in the closed system approach. This intermediate again accepts a proton after 90 fs to form the [*Cu*(OH)(OH)] intermediate (blue triangles, indicated with grey arrow). It should be noted that the values for <λ> are significantly higher than those obtained in Figure S4. <λ> for the ionised intermediate ([*Cu*(OH)(O)]$^+$ + Mn^{2+}) is again indicated by red circles. By thermodynamic integration along this reaction coordinate, we obtain a prohibitively high free energy change. The [*Cu*(OH)(O)] → [*Cu*(O)(O)] step would therefore be highly unlikely via this pathway. *NB.* For the [*Cu*(OH)(O)]^0 + Mn^{3+} system, the average O – O bond length *before* enforcing any constraints is 2.36 Å, while for [*Cu*(OH)(O)]$^+$ + Mn^{2+} this is 2.39 Å.**

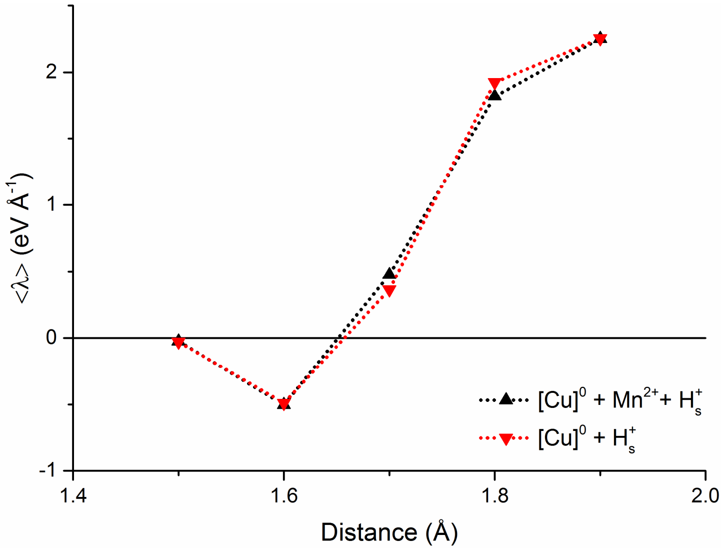


Figure S6 The time-averaged constraint force (<λ>) as a function of the O – O distance in the OOH ligating group of the [*Cu*(OH)(OOH)] intermediate, as d(O – O) is lengthened. The black triangles indicate the process as calculated in the closed system approach (($[Cu]^0 + Mn^{2+} + H^+_s$), charge = 3^+, septet multiplicity), while the red triangles the process calculated without the metal ion (($[Cu]^0 + H^+_s$), charge = 1^+, triplet multiplicity).

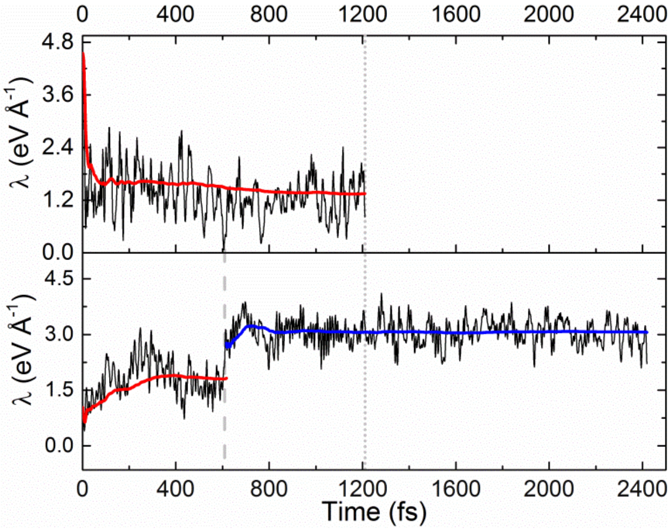


Figure S7 The constraint force (λ) as a function of time for two different O – O distance constraints (d(O – O) between the oxo ligand and the oxygen of the incoming water molecule), observed in the investigation of the [*Cu*(OH)(O)] intermediate (System 3, with septet ($[Cu]^+ + Mn^{2+}$) multiplicity).

(top) d(O – O) = 2.1 Å as the incoming water molecule is brought increasingly closer. This is a typical constraint run for 1.2 ps (until grey dotted line). The running time-average of λ (<λ>, red line) is seen to converge.

(bottom) d(O – O) = 1.8 Å after lengthening the formed bond for the system with septet multiplicity ($[Cu]^0 + Mn^{2+} + H^+_s$). This run shows how sensitive λ is to events that occur within the system. After 600 fs (grey dashed line), a proton is accepted by the O initially part of the incoming water molecule. <λ> after this event (blue line) is seen to converge rapidly, and though the system was allowed to evolve for 1.2 ps beyond the normal run time, no change in <λ> was observed.

References

1 Bon Kweon Koo, *Bull Korean Chem Soc*, 2001, **22**, 113.

2 C. J. Cramer, *Essentials of Computational Chemistry: Theories and Models*, Wiley, Chichester, 2005.