Simple soluble Bi(III) salts as efficient catalysts for the oxidation of alkanes with H_2O_2

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Supplementary Information

Calculations of the ΔG_s value of hydrolysis of 3^8

The CPCM method and the model with one explicit solvent molecule in the second coordination sphere allow the accurate estimates of the activation and reaction energies of the reactions in which the number of species with the same charge is preserved during the reaction (*e.g.* ligand substitution).[3,19,20] However, this method and model fail to predict correctly the energetic parameters of reactions accompanied by the change of the overall charges of species involved in the process (*e.g.* hydrolysis).[19] Therefore, in order to estimate the ΔG_s value of hydrolysis of $\mathbf{3^8}$**-H_2O** to $\mathbf{4^6}$**-H_2O**, the experimental pK_a value of Bi(III) (1.1 [Ref. 38]) and the corresponding thermodynamic cycle (Figure S10) were used.

The ΔG_s value of hydrolysis of $\mathbf{1^8}$**-H_2O** in water solution [ΔG_s(H$\mathbf{1^8}$**-H_2O**)] was estimated from the experimental pK_a value using the equation $pK_a = \Delta G_s/(2.303RT) - 1.74$. The ΔG_s values of the processes

$$[Bi(H_2O)_8](H_2O)^{3+} + H_2O_2 \rightarrow [Bi(H_2O)_7(H_2O_2)](H_2O)^{3+} + H_2O \qquad \Delta G_s(1)$$

and

$$[Bi(H_2O)_5(OH)](H_2O)^{2+} + H_2O_2 \rightarrow [Bi(H_2O)_5(OOH)](H_2O)^{2+} + H_2O \qquad \Delta G_s(2)$$

in water solution involved into the thermodynamic cycle were calculated at the CPCM level as described in Computational Details section (note that the number of species with the same charge is preserved in these processes). The ΔG_s of hydrolysis of $\mathbf{3^8\text{-}H_2O}$ was calculated as $\Delta G_s(\mathrm{H}\mathbf{3^8\text{-}H_2O}) = \Delta G_s(\mathrm{H}\mathbf{1^8\text{-}H_2O}) + \Delta G_s(2) - \Delta G_s(1)$.

Calculations of the ΔG_s value of the reaction $[Bi(H_2O)_7(H_2O_2)](H_2O)^{3+} \rightarrow [Bi(H_2O)_3(OH)_3](H_2O)^{2+} + 2H_2O + H_3O^+$

The ΔG_s value of this reaction in water solution [$\Delta G_s(\mathrm{R}\mathbf{3}\rightarrow\mathbf{9})$] was estimated from the thermodynamic cycle (Figure S11) using experimental pK_a value of **1** (1.1) and the equation $pK_a = \Delta G_s/(2.303RT) - 1.74$. The ΔG_s values of the processes

$$[Bi(H_2O)_8](H_2O)^{3+} + H_2O_2 \rightarrow [Bi(H_2O)_7(H_2O_2)](H_2O)^{3+} + H_2O \qquad \Delta G_s(1)$$

and

$$[Bi(H_2O)_5(OH)](H_2O)^{2+} + H_2O_2 \rightarrow [Bi(H_2O)_3(OH)_3](H_2O)^{2+} + 2H_2O \qquad \Delta G_s(3)$$

in water solution involved into the thermodynamic cycle were calculated at the CPCM level as described in Computational Details section. The ΔG_s of hydrolysis of $\mathbf{3^8\text{-}H_2O}$ was calculated as $\Delta G_s(\mathrm{R}\mathbf{3}\rightarrow\mathbf{9}) = \Delta G_s(\mathrm{H}\mathbf{1^8\text{-}H_2O}) + \Delta G_s(3) - \Delta G_s(1)$.

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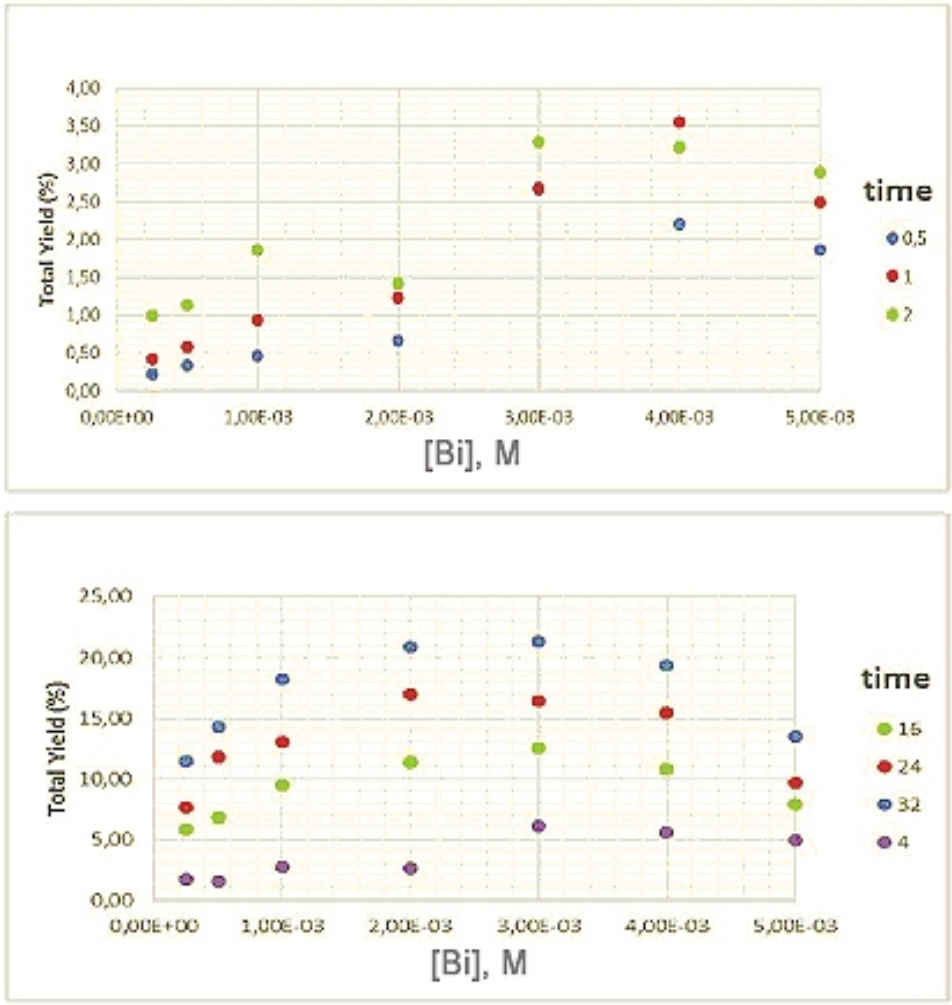
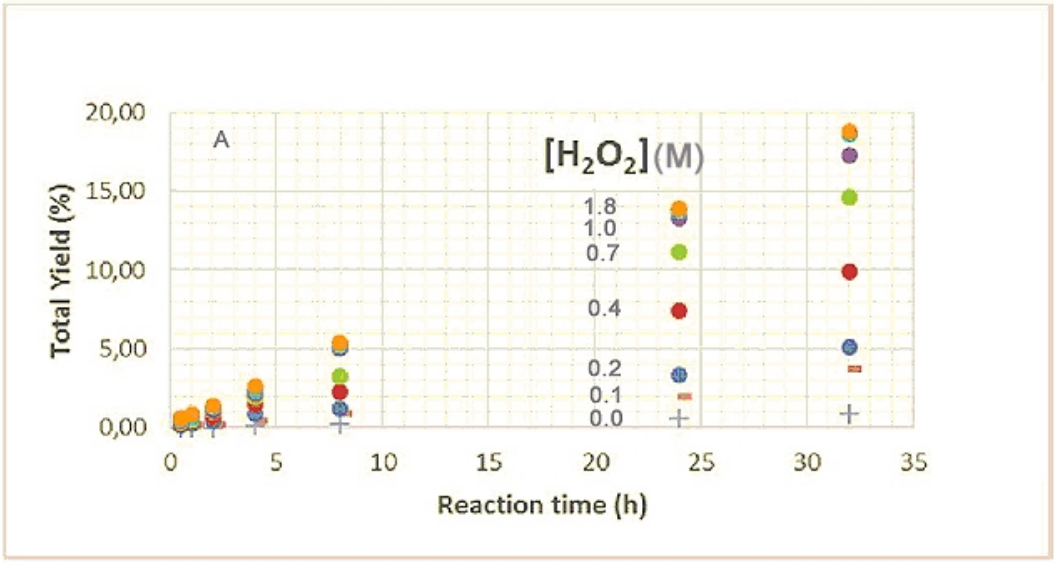
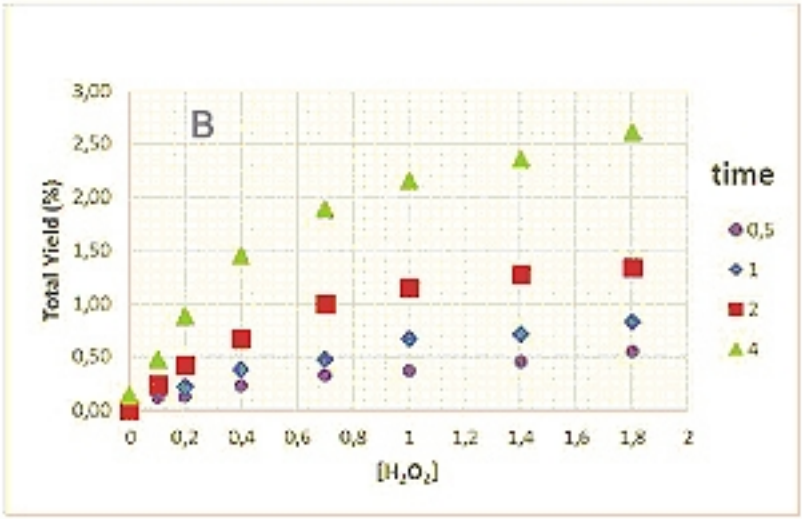


Fig. S1 Dependence of the oxygenate yield on concentration of the bismuth salt and after different time of the reaction time (0.5, 1, 2, 4, 16, 24 and 32 h). Conditions. $[cyclooctane]_0$ = 0.25 M; $[H_2O_2]_0$ = 1.19 M; $[H_2O]_{total}$ = 2.38 M; $[HNO_3]_0$ = 0.072 M; 60 °C.





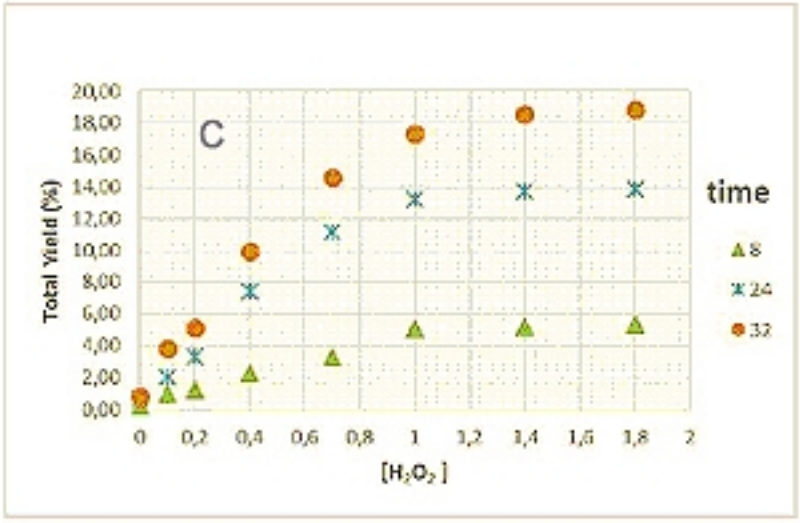


Fig. S2 Dependence of the oxygenate yield on initial concentration of H_2O_2. Graph A: kinetic curves of oxygenate accumulation at different $[H_2O_2]_0$. Graphs B and C: dependence of oxygenate yield on initial concentration of H_2O_2 at different reaction times (0.5, 1, 2, 4, 8, 24 and 32 h).

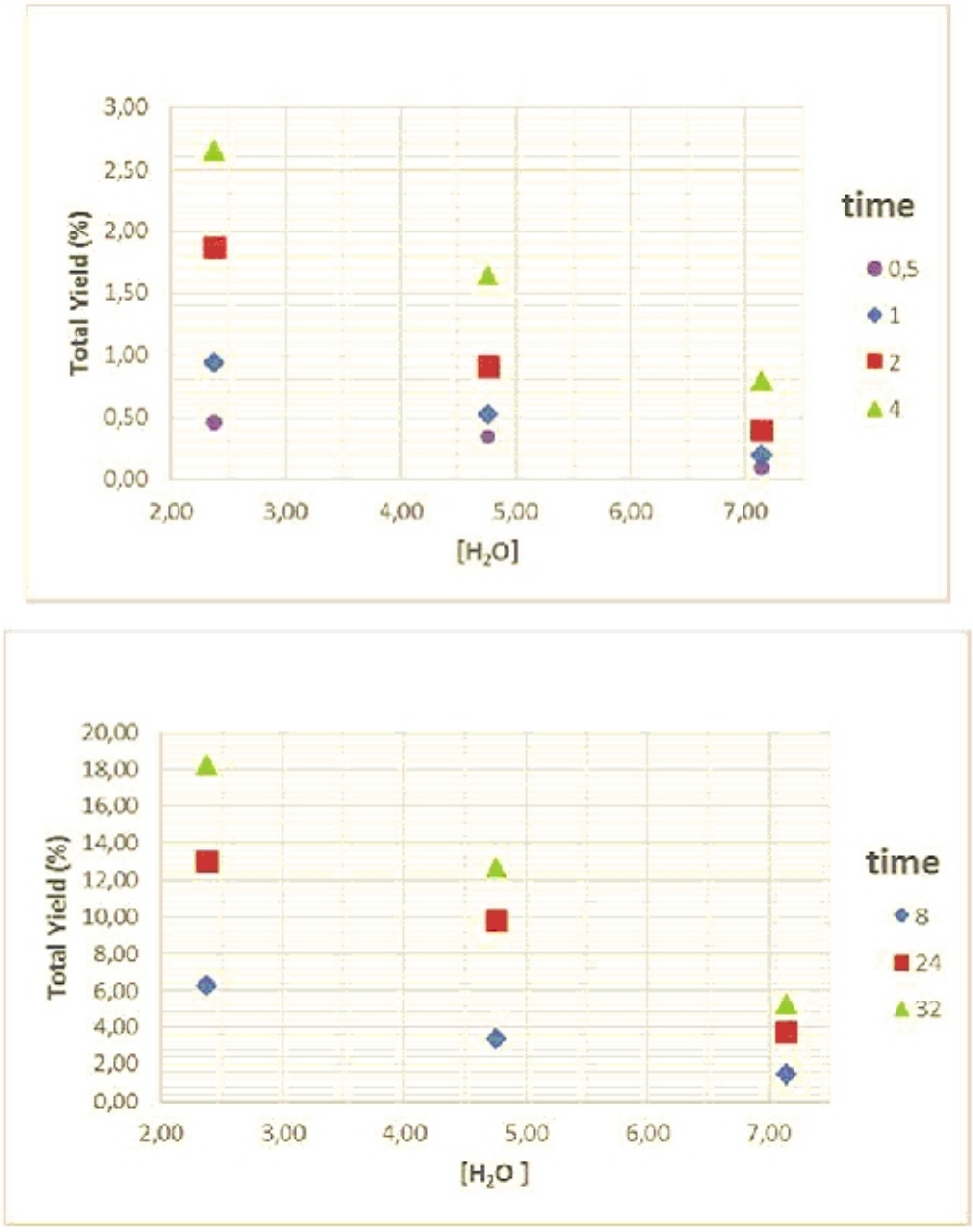


Fig. S3 Dependence of the oxygenate yield on concentration of H_2O at different reaction times (0.5, 1, 2, 4, 8, 24 and 32 h).

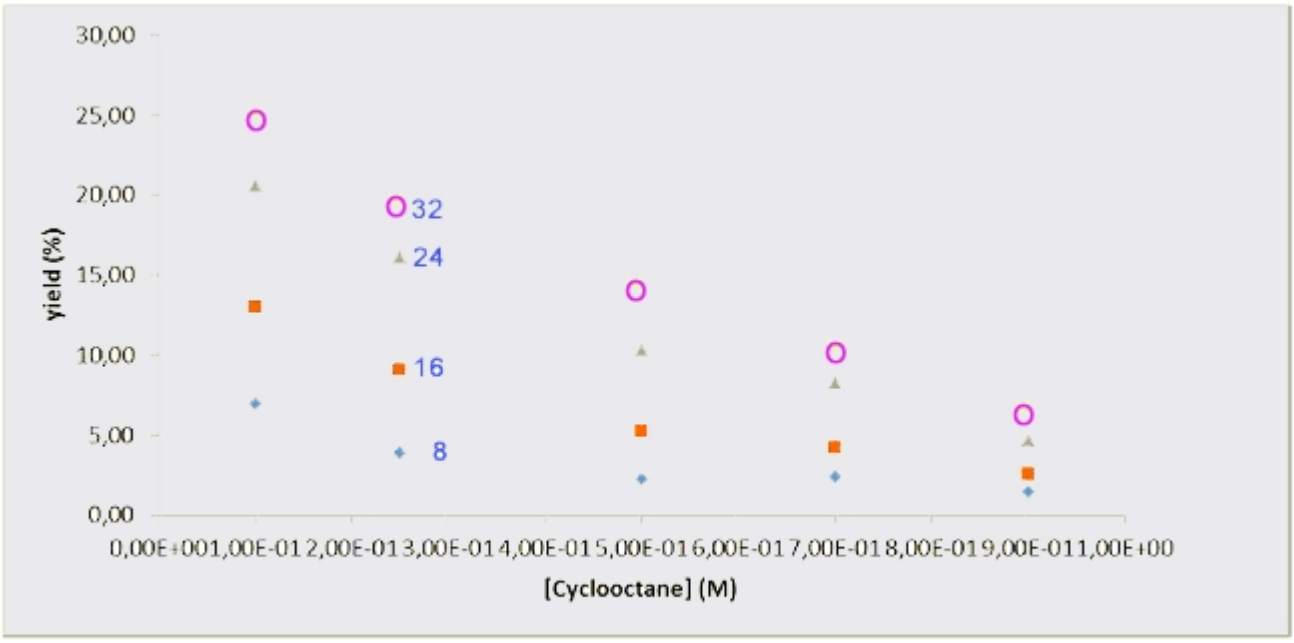
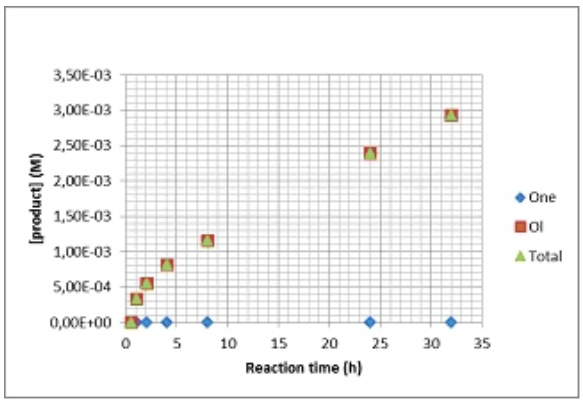
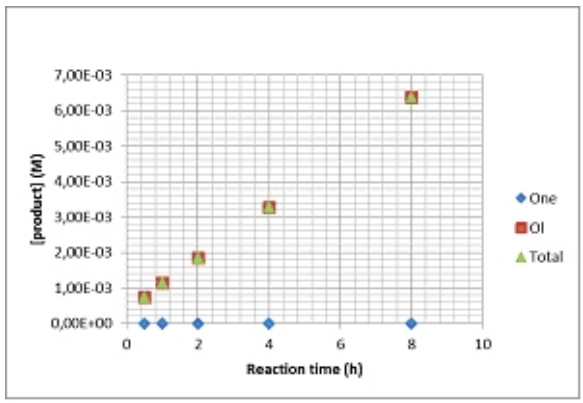


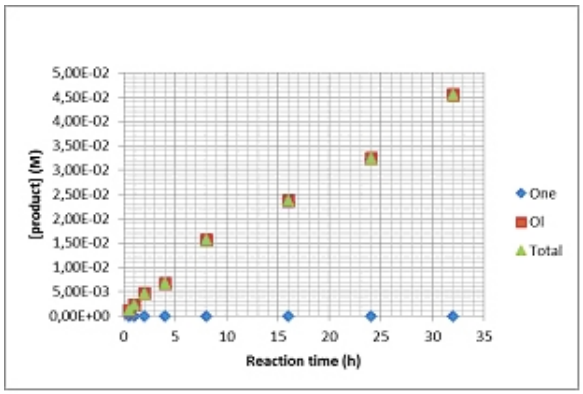
Fig. S4. Dependence of the oxygenate yield (based on starting cyclooctane) on initial concentration of cyclooctane after 8, 16, 24 and 32 h of reaction time.



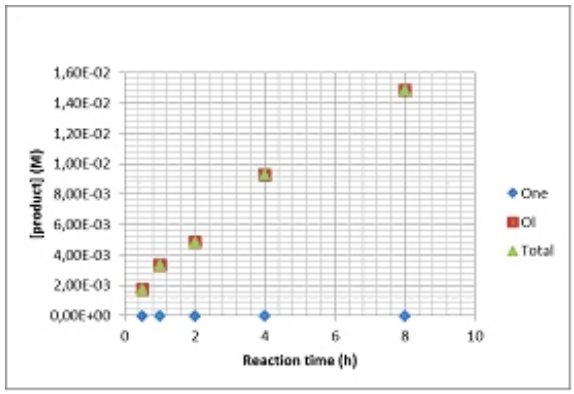
40 °C



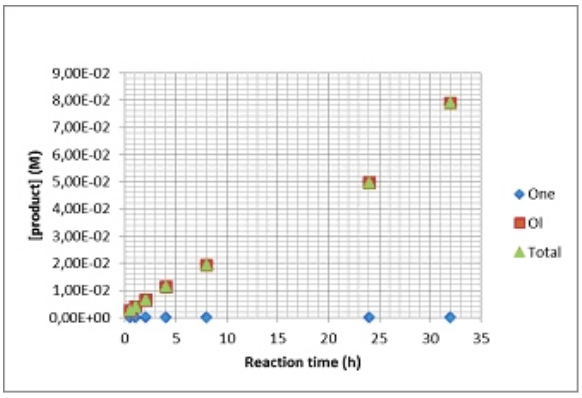
55 °C



60 °C



65 °C



75 °C

Fig. S5 Cyclooctane oxidation with H_2O_2 catalyzed by complex $Bi(NO_3)_3$ at different temperatures Conditions: $[Bi(NO_3)_3]_0$ = 1.0 × 10^{-3} M; $[cyclooctane]_0$ = 0.25 M; $[H_2O_2]_0$ = 1.2 M; $[HNO_3]_0$ = 0.072 M) in acetonitrile (contains H_2O, 2.4 M). The initial rate W_0 was determined from the slope of tangent (as, for example, presented by dotted line 1b in Figure 3) to the kinetic curve of accumulation of the sum of cyclooctyl hydroperoxide, cyclooctanol and cyclooctanone (in order to obtain the value of concentration of all products we measured concentration of the sum cyclooctanol + cyclooctanone after reduction of the sample with PPh_3). Concentrations of the products (cyclooctanol and cyclooctanone) were measured after reduction with PPh_3. The Arrhenius plot is presented in Figure 9. This dependence corresponds to the effective activation energy E_a = 20 ± 2.5 kcal mol^{-1}.

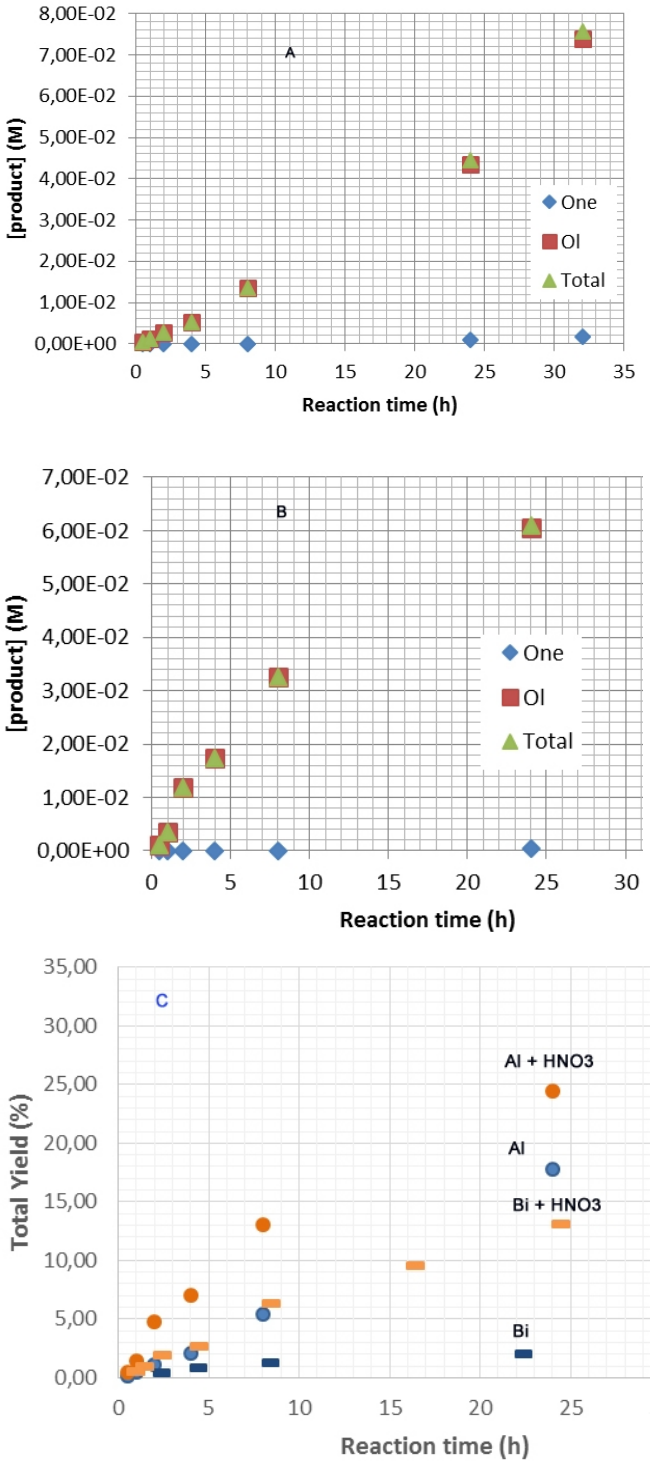
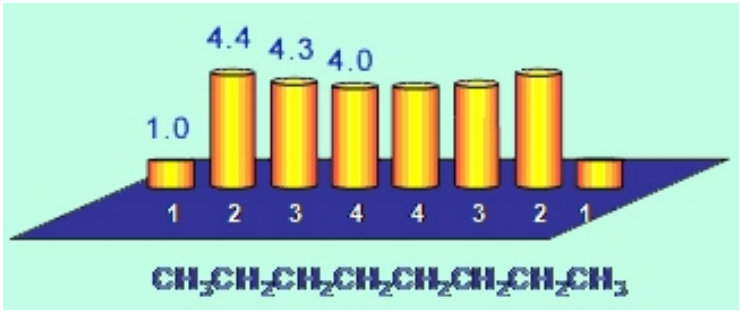


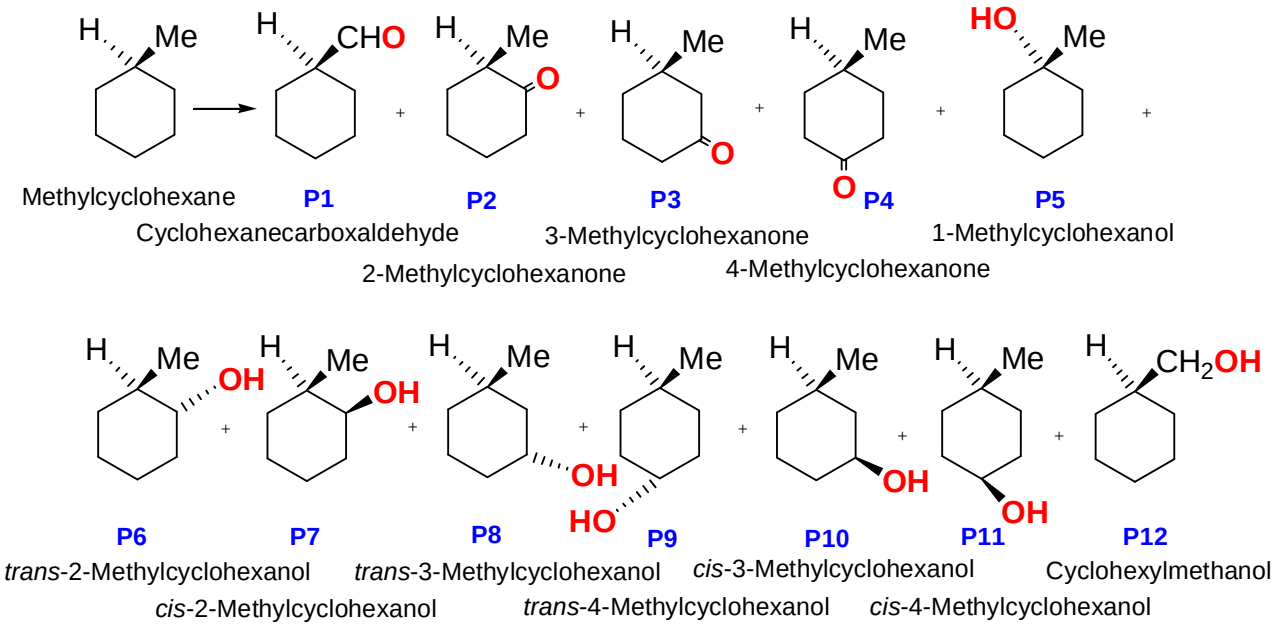
Fig. S6 Kinetic curves of cyclooctane oxidation with H_2O_2 catalyzed by complexes $Bi(NO_3)_3$ and $Al(NO_3)_3$ in the absence and in the presence (0.072 M) HNO_3 at 60 °C. Graph A: $[Al(NO_3)_3]_0$ = 1.0 × 10^{-3} M; $[cyclooctane]_0$ = 0.25 M; $[H_2O_2]_0$ = 1.2 M; $[HNO_3]_0$ = 0 M) in acetonitrile (contains H_2O, 2.4 M).Graph B: $[Al(NO_3)_3]_0$ = 1.0 × 10^{-3} M; $[cyclooctane]_0$ = 0.25 M; $[H_2O_2]_0$ = 1.2 M; $[HNO_3]_0$ = 0.072 M) in acetonitrile (contains H_2O, 2.4 M). Graph C: Kinetic curves of cyclooctane oxidation with H_2O_2 catalyzed by complexes $Bi(NO_3)_3$ and $Al(NO_3)_3$ both in the absence and in the presence (0.072 M) HNO_3 at 60 °C.

a

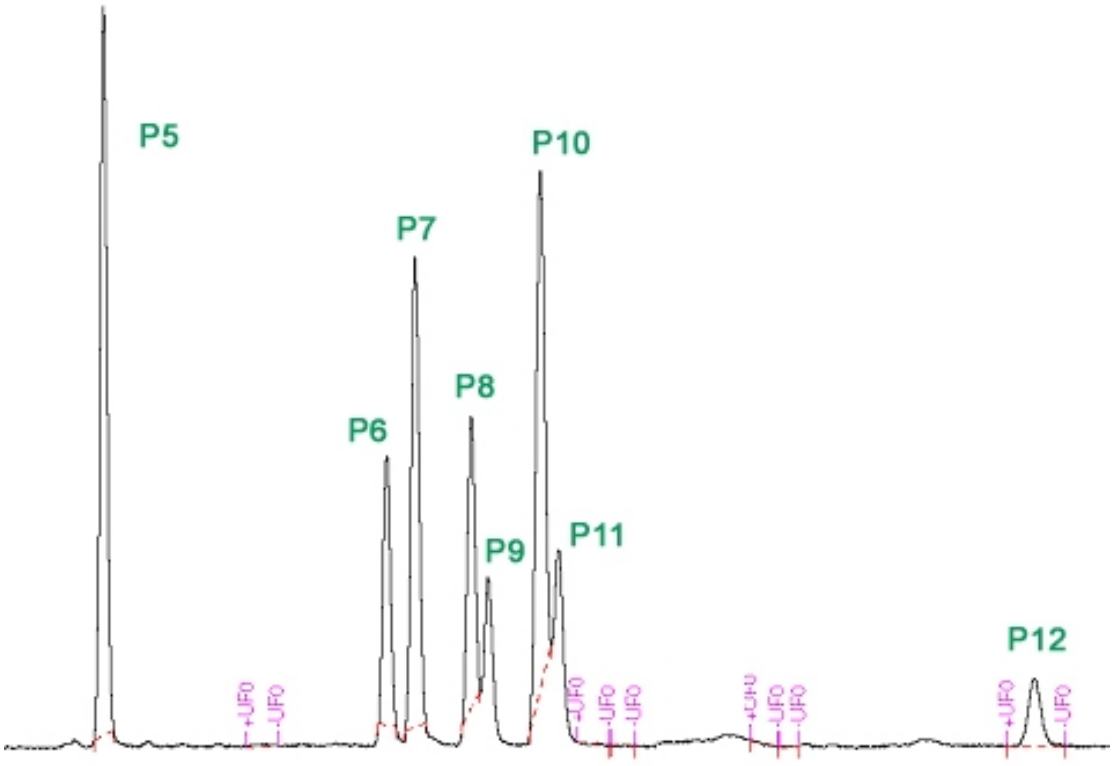


b

Fig. S7 A chromatogram of the *n*-octane oxidation with H_2O_2 catalyzed by the bismuth salt in the presence of nitric acid (octanols after reduction with PPh_3) (*a*) and the profile of reactivities (*b*).



a



b

Fig. S8 Products obtained in the methylcyclohexane oxidation (*a*). A chromatogram of products **P5**–**P12** obtained in the oxidation of methycyclohexane with H_2O_2 catalyzed by the bismuth salt in the presence of nitric acid (*b*).

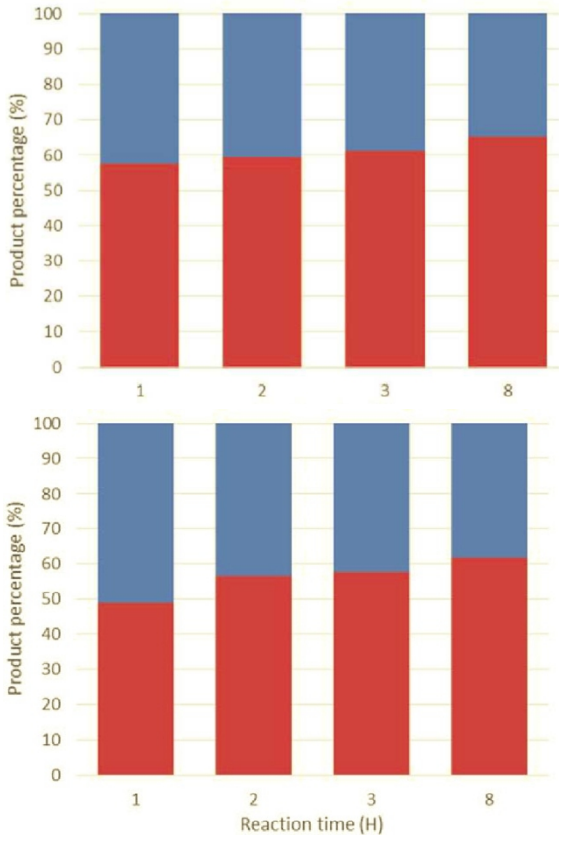


Fig. S9 The ratio of products *trans*-1,2-dimethylhydroxycyclohexane (blue bar) and *cis*-1,2-dimethyl-hydroxycyclohexane (red bar) obtained in the oxidation of *cis*- (*a*) and *trans*- (*b*) isomers of 1,2-dimethylcyclohexane (see Table 1).

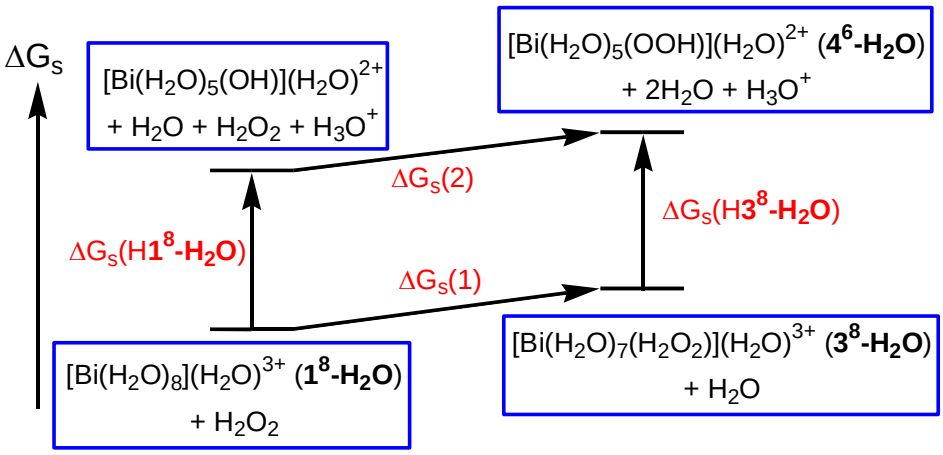


Fig. S10 Thermodynamic cycle for the calculations of ΔG_s value of hydrolysis of $\mathbf{3^8\text{-}H_2O}$ [ΔG_s(H$\mathbf{3^8\text{-}H_2O}$)] using the experimental value ΔG_s(H$\mathbf{1^8\text{-}H_2O}$) and calculated values ΔG_s(1) and ΔG_s(2).

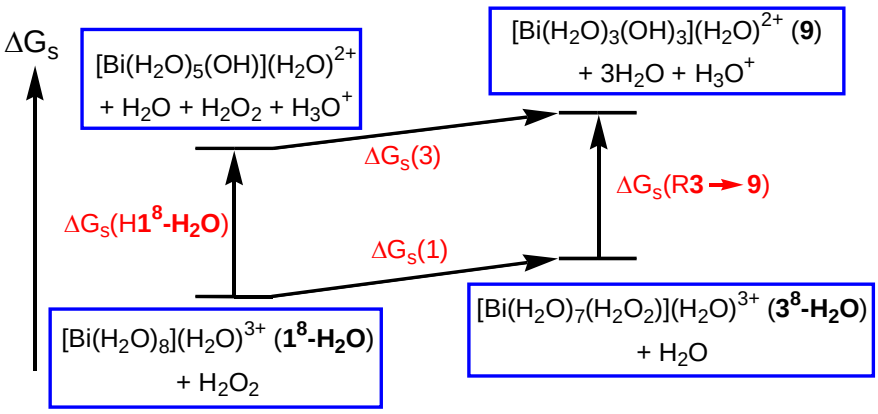


Fig. S11 Thermodynamic cycle for the calculations of the ΔG_s value of reaction $\mathbf{3^8\text{-}H_2O} \rightarrow \mathbf{9}$ [ΔG_s(R**3**→**9**)] using the experimental value ΔG_s(H$\mathbf{1^8\text{-}H_2O}$) and calculated values ΔG_s(1) and ΔG_s(3).

Table S1 Calculated total energies and enthalpies in gas phase (E_g, H_g) and CH_3CN solution (H_s) (in Hartree) and solvent effect (δE_s) calculated as difference of the total energies in CH_3CN solution and gas phase ($E_s - E_g$, in kcal/mol). Values calculated for the H_2O solution are given in parentheses

	E_g	δE_s	H_g	H_s
H_2O_2	–151.603684	–4.43 (–11.87)	–151.573050	–151.580113 (-151.591966)
H_2O	–76.459175	–2.69 (–6.73)	–76.434118	–76.438398 (-76.444843)
$HO^{\bullet}$	–75.763068	–1.80	–75.751316	–75.754178
$HOO^{\bullet}$	–150.959702	–3.57	–150.941815	–150.947500
$[Bi(H_2O)_9]^{3+}$ (**1^9**)	–692.646808	–326.55	–692.395973	–692.916364
$[Bi(H_2O)_9](H_2O)^{3+}$ (**1^9-H_2O**)	–769.153817	–313.36	–768.874684	–769.374055
$[Bi(H_2O)_8](H_2O)^{3+}$ (**1^8-H_2O**)	–692.661563	–319.42 (–367.87)	–692.410535	–692.919563 (–692.996773)
$[Bi(H_2O)_8](H_2O)_2^{3+}$ (**1^8-$2H_2O$**)	–769.169837	–305.50	–768.890547	–769.377392
$[Bi(H_2O)_8](H_2O_2)^{3+}$ (**1^8-H_2O_2**)	–767.806700	–316.79	–767.550712	–768.055549
TS1	–767.801662	–314.27	–767.546700	–768.047521
$[Bi(H_2O)_7](H_2O)(H_2O_2)^{3+}$ (**2^7-H_2O-H_2O_2**)	–767.817476	–308.80	–767.561509	–768.053613
TS2	–767.800676	–315.71	–767.545669	–768.048785
$[Bi(H_2O)_7(H_2O_2)](H_2O)^{3+}$ (**3^8-H_2O**)	–767.805689	–317.31 (–367.17)	–767.549354	–768.055020 (–768.134477)
$[Bi(H_2O)_5(OOH)](H_2O)^{2+}$ (**4^6-H_2O**)	–614.716006	–146.33 (–177.14)	–614.527649	–614.760841 (–614.809940)
TS3	–689.852452	–143.59	–689.660288	–689.889113
$[Bi(H_2O)_4(OOH)](H_2O)(H_2O_2)^{2+}$ (**5^5-H_2O-H_2O_2**)	–689.857296	–141.89	–689.664045	–689.890161
TS4	–689.852335	–141.42	–689.660258	–689.885625
$[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2+}$ (**6^6-H_2O**)	–689.854706	–145.26	–689.661184	–689.892671
$[Bi(H_2O)_4(OH)(OOH)](H_2O)^{2+}$ (**7^6-H_2Ob**)	–614.058916	–149.98	–613.883289	–614.122297
$[Bi(H_2O)_4(OH)(OOH)](H_2O)^{2+}$ (**7^6-H_2Oa**)	–614.061215	–145.83	–613.885564	–614.117959
$[Bi(H_2O)_7(OH)](H_2O)^{3+}$	–691.949367	–321.97	–691.712428	–692.225520
$[Bi(H_2O)_5(=O)](H_2O)^{2+}$	–538.863118	–150.51	–538.691971	–538.931824
$[Bi(H_2O)_4(H_2O_2)(=O)](H_2O)^{2+}$	–614.006887	–148.74	–613.830333	–614.067365
$[Bi(H_2O)_4(H_2O_2)](H_2O)^{2+}$	–538.811394	–148.07	–538.638206	–538.874171
$[Bi(H_2O)_5](H_2O)^{2+}$	–463.667933	–148.72	–463.500252	–463.737252
$[Bi(H_2O)_5(OH)](H_2O)^{2+}$	–539.567458	–148.43 (–179.12)	–539.384245	–539.620783 (–539.669691)
$[Bi(H_2O)_3(OH)_3](H_2O)^{2+}$ (**9**)	–538.164581	–162.56 (–198.90)	–538.006702	–538.265758 (–538.323669)

Table S2 Calculated entropies (in cal/mol•K) and Gibbs free energies (in Hartree) in gas phase (S_g, G_g) and CH_3CN solution (S_s, G_s). Values calculated for the H_2O solution are given in parentheses

	S_g	S_s	G_g	G_s
H_2O_2	55.77	39.41 (30.37)	–151.599505	–151.598839 (–151.606392)
H_2O	45.09	31.19 (24.61)	–76.455541	–76.453216 (–76.456527)
$HO^{\bullet}$	42.58	29.25	–75.771550	–75.768078
$HOO^{\bullet}$	54.68	38.57	–150.967795	–150.965826
$[Bi(H_2O)_9]^{3+}$ (**1^9**)	172.67	129.42	–692.478014	–692.977856
$[Bi(H_2O)_9](H_2O)^{3+}$ (**1^9-H_2O**)	182.56	137.04	–768.961425	–769.439167
$[Bi(H_2O)_8](H_2O)^{3+}$ (**1^8-H_2O**)	169.88	127.28 (91.99)	–692.491252	–692.980038 (–693.040482)
$[Bi(H_2O)_8](H_2O)_2^{3+}$ (**1^8-2H_2O**)	182.22	136.78	–768.977125	–769.442381
$[Bi(H_2O)_8](H_2O_2)^{3+}$ (**1^8-H_2O_2**)	177.36	133.04	–767.634982	–768.118761
TS1	174.09	130.52	–767.629415	–768.109535
$[Bi(H_2O)_7](H_2O)(H_2O_2)^{3+}$ (**2^7-H_2O-H_2O_2**)	177.28	132.97	–767.645739	–768.116791
TS2	171.74	128.71	–767.627267	–768.109939
$[Bi(H_2O)_7(H_2O_2)](H_2O)^{3+}$ (**3^8-H_2O**)	174.98	131.20 (94.75)	–767.632492	–768.117357 (–768.179494)
$[Bi(H_2O)_5(OOH)](H_2O)^{2+}$ (**4^6-H_2O**)	144.47	107.71 (78.27)	–614.596293	–614.812017 (–614.847129)
TS3	149.24	111.38	–689.731196	–689.942035
$[Bi(H_2O)_4(OOH)](H_2O)(H_2O_2)^{2+}$ (**5^5-H_2O-H_2O_2**)	154.61	115.52	–689.737506	–689.945047
TS4	153.91	114.98	–689.733384	–689.940255
$[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2+}$ (**6^6-H_2O**)	154.30	115.28	–689.734495	–689.947443
$[Bi(H_2O)_4(OH)(OOH)](H_2O)^{2+}$ (**7^6-H_2Ob**)	145.06	108.16	–613.952211	–614.173690
$[Bi(H_2O)_4(OH)(OOH)](H_2O)^{2+}$ (**7^6-H_2Oa**)	149.06	111.24	–613.956388	–614.170815
$[Bi(H_2O)_7(OH)](H_2O)^{3+}$	169.64	127.09	–691.793030	–692.285905
$[Bi(H_2O)_5(=O)](H_2O)^{2+}$	143.55	107.00	–538.760175	–538.982664
$[Bi(H_2O)_4(H_2O_2)(=O)](H_2O)^{2+}$	146.31	109.13	–613.899852	–614.119215
$[Bi(H_2O)_4(H_2O_2)](H_2O)^{2+}$	142.02	105.82	–538.705686	–538.924451
$[Bi(H_2O)_5](H_2O)^{2+}$	139.18	103.64	–463.566379	–463.786494
$[Bi(H_2O)_5(OH)](H_2O)^{2+}$	141.17	105.17 (76.49)	–539.451321	–539.670753 (–539.706034)
$[Bi(H_2O)_3(OH)_3](H_2O)^{2+}$ (**9**)	126.44	93.83 (68.54)	–538.066779	–538.310338 (–538.356233)

Table S3 Cartesian atomic coordinates (in Å) of the calculated equilibrium structures (nuclear charges of elements are shown in the second column)

1^9

Bi	0.000359	-0.001114	-0.000121
O	1.806164	-1.656503	0.564092
H	1.864893	-2.158935	1.391034
H	2.597505	-1.875078	0.048604
O	-1.845685	0.320817	-1.683713
H	-2.653214	-0.203287	-1.796754
H	-1.899576	1.054357	-2.315220
O	-0.039494	-1.948354	-1.664025
H	0.485530	-2.761987	-1.622112
H	-0.593000	-2.019958	-2.456495
O	1.772516	0.302883	-1.759513
H	2.576936	0.841276	-1.709059
H	1.799246	-0.158982	-2.611101
O	-1.782316	-1.657801	0.633952
H	-1.830866	-2.573955	0.321066
H	-2.575808	-1.504019	1.169157
O	-0.018391	2.412619	-0.864343
H	-0.543618	3.149067	-0.516380
H	0.499164	2.769647	-1.601841
O	0.057840	-0.436227	2.523862
H	-0.460100	-1.092859	3.013442
H	0.602391	0.026814	3.178133
O	-1.791719	1.329460	1.168992
H	-2.600864	1.702903	0.787280
H	-1.818798	1.519012	2.119455
O	1.838861	1.340195	1.079812
H	2.648785	1.012887	1.500369
H	1.885209	2.308266	1.101782

1^9-H_2O

Bi	0.653176	-0.457430	-0.442186
O	-1.568337	0.649096	0.075932
H	-2.262552	0.216908	0.595620
H	-1.946395	1.478615	-0.252717
O	3.022364	0.005224	-0.289034
H	3.463617	0.688743	0.273838
H	3.632268	-0.246862	-0.996441
O	1.039648	1.683499	0.739887
H	0.352357	2.261878	1.098249
H	1.915825	2.019583	1.046145
O	0.572118	1.360787	-2.119404
H	0.063573	1.340293	-2.943527
H	0.960888	2.244362	-2.039195
O	0.833329	-0.908669	2.004676
H	0.707219	-0.281838	2.731926
H	1.273771	-1.688368	2.373473
O	1.883489	-1.325304	-2.563371

H	2.199935	-2.231471	-2.693633
H	2.079601	-0.846609	-3.382647
O	-1.073263	-2.259094	0.311296
H	-1.233852	-2.578462	1.211493
H	-1.688061	-2.738414	-0.263090
O	1.795568	-2.732614	-0.032499
H	2.737210	-2.917406	0.102501
H	1.335748	-3.583766	0.019614
O	-1.005547	-1.088070	-2.364751
H	-1.952205	-0.892719	-2.426542
H	-0.788123	-1.620233	-3.144086
O	3.702768	2.132565	1.289760
H	4.164704	2.895403	0.906351
H	4.087397	2.030800	2.174846

1^{8}-H_2O

Bi	0.232244	-0.155259	-0.098686
O	-1.525373	1.108773	-1.430786
O	-1.777666	-1.692574	-0.052889
O	-1.240464	0.950296	1.595046
O	0.396356	-1.650308	1.874820
O	1.345802	1.221917	-1.843024
O	1.614970	1.345057	1.259098
O	0.270374	-1.553882	-2.139618
O	2.467164	-1.105497	-0.111416
H	-1.836564	0.926445	-2.331594
H	-2.053904	1.858106	-1.113575
H	-1.878425	-2.452477	0.541016
H	-2.604724	-1.628950	-0.555378
H	-0.939719	1.520930	2.319476
H	-2.197993	0.844449	1.709120
H	1.032524	-2.370499	2.004475
H	-0.085133	-1.546814	2.710521
H	0.903409	1.894284	-2.383928
H	2.298434	1.339068	-1.980093
H	1.591702	2.313902	1.277346
H	2.509983	1.071124	1.581261
H	-0.222659	-2.377760	-2.278882
H	0.757176	-1.373605	-2.959280
H	2.807950	-1.812464	-0.679665
H	3.193086	-0.809355	0.494610
H	4.868289	0.624109	1.413151
O	4.062284	0.169597	1.708956
H	4.302864	-0.218373	2.566017

1^{8}-$2H_2O$

Bi	0.281556	-0.485474	-0.078085
O	-1.106843	1.177064	-1.180577
O	-2.076791	-1.261379	-0.015829
O	-0.477274	-0.158411	2.241365
O	0.398278	-2.778391	0.969097
O	1.728890	0.112773	-2.057803

O	1.193384	1.660602	0.749590
O	0.055310	-2.218740	-1.882301
O	2.626237	-0.806945	0.603312
H	-0.822264	1.991746	-1.619235
H	-2.092530	1.112314	-1.277455
H	-2.408907	-2.087742	0.362837
H	-2.848249	-0.757120	-0.369736
H	-0.066626	0.457315	2.866780
H	-1.311751	-0.451815	2.637084
H	0.474526	-3.611400	0.479336
H	0.466720	-3.000113	1.910403
H	1.484134	0.457105	-2.930093
H	2.696881	0.091508	-2.032343
H	0.730122	2.508740	0.800881
H	2.137544	1.820206	0.992652
H	-0.752496	-2.694526	-2.126954
H	0.689353	-2.359804	-2.601634
H	3.031952	-1.663070	0.802704
H	3.242633	-0.099935	0.916458
H	4.559134	1.937191	0.884110
O	3.860163	1.507869	1.402837
H	4.135809	1.619137	2.326947
O	-3.755773	0.570908	-1.189774
H	-4.221722	0.369923	-2.017368
H	-4.385874	1.093552	-0.668035

1^{8}-H_2O_2

Bi	-0.023708	0.042452	0.037475
O	-0.576153	2.171701	1.307975
O	-1.918217	1.104996	-1.288989
O	-2.076061	-0.411632	1.429651
O	-1.024166	-1.663749	-1.459283
O	1.941696	0.742051	1.345779
O	0.387672	-1.905543	1.396845
O	1.001516	1.745258	-1.479675
O	1.834482	-1.069891	-1.061090
H	-0.218890	3.062834	1.169216
H	-1.230916	2.250774	2.018946
H	-2.328618	0.770413	-2.101529
H	-2.329464	1.965471	-1.112811
H	-2.126172	-0.801654	2.316858
H	-2.987764	-0.194720	1.179002
H	-0.484531	-2.208970	-2.052794
H	-1.922850	-2.027665	-1.491912
H	1.893706	1.299176	2.138414
H	2.858922	0.437477	1.271635
H	-0.261122	-2.613894	1.524137
H	1.273027	-2.307074	1.585575
H	0.546336	2.163464	-2.227242
H	1.866547	2.178713	-1.408928
H	2.305242	-0.724068	-1.834370

H	2.342377	-1.854505	-0.725507
O	2.768209	-3.208026	1.455531
O	3.281219	-3.072535	0.116357
H	3.569480	-3.256904	2.010228
H	3.401881	-3.995659	-0.177614

2^{7}-H_2O-H_2O_2

Bi	-0.498247	-1.142009	0.900612
O	0.748996	0.135281	2.454547
O	-2.365495	-0.417765	-0.667155
O	-2.297028	-0.482063	2.470231
O	-1.426616	-3.192133	-0.284189
O	-0.062100	-2.718469	2.659088
O	0.441927	0.728732	-0.314210
O	1.474105	-2.158972	0.080272
H	1.190147	1.006103	2.260496
H	1.072825	-0.197920	3.305140
H	-2.817494	-1.028427	-1.270137
H	-2.777688	0.449743	-0.805337
H	-2.198620	-0.029559	3.323529
H	-3.250516	-0.512430	2.288815
H	-1.019368	-3.618271	-1.054967
H	-2.135276	-3.790459	0.002242
H	-0.703944	-2.987336	3.334877
H	0.666358	-3.396794	2.656831
H	0.221109	0.996252	-1.219686
H	0.990370	1.445132	0.095604
H	2.130329	-1.704057	-0.470297
H	1.873151	-3.021937	0.380936
O	1.796555	2.382636	1.384038
H	1.439736	3.259936	1.600581
H	2.757650	2.511102	1.325337
O	1.928200	-4.555742	2.446770
H	2.700421	-4.669003	3.033338
O	2.518685	-4.403671	1.142854
H	2.552321	-5.316588	0.798997

3^{8}-H_2O

Bi	-0.255153	-0.315400	0.057640
O	-0.215150	-2.768913	-0.333067
O	1.940872	-0.823148	-0.914705
O	0.609776	-1.465326	2.097477
O	1.330304	1.363691	0.933572
O	-2.671893	-0.790000	-0.125970
O	-1.458206	0.738418	1.945667
O	-0.805306	-0.452398	-2.354423
H	-0.586467	-3.242065	-1.093527
H	-0.061056	-3.433444	0.356445
H	2.694966	-0.215273	-0.977034
H	2.231126	-1.676059	-1.275146
H	0.161033	-1.472771	2.958308
H	1.480503	-1.869357	2.242439

H	1.165230	2.299544	0.706943
H	2.080142	1.328391	1.546235
H	-3.159607	-0.746167	-0.986139
H	-3.224130	-1.302331	0.483942
H	-1.073110	1.283549	2.649599
H	-2.416393	0.885900	1.971983
H	-0.192593	-0.564141	-3.096914
H	-1.729019	-0.526882	-2.706081
O	-0.732629	2.011827	-1.013159
H	-0.565591	2.139281	-1.965485
O	-0.132332	3.177037	-0.411495
H	-0.874169	3.808018	-0.338190
O	-3.504111	-0.653242	-2.740075
H	-4.031584	0.095653	-3.062344
H	-3.897491	-1.432133	-3.166693

4^6-H_2O

Bi	0.195974	-0.209251	-0.190487
O	-3.686093	-1.966214	0.011210
O	-2.170274	0.329786	-0.267955
O	-0.095816	2.175755	0.401895
O	1.738388	-2.143600	-0.533661
O	2.553338	0.440071	0.272725
O	-0.977472	-2.227885	0.201484
O	0.245633	-0.376201	1.887361
H	-4.268957	-2.092479	0.774995
H	-4.152482	-2.364346	-0.739337
H	-2.496225	1.223332	-0.094630
H	-2.918742	-0.302521	-0.208310
H	0.137214	2.334259	1.333390
H	0.034029	3.001269	-0.086695
H	1.620874	-2.961053	-1.038402
H	2.670132	-2.087004	-0.278312
H	2.666204	0.692171	1.205974
H	3.245648	0.873018	-0.246630
H	-1.964443	-2.296452	0.199084
H	-0.627059	-2.849689	0.856131
O	1.000165	0.734380	2.470568
H	0.921802	0.522516	3.415995

5^5-H_2O-H_2O_2

Bi	-0.044422	1.386076	0.347346
O	4.107567	1.808845	-0.684199
O	-3.742566	0.243585	-0.495869
O	1.548861	1.011400	-1.288582
O	-2.109727	1.142730	1.544578
O	-1.568833	1.605450	-1.442483
O	1.823834	0.846427	1.825923
O	-0.513702	-0.634747	0.209765
O	4.184923	1.883816	0.753692
H	4.920343	1.327608	-0.922889
H	-4.644958	0.581302	-0.601362

H	-3.799404	-0.707723	-0.671182
H	1.500531	0.079454	-1.579572
H	2.496378	1.280164	-1.193313
H	-2.401957	1.391850	2.432444
H	-2.848631	0.703968	1.064970
H	-1.498414	2.024532	-2.311734
H	-2.425385	1.119643	-1.363939
H	2.725749	1.185321	1.635439
H	1.888985	0.175186	2.520208
O	0.227284	-1.267107	-0.871009
H	0.347863	-2.162472	-0.514427
H	4.598151	2.752680	0.904046

6^6-H_2O

Bi	-0.175887	0.557539	-0.909025
O	0.831938	1.771268	0.441292
O	0.288855	1.944334	-2.925640
O	-1.270843	2.910894	-0.589279
O	0.393325	-1.463834	0.187859
O	-1.774538	0.257614	1.043666
O	1.889101	-0.118913	-1.813864
O	1.887382	1.026049	1.115415
H	-0.130499	2.825454	-2.921586
H	0.414823	1.680919	-3.848402
H	-0.758776	3.394153	0.087808
O	-1.253423	3.820866	-1.709237
H	1.277010	-1.898660	0.157307
H	-0.086973	-1.760112	0.973462
H	2.474182	0.545389	-2.205661
H	2.441164	-0.839477	-1.421914
H	-2.714857	0.023952	1.034344
H	-1.606020	0.693425	1.892671
H	-2.159683	4.178430	-1.709230
O	2.931018	-2.241235	-0.460846
H	3.669096	-2.140635	0.158770
H	3.084963	-3.081083	-0.919840
H	2.432194	1.759704	1.444528

7^6-H_2Oa

Bi	-0.284804	0.650279	-0.327673
O	-0.745385	2.975868	0.971728
O	1.390873	-0.754416	-1.460440
O	0.754188	-0.076646	1.245857
O	-2.370988	0.453767	0.885537
O	1.727523	2.060589	-0.192494
O	-1.280200	-1.467289	-0.874706
O	-1.836254	3.135678	1.693523
H	2.056063	-1.119702	-0.855188
H	1.808720	-0.663706	-2.330083
H	0.294516	-0.511750	1.976095
H	-3.020423	-0.280197	0.786798
H	-2.754048	1.145812	1.443618

H	-0.782320	-2.163717	-1.324209
H	-2.168150	-1.805108	-0.618064
H	2.030807	2.871220	-0.625676
H	2.279951	1.914797	0.590984
O	-3.774363	-1.814352	0.212936
H	-3.950890	-2.512641	0.861273
H	-4.570144	-1.765820	-0.338054
H	-1.799005	4.047307	2.063064

7^6-H_2Ob

Bi	0.083122	-0.210332	-0.542108
O	-0.085218	1.454001	-1.732238
O	-1.103307	-1.475710	-2.213501
O	-2.268117	-0.169053	0.059375
O	-3.743850	-1.814704	-1.589766
O	2.273748	0.974287	-0.581334
O	-0.116921	1.427692	1.328971
O	1.806491	-1.454989	-1.910272
H	-0.818959	1.601222	-2.342871
H	-2.059789	-1.718659	-2.171799
H	-0.757058	-1.697477	-3.089241
H	-2.628742	0.313738	0.815998
H	-2.988347	-0.684141	-0.369334
H	-4.070164	-2.671737	-1.275220
H	-4.449739	-1.462533	-2.153159
O	2.364466	2.071788	-1.291037
H	-0.233517	2.376982	1.169292
H	0.244102	1.341626	2.225018
H	1.882208	-2.412710	-2.035574
H	2.687184	-1.088631	-2.084580
H	1.450552	2.187817	-1.704926

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Bi	0.809040	-0.497858	0.242856
O	1.732217	1.189528	-0.950903
O	1.858318	-1.706621	-1.009847
O	-0.598899	1.275543	0.516091
O	-0.510189	-0.669288	-1.640507
O	2.020305	0.183597	1.718711
O	-0.633637	-1.445326	1.305216
H	1.724039	2.113011	-0.579499
H	2.552216	1.018129	-1.444261
H	2.594112	-2.187952	-0.588127
H	-1.312918	1.155580	1.166881
H	-0.205714	2.188195	0.592218
H	-1.224021	-0.079141	-1.930531
H	-0.182426	-1.186026	-2.396754
H	1.821153	-0.202533	2.592055
H	-1.014030	-2.241146	0.890757
O	0.997252	3.436961	0.313026
H	0.720417	4.217492	-0.194207
H	1.488326	3.782364	1.076144

$[Bi(H_2O)_7(OH)](H_2O)^{3+}$

Bi	-0.237375	-0.391130	0.078505
O	-0.149599	-2.858004	-0.343005
O	1.983037	-0.870906	-0.886310
O	0.570764	-1.401449	2.193664
O	1.342827	1.398678	0.892619
O	-2.620944	-0.924606	-0.084280
O	-1.455171	0.801474	1.835774
O	-0.811240	-0.460682	-2.386626
H	-0.472983	-3.310003	-1.138113
H	-0.002795	-3.552702	0.318322
H	2.739155	-0.266473	-0.955523
H	2.273237	-1.725402	-1.243510
H	0.107990	-1.322340	3.044074
H	1.378940	-1.910228	2.370542
H	1.369355	2.335098	0.639444
H	2.025286	1.289704	1.574146
H	-3.131848	-0.769958	-0.918279
H	-3.121321	-1.565514	0.444346
H	-1.118885	1.469823	2.453804
H	-2.422820	0.878715	1.834593
H	-0.229281	-0.416379	-3.163156
H	-1.758417	-0.448029	-2.699786
O	-1.007271	1.577374	-1.184547
H	-0.714220	2.255531	-1.830804
O	-3.493669	-0.500569	-2.663274
H	-3.992764	0.300816	-2.892191
H	-3.935526	-1.215636	-3.150941

$[Bi(H_2O)_5(=O)](H_2O)^{2+}$

Bi	0.198228	-0.196718	-0.229838
O	-3.668658	-1.943346	0.218602
O	-2.159668	0.296536	-0.301511
O	-0.077737	2.254631	0.246452
O	1.745802	-2.143622	-0.640701
O	2.527750	0.378259	0.546410
O	-0.975001	-2.225474	0.072982
O	0.211881	-0.331217	1.834012
H	-4.148918	-2.037518	1.055369
H	-4.236613	-2.346393	-0.455767
H	-2.509691	1.197588	-0.318202
H	-2.898338	-0.333471	-0.143505
H	-0.186359	2.563949	1.159049
H	0.131828	3.032766	-0.291486
H	1.690723	-2.833828	-1.317969
H	2.661683	-2.126198	-0.327620
H	2.736989	0.306209	1.490875
H	3.202381	0.950606	0.151506
H	-1.955627	-2.307144	0.184722
H	-0.540784	-2.962649	0.526449

$[Bi(H_2O)_4(H_2O_2)(=O)](H_2O)^{2+}$

Bi	-0.252749	0.444603	-0.929679
O	0.789474	1.770078	0.258424
O	0.084576	1.823764	-2.939787
O	-1.293289	2.938086	-0.563178
O	0.601011	-1.341664	0.375483
O	-1.787168	0.229917	1.076855
O	1.802066	-0.176404	-1.890310
H	-0.233696	2.746218	-2.869268
H	0.055164	1.566999	-3.872908
H	-0.860534	3.423061	0.165688
O	-1.162294	3.859880	-1.665882
H	1.469594	-1.794471	0.257621
H	0.161316	-1.672647	1.170935
H	2.319987	0.498535	-2.353789
H	2.411597	-0.870008	-1.538162
H	-2.707058	-0.073973	1.106463
H	-1.622367	0.693897	1.911673
H	-2.053552	4.251205	-1.725477
O	3.039351	-2.181018	-0.513272
H	3.847154	-2.020992	-0.001488
H	3.155394	-3.054779	-0.917285

$[Bi(H_2O)_4(H_2O_2)](H_2O)^{2+}$

Bi	0.002763	0.680813	-0.742546
O	0.438039	2.039184	-2.717027
O	-1.561038	2.947743	-0.736331
O	0.595199	-1.355522	0.406007
O	-1.702027	0.460388	1.137248
O	2.022788	-0.101659	-1.731998
H	-0.037069	2.896063	-2.724313
H	0.509541	1.730581	-3.631561
H	-1.560236	3.531325	0.043215
O	-1.328410	3.880566	-1.815044
H	1.377531	-1.917961	0.206258
H	-0.001089	-1.838997	0.993264
H	2.654006	0.505571	-2.143202
H	2.493347	-0.930984	-1.475191
H	-2.639536	0.244018	1.024800
H	-1.578784	0.667443	2.075241
H	-2.227749	4.056100	-2.148129
O	2.893232	-2.447843	-0.640958
H	3.707824	-2.492126	-0.117487
H	2.873706	-3.265683	-1.160883

$[Bi(H_2O)_5](H_2O)^{2+}$

Bi	0.214342	-0.278069	0.097292
O	-3.771202	-1.909147	0.010107
O	-2.124483	0.280532	0.116745
O	-0.087032	2.213560	0.441240
O	1.759638	-2.260549	-0.220283
O	2.578450	0.689468	0.149676
O	-1.058861	-2.316012	-0.001313

H	-4.321769	-2.152429	0.769540
H	-4.305021	-2.109282	-0.773496
H	-2.445291	1.182577	-0.013418
H	-2.882036	-0.347424	0.077836
H	-0.276743	2.651921	1.283785
H	0.264555	2.894765	-0.150567
H	1.963182	-2.693235	-1.062529
H	2.465147	-2.509446	0.394686
H	2.988075	1.181782	0.875116
H	3.242876	0.636451	-0.551864
H	-2.039922	-2.400267	-0.000154
H	-0.659667	-3.186029	0.130070

$[Bi(H_2O)_5(OH)](H_2O)^{2+}$

Bi	0.022558	-0.558784	-0.131791
O	-1.092242	0.214878	1.366538
O	-1.691298	-2.118427	-0.785893
O	0.044898	-2.641883	1.312296
O	-3.228138	-1.301080	-2.911825
O	0.628748	1.862750	-0.571250
O	1.599505	0.004308	1.706883
O	-1.360167	0.410710	-1.848450
H	-2.050224	0.294771	1.267339
H	-2.342846	-2.045969	-1.519844
H	-1.818119	-2.950190	-0.310170
H	-0.255630	-2.549556	2.229175
H	0.666693	-3.384743	1.299457
H	-4.179462	-1.139503	-2.824066
H	-3.111786	-1.686962	-3.793020
H	0.396188	2.509029	0.112569
H	1.392471	2.224695	-1.044837
H	1.198138	0.389865	2.500262
H	2.553796	-0.055294	1.853351
H	-2.076287	-0.011525	-2.374979
H	-1.259854	1.336493	-2.107434

TS1

Bi	-0.700800	-0.951240	0.897213
O	-1.330073	1.027187	2.256891
O	-2.489730	-0.143505	-0.573672
O	-2.676896	-1.655540	2.249568
O	-1.604405	-2.925516	-0.204540
O	0.228858	-2.306190	2.676831
O	0.399657	0.839631	-0.308999
O	1.098896	-2.084884	-0.267706
H	-1.048470	1.944540	2.114359
H	-1.903099	1.035806	3.039989
H	-2.929851	-0.666625	-1.262755
H	-2.854238	0.754531	-0.631521
H	-2.654027	-2.315018	2.961398
H	-3.598717	-1.361052	2.173752
H	-1.149698	-3.422630	-0.902757

H	-2.401688	-3.422993	0.037536
H	0.372075	-2.015668	3.590818
H	0.800008	-3.109146	2.537819
H	0.282376	1.356861	-1.120594
H	1.215231	1.120315	0.161247
H	1.618727	-1.687447	-0.982828
H	1.580531	-2.897900	0.040057
O	2.005700	0.600775	1.775426
H	2.102983	1.284207	2.456066
H	2.896841	0.229572	1.690403
O	1.806641	-4.465519	2.115954
H	2.595744	-4.686434	2.647322
O	2.344037	-4.266323	0.792616
H	2.353003	-5.166254	0.414349

TS2

Bi	0.604718	-0.550111	-0.202257
O	0.192224	1.560215	0.762649
O	-0.679996	-2.330627	-1.446098
O	-0.041644	-1.827584	1.781103
O	2.238395	-2.346953	-0.777453
O	2.490539	-0.236176	1.355080
O	-0.800023	0.664795	-1.786376
O	2.302123	0.517557	-1.577121
H	-0.572020	2.138405	0.484444
H	0.556062	1.902143	1.592932
H	-0.725613	-3.279306	-1.247233
H	-1.320781	-2.178778	-2.158102
H	-0.965469	-1.677146	2.055720
H	0.306674	-2.583335	2.279966
H	2.154586	-3.008425	-1.482853
H	3.047637	-2.568721	-0.289709
H	2.532358	-0.493586	2.290044
H	3.292254	0.279643	1.171504
H	-0.801178	0.660439	-2.755592
H	-1.337216	1.443685	-1.487588
H	2.310849	1.441620	-1.876060
H	3.014254	0.058573	-2.051523
O	-1.884610	2.747170	-0.432402
H	-2.730326	2.604749	0.022894
H	-1.904870	3.658955	-0.765999
O	-2.351584	-0.569410	1.092187
O	-2.747253	0.748192	1.532830
H	-3.156055	-0.914545	0.664766
H	-3.185231	0.583896	2.388674

TS3

Bi	-0.274024	0.047084	-0.474832
O	4.006115	0.806041	0.519683
O	1.640552	-1.394071	-0.515946
O	-1.435767	-2.076733	-0.613772
O	-1.371831	2.155988	-0.092325

O	-3.379242	0.610607	0.552720
O	1.388029	1.453826	0.329103
O	-0.529116	-0.218692	1.572809
H	4.738214	1.077898	-0.062839
O	4.076040	-0.631869	0.482467
H	1.643102	-2.276363	-0.913884
H	2.526637	-1.236206	-0.110242
H	-1.768453	-2.338692	0.264855
H	-1.938007	-2.541578	-1.298470
H	-1.389147	2.998845	-0.567720
H	-2.274424	1.944409	0.251826
H	-3.400509	0.227429	1.441558
H	-4.299285	0.673903	0.262191
H	2.364026	1.284912	0.385291
H	1.141761	2.098582	1.010133
O	-1.534552	-1.215861	1.913506
H	-1.192127	-1.524011	2.769610
H	4.523798	-0.849719	1.319673

TS4

Bi	-0.029553	0.028302	-0.650372
O	0.795260	1.301669	0.765542
O	-0.019340	1.747916	-2.245814
O	-1.952477	3.893393	-0.722686
O	0.741526	-2.010709	0.482759
O	-1.751537	0.545652	0.994195
O	2.134843	-0.179021	-1.441563
O	2.051447	1.848896	0.273885
H	-0.563875	2.593881	-2.214707
H	0.660975	1.850349	-2.926685
H	-1.721905	4.778303	-0.391547
O	-1.439392	3.946133	-2.072194
H	1.544031	-2.488784	0.183703
H	0.405745	-2.440317	1.282140
H	2.676908	0.508184	-1.001476
H	2.613660	-1.044984	-1.400903
H	-2.677265	0.277081	1.090933
H	-1.577657	1.256506	1.631327
H	-2.230303	4.129475	-2.608342
O	3.059028	-2.702939	-0.929673
H	3.909449	-2.820649	-0.479475
H	3.034824	-3.395021	-1.608074
H	2.419160	2.222727	1.091622