RSC Electronic Supplementary Information (EIS):

Searching for the thermodynamic limit – a DFT study of the step-wise water oxidation of the bipyramidal Cu_7 cluster

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This document contains supplementary information to the main article. Some extra figures of structures mentioned but not shown in the main article are included – these are the TS for H-diffusion, the adsorption structures for the various addition isomers of two and three water molecules and a electrostatic potential map over the $Cu_7(H_2O)_5$ cluster. Details of the NBO analysis - charges and electron populations - are provided, as is an analysis of the preferred adsorption sites of the $H^{\cdot}$, H^+, H_2,$OH^{\cdot}$ and H_2O species. Complimentary graphs and diagrams for the adsorption energies included as well as the relative enthalpies for the different stages of the gas phase oxidation reactions are also included. Additionally, we provide a Gibbs free energy diagram for the sequential oxidation of the Cu_7 cluster for atmospheric pressure of H_2 gas. All reported energies are determined at the PBE0/LACV3P**++//PBE0/LACVP*+ level of theory if not otherwise specified.

Contents

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1 Additional figures

1.1 Alternative adsorption structures

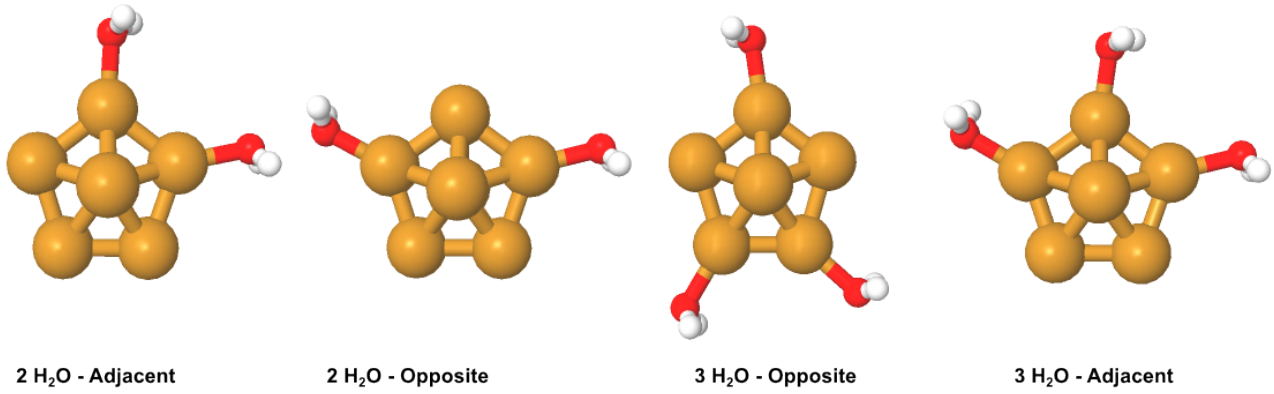

Figure 1: Different structures for adsorption of two and three water molecules to Cu_7.

Table 1: SCF energies (*i.e.* no thermal or zero-point corrections are added to the electronic energies) for the alternative adsorption sites in a.u.

	2 H_2O_{ad}		3 H_2O_{ad}	
	Gas	water	Gas	Water
Adjacent	-1525.611557	-1525.640422	-1601.997421	-1602.038048
Opposite	-1525.611650	-1525.631002	-1601.996582	-1602.041123

1.2 H-diffusion

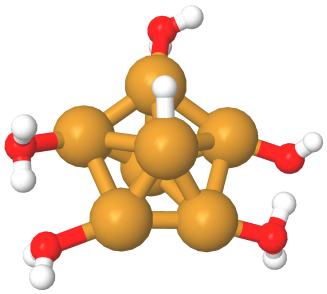

Figure 2: TS for H-diffusion on a Cu_7 complex (I1 - *i.e.* after first dissociation) at high water coverage. The (standard free energy) diffusion barrier in gas phase is *ca.* 0.45 eV.

2 Site analysis

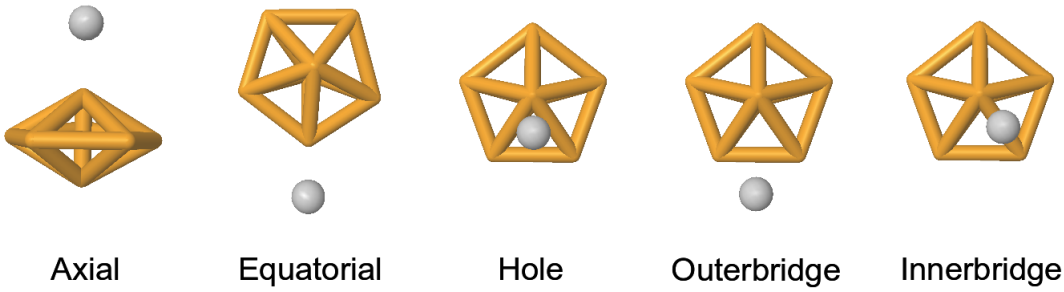

Figure 3: Different adsorption sites on Cu_7

Table 2: Relative adsorption enthalpies, ΔH, (compared to the most favored site for each series) for different adsorption sites for the H_2O, $OH^\bullet$, $H^\bullet$, H^+ and H_2 species onto Cu_7 in gas phase.

	H_2O	$OH^\bullet$	$H^\bullet$	H^+	H_2
Equatorial	0.00	0.56	*n.a.*	*n.a.*	0.00[b)]
Axial	0.14[a)]	0.28	0.10	*n.a.*	0.12[b)]
Outerbridge	*n.a.*	0.03	1.08	0.03	*n.a.*
Innerbridge	*n.a.*	0.05	0.00	0.02	*n.a.*
Hole	*n.a.*	0.00	*n.a.*	0.00	*n.a.*

[a)] In water phase the corresponding *free* energy difference is *ca.* 0.17 eV.[b)] Parallel adsorption favoured (perpendicular =0.11eV). [c)] Perpendicular adsorption only.

3 Complimentary graphs and diagrams

3.1 Adsorption

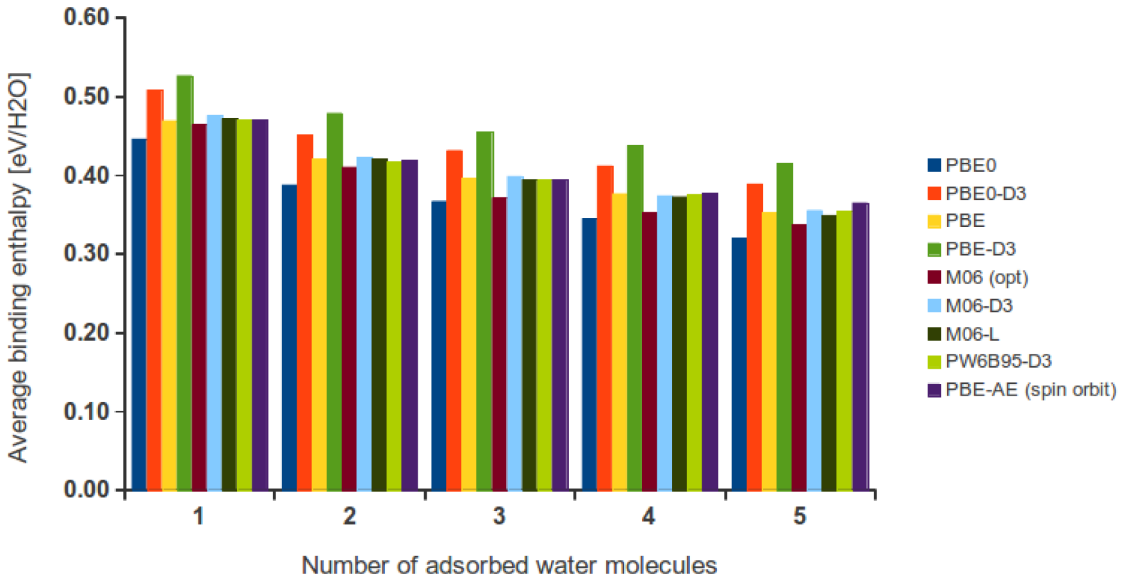

Figure 4: Adsorption enthalpies at 298.15 K

3.2 Step-wise oxidation

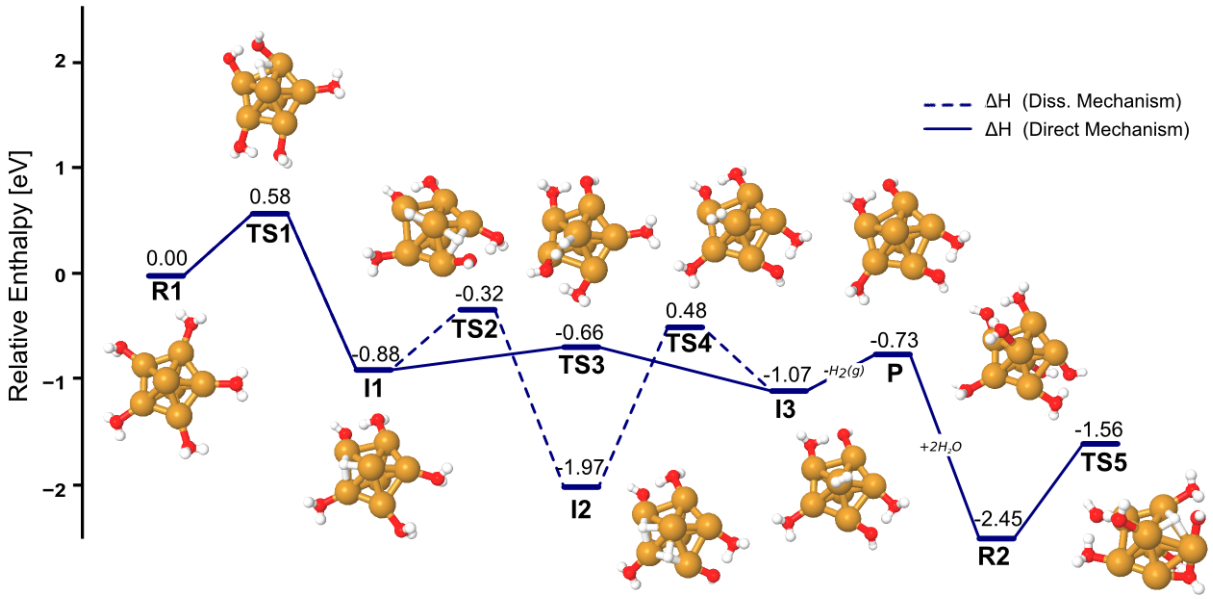

Figure 5: Gas phase enthalpy diagram over the first H_2 generation reaction on Cu_7.

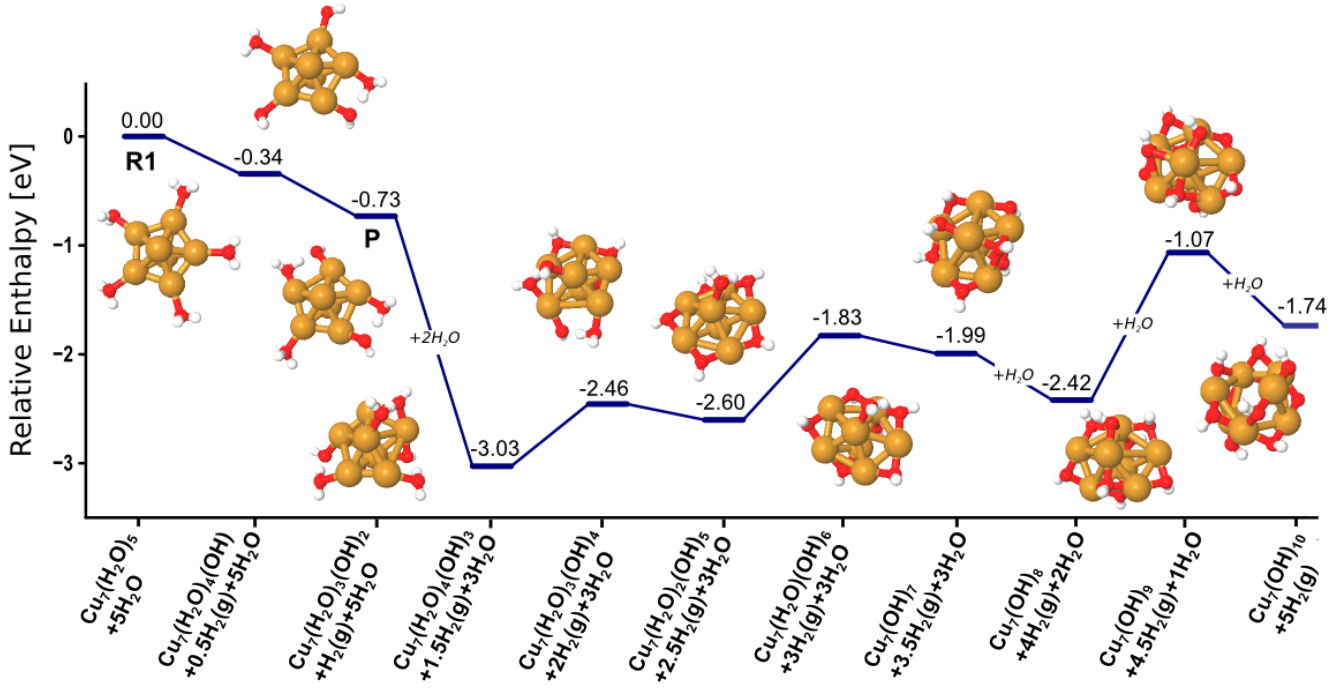

Figure 6: Gas phase enthalpy diagram over the oxidation process from 0OH to 10OH on Cu_7.

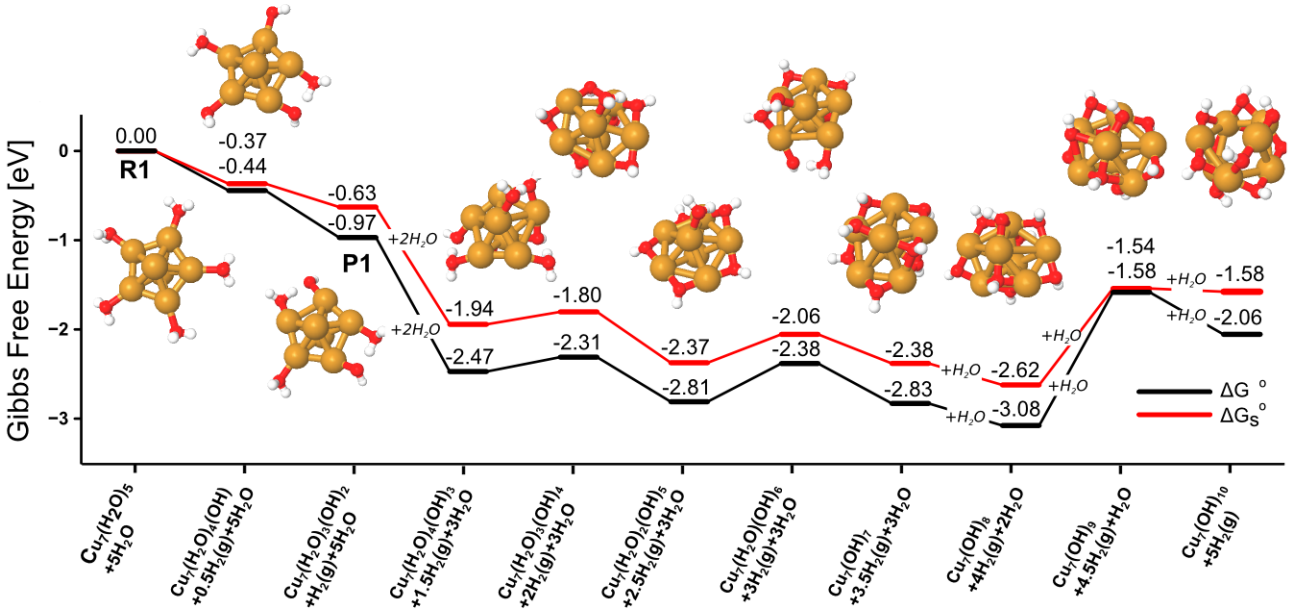

Figure 7: Gibbs free energy diagram over the oxidation process from 0OH to 10OH on Cu_7 using the atmospheric pressure of 5.31×10^{-7} bar for H_2.

4 NBO data

4.1 Mechanism at high coverage

R - $Cu_7(H_2O)_5$

Atom	No	Charge	Total Population
Cu	1	0.13673	28.86327
Cu	2	0.13918	28.86082
Cu	3	0.14516	28.85484
Cu	4	0.13715	28.86285
Cu	5	0.14001	28.85999
Cu	6	-0.49607	29.49607
Cu	7	-0.49433	29.49433
O	8	-0.91867	8.91867
H	9	0.48663	0.51337
H	10	0.49038	0.50962
O	11	-0.91844	8.91844
O	12	-0.91780	8.91780
O	13	-0.91833	8.91833
O	14	-0.91821	8.91821
H	15	0.48695	0.51305
H	16	0.49007	0.50993
H	17	0.48896	0.51104
H	18	0.48734	0.51266
H	19	0.49005	0.50995
H	20	0.48644	0.51356
H	21	0.48746	0.51254
H	22	0.48934	0.51066

I1 - $Cu_7(H_2O)_4(OH)(H)$

Atom	No	Charge	Total Population
Cu	1	0.18817	28.81183
Cu	2	0.11182	28.88818
Cu	3	0.31373	28.68627
Cu	4	0.52477	28.47523
Cu	5	0.13381	28.86619
Cu	6	-0.06071	29.06071
Cu	7	-0.44445	29.44445
O	8	-0.93094	8.93094
H	9	0.50536	0.49464
H	10	0.48566	0.51434
O	11	-0.93679	8.93679
O	12	-1.13764	9.13764
O	13	-0.90263	8.90263
O	14	-1.00535	9.00535
H	15	0.50103	0.49897
H	16	0.50424	0.49576
H	17	0.46406	0.53594
H	18	0.49336	0.50664
H	19	0.49219	0.50781
H	20	0.47551	0.52449
H	21	0.51139	0.48861
H	22	-0.28657	1.28657

I2 - $Cu_7(H_2O)_3(OH)_2(H)_2$

Atom	No	Charge	Total Population
Cu	1	0.47494	28.52506
Cu	2	0.34165	28.65835
Cu	3	0.34549	28.65451
Cu	4	0.48201	28.51799
Cu	5	0.19883	28.80117
Cu	6	0.13823	28.86177
Cu	7	-0.22688	29.22688
O	8	-1.12792	9.12792
H	9	0.47086	0.52914
H	10	-0.26295	1.26295
O	11	-1.00361	9.00361
O	12	-1.13047	9.13047
O	13	-1.00414	9.00414
H	14	0.48230	0.51770
H	15	0.51355	0.48645
H	16	0.46884	0.53116
H	17	0.48127	0.51873
H	18	0.51245	0.48755
H	19	-0.26304	1.26304
O	20	-0.89175	8.89175
H	21	0.50084	0.49916
H	22	0.49949	0.50051

I3 - $Cu_7(H_2O)_3(OH)_2(H_2)_{ad}$

Atom	No	Charge	Total Population
Cu	1	0.42579	28.57421
Cu	2	0.19289	28.80711
Cu	3	0.40665	28.59335
Cu	4	0.35400	28.64600
Cu	5	0.35244	28.64756
Cu	6	-0.02630	29.02630
Cu	7	-0.48837	29.48837
O	8	-1.14025	9.14025
H	9	0.51127	0.48873
H	10	0.46506	0.53494
O	11	-1.01212	9.01212
O	12	-1.01221	9.01221
O	13	-1.14549	9.14549
H	14	0.47852	0.52148
H	15	0.47887	0.52113
H	16	0.51168	0.48832
O	17	-0.92122	8.92122
H	18	0.49541	0.50459
H	19	0.49362	0.50638
H	20	0.46415	0.53585
H	21	0.05545	0.94455
H	22	0.06016	0.93984

TS1 - $Cu_7(H_2O)_4(OH\cdots H)$

Atom	No	Charge	Total Population
Cu	1	0.33147	28.66853
Cu	2	0.29364	28.70636
Cu	3	0.23140	28.76860
Cu	4	0.12068	28.87932
Cu	5	0.13445	28.86555
Cu	6	-0.27687	29.27687
Cu	7	-0.50196	29.50196
O	8	-1.13730	9.13730
H	9	0.12431	0.87569
H	10	0.47795	0.52205
O	11	-0.96552	8.96552
O	12	-0.94291	8.94291
O	13	-0.93814	8.93814
H	14	0.52507	0.47493
H	15	0.47934	0.52066
H	16	0.49725	0.50275
H	17	0.48397	0.51603
H	18	0.51098	0.48902
O	19	-0.91282	8.91282
H	20	0.48941	0.51059
H	21	0.48957	0.51043
H	22	0.48601	0.51399

TS2 - $Cu_7(H_2O)_3(OH)(HO\cdots H\cdots H)$

Atom	No	Charge	Total Population
Cu	1	0.33040	28.66960
Cu	2	0.27653	28.72347
Cu	3	0.36355	28.63645
Cu	4	0.49310	28.50690
Cu	5	0.25099	28.74901
Cu	6	0.03464	28.96536
Cu	7	-0.42953	29.42953
O	8	-1.09062	9.09062
H	9	0.13253	0.86747
H	10	0.48401	0.51599
O	11	-0.95452	8.95452
O	12	-1.13765	9.13765
O	13	-1.00199	9.00199
H	14	0.52636	0.47364
H	15	0.48551	0.51449
H	16	0.46775	0.53225
H	17	0.47940	0.52060
H	18	0.51342	0.48658
H	19	-0.29450	1.29450
O	20	-0.92460	8.92460
H	21	0.50404	0.49596
H	22	0.49118	0.50882

TS3 - $Cu_7(H_2O)_3(OH)(H)(OH\cdots H)$

Atom	No	Charge	Total Population
Cu	1	0.36014	28.63986
Cu	2	0.19048	28.80952
Cu	3	0.39585	28.60415
Cu	4	0.32534	28.67466
Cu	5	0.34508	28.65492
Cu	6	-0.20191	29.20191
Cu	7	-0.26885	29.26885
O	8	-0.97058	8.97058
H	9	0.52609	0.47391
H	10	0.48380	0.51620
O	11	-1.00603	9.00603
O	12	-1.12366	9.12366
O	13	-1.14774	9.14774
H	14	0.47931	0.52069
H	15	0.30563	0.69437
H	16	0.48855	0.51145
H	17	0.46398	0.53602
H	18	0.51444	0.48556
H	19	-0.22771	1.22771
O	20	-0.92179	8.92179
H	21	0.49829	0.50171
H	22	0.49129	0.50871

TS4 - $Cu_7(H_2O)_3(OH)_2(H\cdots H)$

Atom	No	Charge	Total Population
Cu	1	0.41724	28.58276
Cu	2	0.37471	28.62529
Cu	3	0.38937	28.61063
Cu	4	0.46466	28.53534
Cu	5	0.20368	28.79632
Cu	6	0.11248	28.88752
Cu	7	-0.51087	29.51087
O	8	-1.13735	9.13735
H	9	0.46661	0.53339
H	10	-0.07283	1.07283
O	11	-1.01486	9.01486
O	12	-1.13167	9.13167
O	13	-1.00976	9.00976
H	14	0.48125	0.51875
H	15	0.51011	0.48989
H	16	0.46866	0.53134
H	17	0.48026	0.51974
H	18	0.51237	0.48763
H	19	-0.08539	1.08539
O	20	-0.91243	8.91243
H	21	0.49760	0.50240
H	22	0.49615	0.50385

P - $Cu_7(H_2O)_3(OH)_2$

Atom	No	Charge	Total Population
Cu	1	0.37782	28.62218
Cu	2	0.15602	28.84398
Cu	3	0.35825	28.64175
Cu	4	0.27795	28.72205
Cu	5	0.30421	28.69579
Cu	6	-0.09003	29.09003
Cu	7	-0.09119	29.09119
O	8	-1.13487	9.13487
H	9	0.51179	0.48821
H	10	0.46737	0.53263
O	11	-1.00014	9.00014
O	12	-1.00745	9.00745
O	13	-1.14214	9.14214
H	14	0.48113	0.51887
H	15	0.48032	0.51968
H	16	0.51462	0.48538
O	17	-0.91924	8.91924
H	18	0.49649	0.50351
H	19	0.49529	0.50471
H	20	0.46380	0.53620

4.2 Thermodynamic limit

0OH - $Cu_7(H_2O)_5$

Atom	No	Charge	Total Population
Cu	1	0.13673	28.86327
Cu	2	0.13918	28.86082
Cu	3	0.14516	28.85484
Cu	4	0.13715	28.86285
Cu	5	0.14001	28.85999
Cu	6	-0.49607	29.49607
Cu	7	-0.49433	29.49433
O	8	-0.91867	8.91867
H	9	0.48663	0.51337
H	10	0.49038	0.50962
O	11	-0.91844	8.91844
O	12	-0.91780	8.91780
O	13	-0.91833	8.91833
O	14	-0.91821	8.91821
H	15	0.48695	0.51305
H	16	0.49007	0.50993
H	17	0.48896	0.51104
H	18	0.48734	0.51266
H	19	0.49005	0.50995
H	20	0.48644	0.51356
H	21	0.48746	0.51254
H	22	0.48934	0.51066

1OH - $Cu_7(H_2O)_4(OH)_1$

Atom	No	Charge	Total Population
Cu	1	0.16118	28.83882
Cu	2	0.14312	28.85688
Cu	3	0.32425	28.67575
Cu	4	0.30627	28.69373
Cu	5	0.12696	28.87304
Cu	6	-0.32541	29.32541
Cu	7	-0.19566	29.19566
O	8	-0.92458	8.92458
H	9	0.48697	0.51303
H	10	0.48930	0.51070
O	11	-0.91970	8.91970
O	12	-1.01430	9.01430
O	13	-0.91772	8.91772
O	14	-1.14291	9.14291
H	15	0.49083	0.50917
H	16	0.48773	0.51227
H	17	0.47348	0.52652
H	18	0.48964	0.51036
H	19	0.48822	0.51178
H	20	0.46172	0.53828
H	21	0.51060	0.48940

2OH - $Cu_7(H_2O)_3(OH)_2$

Atom	No	Charge	Total Population
Cu	1	0.37782	28.62218
Cu	2	0.15602	28.84398
Cu	3	0.35825	28.64175
Cu	4	0.27795	28.72205
Cu	5	0.30421	28.69579
Cu	6	-0.09003	29.09003
Cu	7	-0.09119	29.09119
O	8	-1.13487	9.13487
H	9	0.51179	0.48821
H	10	0.46737	0.53263
O	11	-1.00014	9.00014
O	12	-1.00745	9.00745
O	13	-1.14214	9.14214
H	14	0.48113	0.51887
H	15	0.48032	0.51968
H	16	0.51462	0.48538
O	17	-0.91924	8.91924
H	18	0.49649	0.50351
H	19	0.49529	0.50471
H	20	0.46380	0.53620

2OH* - $Cu_7(H_2O)_5(OH)_2$

Atom	No	Charge	Total Population
Cu	1	0.37373	28.62627
Cu	2	0.18655	28.81345
Cu	3	0.35430	28.64570
Cu	4	0.31694	28.68306
Cu	5	0.32511	28.67489
Cu	6	-0.18164	29.18164
Cu	7	-0.16944	29.16944
O	8	-0.98575	8.98575
H	9	0.48042	0.51958
H	10	0.52085	0.47915
O	11	-0.97925	8.97925
O	12	-1.18982	9.18982
O	13	-1.19605	9.19605
H	14	0.52229	0.47771
H	15	0.47670	0.52330
H	16	0.47956	0.52044
O	17	-0.93916	8.93916
O	18	-0.94227	8.94227
O	19	-0.91990	8.91990
H	20	0.48878	0.51122
H	21	0.52599	0.47401
H	22	0.48170	0.51830
H	23	0.52510	0.47490
H	24	0.47831	0.52169
H	25	0.49305	0.50695
H	26	0.47390	0.52610

3OH - $Cu_7(H_2O)_4(OH)_3$

Atom	No	Charge	Total Population
Cu	1	0.73915	28.26085
Cu	2	0.24375	28.75625
Cu	3	0.27014	28.72986
Cu	4	0.31192	28.68808
Cu	5	0.34535	28.65465
Cu	6	0.05122	28.94878
Cu	7	-0.03982	29.03982
O	8	-1.16015	9.16015
H	9	0.52550	0.47450
H	10	0.48263	0.51737
O	11	-0.98781	8.98781
O	12	-0.97148	8.97148
O	13	-1.18765	9.18765
H	14	0.48068	0.51932
H	15	0.48142	0.51858
H	16	0.47643	0.52357
H	17	0.52009	0.47991
O	18	-0.93615	8.93615
H	19	0.48317	0.51683
H	20	0.52749	0.47251
O	21	-1.20039	9.20039
H	22	0.48528	0.51472
O	23	-0.94148	8.94148
H	24	0.52361	0.47639
H	25	0.47712	0.52288

4OH - $Cu_7(H_2O)_3(OH)_4$

Atom	No	Charge	Total Population
Cu	1	0.58224	28.41776
Cu	2	0.67397	28.32603
Cu	3	0.32391	28.67609
Cu	4	0.26627	28.73373
Cu	5	0.70682	28.29318
Cu	6	-0.02575	29.02575
Cu	7	0.06421	28.93579
O	8	-1.14237	9.14237
H	9	0.51328	0.48672
H	10	0.47449	0.52551
O	11	-1.19879	9.19879
O	12	-1.12076	9.12076
O	13	-1.00996	9.00996
H	14	0.52765	0.47235
H	15	0.46953	0.53047
H	16	0.48002	0.51998
H	17	0.48885	0.51115
O	18	-0.95115	8.95115
H	19	0.48750	0.51250
H	20	0.53048	0.46952
O	21	-1.18073	9.18073
H	22	0.48816	0.51184
O	23	-0.93395	8.93395
H	24	0.48608	0.51392

5OH - $Cu_7(H_2O)_2(OH)_5$

Atom	No	Charge	Total Population
Cu	1	0.67015	28.32985
Cu	2	0.68654	28.31346
Cu	3	0.64772	28.35228
Cu	4	0.58522	28.41478
Cu	5	0.61873	28.38127
Cu	6	0.04890	28.95110
Cu	7	0.09428	28.90572
O	8	-1.16642	9.16642
H	9	0.47541	0.52459
O	10	-1.16439	9.16439
O	11	-1.19218	9.19218
O	12	-1.16811	9.16811
O	13	-1.19185	9.19185
H	14	0.47506	0.52494
H	15	0.48442	0.51558
H	16	0.47290	0.52710
H	17	0.48497	0.51503
O	18	-0.94517	8.94517
H	19	0.52824	0.47176
H	20	0.48429	0.51571
O	21	-0.94182	8.94182
H	22	0.48415	0.51585
H	23	0.52897	0.47103

6OH - $Cu_7(H_2O)(OH)_6$

Atom	No	Charge	Total Population
Cu	1	0.68451	28.31549
Cu	2	0.72754	28.27246
Cu	3	0.61521	28.38479
Cu	4	0.58433	28.41567
Cu	5	0.70270	28.29730
Cu	6	0.64278	28.35722
Cu	7	-0.01050	29.01050
O	8	-1.12234	9.12234
H	9	0.48145	0.51855
O	10	-1.11801	9.11801
O	11	-1.13088	9.13088
O	12	-1.18195	9.18195
O	13	-1.19092	9.19092
H	14	0.48053	0.51947
H	15	0.47601	0.52399
H	16	0.49108	0.50892
H	17	0.50239	0.49761
O	18	-0.94191	8.94191
H	19	0.52796	0.47204
O	20	-1.16814	9.16814
H	21	0.46534	0.53466
H	22	0.48282	0.51718

7OH - $Cu_7(OH)_7$

Atom	No	Charge	Total Population
Cu	1	0.73066	28.26934
Cu	2	0.72584	28.27416
Cu	3	0.71791	28.28209
Cu	4	0.70642	28.29358
Cu	5	0.68748	28.31252
Cu	6	0.66466	28.33534
Cu	7	0.30928	28.69072
O	8	-1.07768	9.07768
H	9	0.49851	0.50149
O	10	-1.10831	9.10831
O	11	-1.12581	9.12581
O	12	-1.12547	9.12547
O	13	-1.15586	9.15586
H	14	0.48381	0.51619
H	15	0.47633	0.52367
H	16	0.48317	0.51683
H	17	0.49328	0.50672
O	18	-1.15818	9.15818
H	19	0.48124	0.51876
O	20	-1.17542	9.17542
H	21	0.46815	0.53185

8OH - $Cu_7(OH)_8$

Atom	No	Charge	Total Population
Cu	1	1.10266	27.89734
Cu	2	0.67877	28.32123
Cu	3	0.68533	28.31467
Cu	4	0.67647	28.32353
Cu	5	0.68952	28.31048
Cu	6	0.64539	28.35461
Cu	7	0.62548	28.37452
O	8	-1.09363	9.09363
H	9	0.48802	0.51198
O	10	-1.12579	9.12579
O	11	-1.13376	9.13376
O	12	-1.09950	9.09950
O	13	-1.16869	9.16869
H	14	0.47765	0.52235
H	15	0.47594	0.52406
H	16	0.47332	0.52668
H	17	0.49346	0.50654
O	18	-1.16497	9.16497
H	19	0.48773	0.51227
O	20	-1.10003	9.10003
H	21	0.47546	0.52454
O	22	-1.07036	9.07036
H	23	0.48154	0.51846

9OH - $Cu_7(OH)_9$

Atom	No	Charge	Total Population
Cu	1	0.70349	28.29651
Cu	2	1.14121	27.85879
Cu	3	1.10302	27.89698
Cu	4	0.73692	28.26308
Cu	5	0.68219	28.31781
Cu	6	0.60580	28.39420
Cu	7	0.63165	28.36835
O	8	-1.04836	9.04836
O	9	-1.16857	9.16857
O	10	-1.07435	9.07435
O	11	-1.06537	9.06537
O	12	-1.07591	9.07591
O	13	-1.13638	9.13638
O	14	-1.14951	9.14951
O	15	-1.12181	9.12181
O	16	-1.07962	9.07962
H	17	0.49729	0.50271
H	18	0.47612	0.52388
H	19	0.47551	0.52449
H	20	0.47890	0.52110
H	21	0.47495	0.52505
H	22	0.48753	0.51247
H	23	0.46686	0.53314
H	24	0.47587	0.52413
H	25	0.48256	0.51744

10OH - $Cu_7(OH)_{10}$

Atom	No	Charge	Total Population
Cu	1	0.68517	28.31483
Cu	2	1.11348	27.88652
Cu	3	1.11350	27.88650
Cu	4	0.68540	28.31460
Cu	5	1.07240	27.92760
Cu	6	0.69519	28.30481
Cu	7	0.69514	28.30486
O	8	-1.08537	9.08537
O	9	-1.10126	9.10126
O	10	-1.10363	9.10363
O	11	-1.08524	9.08524
O	12	-1.07470	9.07470
O	13	-1.08529	9.08529
O	14	-1.10342	9.10342
O	15	-1.07470	9.07470
O	16	-1.10120	9.10120
O	17	-1.08543	9.08543
H	18	0.47363	0.52637
H	19	0.48600	0.51400
H	20	0.48942	0.51058
H	21	0.48691	0.51309
H	22	0.48403	0.51597
H	23	0.48940	0.51060
H	24	0.48603	0.51397
H	25	0.47363	0.52637
H	26	0.48408	0.51592
H	27	0.48684	0.51316