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Supporting Information

Radical Reaction Control in the AdoMet Radical Enzyme CDG Synthase (QueE): Consolidate, Destabilize, Accelerate

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Supporting Information

Table S1. Detailed results of *ab initio* and DFT calculations. B3LYP/6-31+G(d) optimizations.

Table S2. Detailed results of *ab initio* and DFT calculations. BMK/6-31+G(2df,p) optimizations.

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Scheme S1. Conformer nomenclature of CPH4.

Additionally, QM calculation output files and molecular structures can be found on figshare:

Jaeger, Christof (2016): Supplementary material for "Radical Reaction Control in the AdoMet Radical Enzyme CDG Synthase (QueE): Consolidate, Destabilize, Accelerate". figshare.

https://dx.doi.org/10.6084/m9.figshare.c.3574113.v1

Table S1. Detailed results of *ab initio* and DFT calculations. B3LYP/6-31+G(d) optimizations.

	B3LYP/6-31+G(d)						
Name	Electronic energy [Hartree]	ZPE [Hartree]	cH [Hartree]	cG [Hartree]	nimag	dE Etot+ZPE [KJ/mol]	RSE Etot+cH [KJ/mol]
1a	-771.1292190	0.1704312	0.183987	0.131174	0	0.0	
1b	-771.1253198	0.1708649	0.184459	0.131174	0	11.4	
3	-770.4927925	0.1568494	0.170626	0.116831	0	0.0	-104.9
4	-770.4307542	0.1550377	0.168316	0.115511	1	158.1	
5	-770.4394744	0.1556640	0.169394	0.115659	0	136.9	
6	-770.4329819	0.1547460	0.168099	0.115314	1	151.5	
7	-770.4194935	0.1541816	0.167977	0.113532	1	185.4	
8	-770.4424673	0.1551995	0.170017	0.111897	0	127.8	25.7
9	-770.4166968	0.1542722	0.168131	0.113853	1	193.0	
10	-770.4601402	0.1546542	0.169002	0.113256	0	80.0	-53.2
(10-H)	-771.1173907	0.1698691	0.183953	0.129815	0	29.6	
11	-770.4602438	0.1541598	0.114271	0.114271	1	78.4	
12	-770.4810930	0.1545484	0.168888	0.111980	0	24.7	
1aHcis	-771.6605858	0.1835654	0.197543	0.143416	0	4.8	
3Hcis	-771.0449564	0.1709745	0.184884	0.131095	0	0.0	-157.6
10Hcis	-770.9969400	0.1685024	0.182797	0.127890	0	119.6	-37.4
(10H-H)cis	-771.6597591	0.1829809	0.197296	0.142945	0	5.4	
4Hcis	-770.9746563	0.1684873	0.181840	0.129344	1	178.0	
5Hcis	-770.9757690	0.1691981	0.182962	0.129467	0	177.0	
6Hcis	-770.9714727	0.1681739	0.181716	0.128720	1	185.6	
1aHtrans	-771.6625348	0.1836874	0.197559	0.144090	0	0.0	
3Htrans	-771.0448138	0.1710401	0.184916	0.131193	0	0.5	-152.1
10Htrans	-770.9959704	0.1683435	0.182675	0.127889	0	121.7	-30.5
(10H-H)trans	-771.6597591	0.1829809	0.197296	0.142945	0	5.4	
4Htrans	-770.9737602	0.1684878	0.181829	0.129362	1	180.4	
5Htrans	-770.9748748	0.1691723	0.182945	0.129352	0	179.3	
6Htrans	-770.9706581	0.1679957	0.181597	0.128386	1	187.2	
7Htrans	-770.9461478	0.1675762	0.181672	0.126512	1	250.5	
13	-568.6961805	0.1416258	0.154021	0.102874	0	0.0	-99.7
(13-H)	-569.3343525	0.1545761	0.167162	0.116311	0	0.0	
14	-568.6520383	0.1400256	0.152059	0.102454	1	111.7	
15	-568.6664871	0.1408978	0.152830	0.104123	0	76.0	

17	-568.6727209	0.1408364	0.153044	0.102542	0	59.5	-44.1
(17-H)	-569.3332422	0.1556521	0.167792	0.118703	0	5.7	
13H	-569.2415038	0.1559037	0.168531	0.117003	0	0.0	-126.9
(13-H)H	-569.8687294	0.1680849	0.181078	0.129042	0	0.0	
14H	-569.1823114	0.1522403	0.164916	0.113665	1	145.8	19.0
15H	-569.1853723	0.1532281	0.166055	0.115410	0	140.3	14.0
16H	-569.1835730	0.1525651	0.164937	0.115095	1	143.3	15.8
17H	-569.1946062	0.1538261	0.166573	0.115810	0	117.7	-33.3
(17-H)H	-569.8591811	0.1685928	0.181272	0.131170	0	26.4	
1Mg4H2O	-1276.8707682	0.2755115	0.300603	0.223995	0	0.0	
3Mg4H2O	-1276.2121848	0.2617722	0.287155	0.209541	0	0.0	-46.9
4Mg4H2O	-1276.1804242	0.2592579	0.284237	0.207489	1	76.8	28.8
5Mg4H2O	-1276.1859157	0.2600679	0.285453	0.207917	0	64.5	17.6
6Mg4H2O	-1276.1838951	0.2591059	0.284242	0.207133	1	67.3	19.7
10Mg4H2O	-1276.2102631	0.2593527	0.285287	0.206559	0	-1.3	-34.2
(10-H)Mg4H2O	-1276.8742305	0.2736847	0.299725	0.221262	0	-13.9	
1Mg3H2O	-1200.4205935	0.2497339	0.272411	0.200735	0	0.0	
(10-H)Mg3H2O	-1200.4271614	0.2482019	0.271504	0.198827	0	-21.3	
3Mg3H2O	-1199.7641487	0.2364140	0.259168	0.186734	0	0.0	-52.0
4Mg3H2O	-1199.7332345	0.2336947	0.256098	0.184616	1	74.0	21.1
5Mg3H2O	-1199.7392633	0.2346667	0.257412	0.185289	0	60.7	8.7
6Mg3H2O	-1199.7368643	0.2336900	0.256167	0.184559	1	64.5	11.8
10Mg3H2O	-1199.7619031	0.2339310	0.257185	0.183968	0	-0.6	-30.5
11Mg3H2O	-1199.7186663	0.2329909	0.255694	0.183194	1	110.4	
12Mg3H2O	-1199.7411615	0.2332050	0.256893	0.181787	0	51.9	2.4
1HMg4H2O	-1277.1584907	0.2875571	0.313149	0.236238	0	0.0	
(10-H)HMg4H2O	-1277.1439893	0.2842331	0.313149	0.236238	0	29.3	
3HMg4H2O	-1276.5067137	0.2730379	0.299759	0.219393	0	0.0	-64.6
10HMg4H2O	-1276.4748031	0.2699830	0.297401	0.214883	0	75.8	-23.9
1Mg2H2OOH	-1200.0177205	0.2387685	0.259850	0.191720	0	0.0	
(10-H)Mg2H2OOH	-1200.0195284	0.2362982	0.258256	0.187573	0	-11.2	
3Mg2H2OOH	-1199.3619619	0.2254943	0.246725	0.177255	0	0.0	-53.5
4Mg2H2OOH	-1199.3273290	0.2220283	0.243207	0.174199	1	81.8	
5Mg2H2OOH	-1199.3351564	0.2227119	0.244185	0.174204	0	63.1	
6Mg2H2OOH	-1199.3316931	0.2216684	0.242899	0.173396	1	69.4	
10Mg2H2OOH	-1199.3570841	0.2219313	0.243905	0.172483	0	3.5	-38.0
13Mg4H2O	-1074.4169550	0.2465247	0.270485	0.195887	0	0.0	-80.2

(13-H)Mg4H2O	-1075.0625680	0.2594717	0.283625	0.209192	0	0.0	
14Mg4H2O	-1074.3813544	0.2427186	0.266947	0.191870	1	83.5	
15Mg4H2O	-1074.3845570	0.2440192	0.268356	0.193188	0	78.5	
16Mg4H2O	-1074.3719365	0.2430890	0.266979	0.192959	1	109.2	
17Mg4H2O	-1074.4039183	0.2455702	0.269299	0.196508	0	31.7	-25.0
(17-H)Mg4H2O	-1075.0718156	0.2608401	0.284169	0.212982	0	-20.7	
3Ca4H2O	-1753.7111031	0.2602369	0.286183	0.206041	0	0.0	-64.3
4Ca4H2O	-1753.6758830	0.2575668	0.255206	0.180040	1	85.5	
5Ca4H2O	-1753.6808380	0.2581670	0.284300	0.203467	0	74.0	10.2
6Ca4H2O	-1753.6786772	0.2572316	0.255204	0.179750	1	77.2	
10Ca4H2O	-1753.7047679	0.2573560	0.284090	0.201853	0	9.1	-35.5
1Ca4H2O	-1754.3625633	0.2726484	0.299118	0.217614	0	0.0	
(10-H)Ca4H2O	-1754.3682527	0.2718358	0.298540	0.217192	0	-17.1	
3Mn4H2O	-2227.0030137	0.2600383	0.286332	0.203626	0	0.0	-49.9
4Mn4H2O	-2226.9701740	0.2574275	0.283181	0.202340	1	79.4	
6Mn4H2O	-2226.9718677	0.2573593	0.283286	0.202120	1	74.7	
10Mn4H2O	-2226.9999322	0.2571365	0.284108	0.200529	0	0.5	-33.7
1Mn4H2O	-2227.6605862	0.2742922	0.299895	0.220134	0	0.0	
(10-H)Mn4H2O	-2227.6640818	0.2714849	0.298520	0.215008	0	-16.5	
3Na4H2O	-1238.5917086	0.2591431	0.285791	0.202417	0	0.0	-140.1
4Na4H2O	-1238.5342172	0.2580153	0.283485	0.203531	1	148.0	
5Na4H2O	-1238.5408460	0.2586374	0.284717	0.203454	0	132.2	
6Na4H2O	-1238.5385240	0.2577078	0.283363	0.203230	1	135.9	
10Na4H2O	-1238.5635559	0.2582064	0.284485	0.203093	0	71.5	-44.4
1Na4H2O	-1239.2143606	0.2736963	0.298782	0.220456	1	0.0	
(10-H)Na4H2O	-1239.2237869	0.2724636	0.299082	0.217000	0	-28.0	
3Na3H2O	-1162.1437422	0.2341230	0.258007	0.180880	0	0.0	-96.6
4Na3H2O	-1162.0914971	0.2315672	0.255025	0.178476	1	130.5	
5Na3H2O	-1162.0953932	0.2324760	0.256427	0.178749	0	122.6	
6Na3H2O	-1162.0925921	0.2319907	0.255319	0.180106	1	128.7	
10Na3H2O	-1162.1180476	0.2323099	0.256363	0.179460	0	62.7	-39.1
1Na3H2O	-1162.7832402	0.2477738	0.271288	0.195634	0	0.0	
(10-H)Na3H2O	-1162.7800836	0.2467395	0.270747	0.194717	0	5.6	
3K4H2O	-1676.1983170	0.2595209	0.285983	0.200659	0	0.0	-136.8
4K4H2O	-1676.1419209	0.2575469	0.283280	0.200938	1	142.9	
5K4H2O	-1676.1493400	0.2579485	0.284315	0.200826	0	124.5	
6K4H2O	-1676.1457916	0.2569084	0.283028	0.200060	1	131.0	
10K4H2O	-1676.1708131	0.2573926	0.284176	0.199871	0	66.6	-36.9

1K4H2O	-1676.8218751	0.2717044	0.298630	0.211703	0	0.0	
(10-H)K4H2O	-1676.8337519	0.2719771	0.298610	0.215024	0	-30.5	
AdoH	-887.6906435	0.2312361	0.248248	0.186006			
AdoR	-888.3634183	0.2465382	0.263125	0.202497			

Table S2. Detailed results of *ab initio* and DFT calculations. BMK/6-31+G(2df,p) optimizations.

	BMK/6-31G+G(2df,p)						
Name	Electronic energy [Hartree]	ZPE [Hartree]	cH [Hartree]	cG [Hartree]	nimag	dE Etot+ZPE [KJ/mol]	RSE Etot+cH [KJ/mol]
1a	-770.7948381	0.1731361	0.186545	0.133934	0	0.0	
1b	-770.7918487	0.1741983	0.187495	0.134823	0	10.6	
3	-770.1557182	0.1595765	0.173206	0.119650	0	0.0	-95.6
4	-770.1005968	0.1585211	0.171491	0.119322	1	142.0	
5	-770.1103175	0.1581125	0.171780	0.118159	0	115.4	
6	-770.1024808	0.1573918	0.170607	0.118130	1	134.0	
7	-770.0788944	0.1570890	0.170742	0.116602	1	195.2	
8	-770.1014591	0.1585074	0.173039	0.115560	0	139.7	
9	-770.0750589	0.1571772	0.170803	0.116981	1	205.5	
10	-770.1263584	0.1578370	0.171722	0.117534	0	72.5	-51.2
(10-H)	-770.7872829	0.1730003	0.186921	0.132688	0	19.5	
11	-770.1174444	0.1566697	0.170058	0.116948	1	92.9	
12	-770.1402944	0.1577396	0.171789	0.115958	0	35.7	
1aHcis	-771.3349790	0.1866726	0.200505	0.146569	0	0.0	-148.7
3Hcis	-770.7167386	0.1740984	0.187831	0.134452	0	0.0	-36.4
10Hcis	-770.6724120	0.1713404	0.185526	0.130976	0	109.1	
(10-H)cis	-771.3384676	0.1861132	0.200244	0.146730	0	-3.9	
4Hcis	-770.6532090	0.1710740	0.184321	0.132052	1	158.9	
5Hcis	-770.6536874	0.1715562	0.185378	0.131299	0	158.9	
6Hcis	-770.6493238	0.1711167	0.184551	0.131680	1	169.2	
1aHtrans	-771.3372400	0.1863534	0.200110	0.146957	0	0.0	-141.3
3Htrans	-770.7167183	0.1742781	0.187962	0.134676	0	0.5	-29.0
10Htrans	-770.6711990	0.1713721	0.185581	0.130988	0	112.4	
(10-H)trans	-771.3399587	0.1859090	0.200158	0.146085	0	-8.3	
4Htrans	-770.6522207	0.1715299	0.184691	0.132667	1	162.6	

5Htrans	-770.6526871	0.1719637	0.185581	0.132408	0	162.6	
6Htrans	-770.6482255	0.1706927	0.184237	0.131072	1	170.9	
13H	-568.9856196	0.1599458	0.172109	0.121834	0	0.0	-116.0
(13-H)H	-569.6150460	0.1708064	0.183540	0.132261	0	0.0	
14H	-568.9263053	0.1558494	0.167719	0.118975	1	145.0	
15H	-568.9375173	0.1558370	0.168389	0.118410	0	115.5	
16H	-568.9355186	0.1552693	0.167309	0.118373	1	119.3	
17H	-568.9412116	0.1563108	0.168882	0.118617	0	107.0	-22.4
(17-H)H	-569.6093995	0.1708173	0.183405	0.133584	0	14.9	
1Mg4H2O	-1276.4017661	0.2822638	0.306504	0.232509	0	0.0	
3Mg4H2O	-1275.7394525	0.2695054	0.293824	0.219736	0	0.0	-33.0
4Mg4H2O	-1275.7148606	0.2657566	0.290074	0.216035	1	54.7	
5Mg4H2O	-1275.7192015	0.2670455	0.291558	0.217101	0	46.7	
6Mg4H2O	-1275.7174750	0.2660831	0.290421	0.216049	1	48.7	
10Mg4H2O	-1275.7421977	0.2667142	0.291774	0.216051	0	-14.5	-32.4
(10-H)Mg4H2O	-1276.4092994	0.2807059	0.306006	0.230137	0	-23.9	
1Mg3H2O	-1199.9735038	0.2564810	0.277001	0.209937	0	0.0	
(10-H)Mg3H2O	-1199.9841622	0.2542650	0.276857	0.206062	0	-33.8	
3Mg3H2O	-1199.3129730	0.2424383	0.264552	0.193733	0	0.0	-37.0
4Mg3H2O	-1199.2898528	0.2399905	0.261606	0.192402	1	54.3	
5Mg3H2O	-1199.2949210	0.2402906	0.262472	0.191885	0	41.8	
6Mg3H2O	-1199.2927638	0.2394727	0.261410	0.191312	1	45.3	
10Mg3H2O	-1199.3157439	0.2397573	0.262237	0.191101	0	-14.3	-30.0
11Mg3H2O	-1199.2566171	0.2381532	0.260268	0.189584	1	136.7	
12Mg3H2O	-1199.2831089	0.2399861	0.262802	0.190158	0	72.0	36.8
1Mg2H2OOH	-1199.5622738	0.2439621	0.264629	0.197732	0	0.0	
(10-H)Mg2H2OOH	-1199.5702953	0.2423228	0.263916	0.194640	0	-25.4	
3Mg2H2OOH	-1198.9024901	0.2304761	0.251674	0.182137	0	0.0	-40.3
4Mg2H2OOH	-1198.8779847	0.2289130	0.249271	0.182200	1	60.2	
5Mg2H2OOH	-1198.8842648	0.2279413	0.249100	0.180207	0	41.2	
6Mg2H2OOH	-1198.8810298	0.2275142	0.248280	0.180322	1	48.6	
10Mg2H2OOH	-1198.9049254	0.2283828	0.249763	0.180335	0	-11.9	-36.8
13Mg4H2O	-1074.0150459	0.2530497	0.276306	0.203820	0	0	-68.8
(13-H)Mg4H2O	-1074.6635129	0.2653546	0.288810	0.216364	0	0.0	
14Mg4H2O	-1073.9879348	0.2495818	0.272525	0.201535	1	62.1	
15Mg4H2O	-1073.9927983	0.2513476	0.274575	0.203087	0	53.9	
16Mg4H2O	-1073.9770355	0.2518489	0.274032	0.204968	1	96.6	
17Mg4H2O	-1074.0063674	0.2515294	0.274632	0.203762	0	18.8	-26.8

(17-H)Mg4H2O	-1074.6772142	0.2680242	0.290470	0.221474	0	-29.0
AdoH	-887.9623953	0.2506013	0.266590	0.207636	0	
AdoR	-887.2897386	0.2356237	0.251919	0.191980	0	-11.0

Table S3. Detailed results of *ab initio* and DFT energy calculations.

	MP2/6-311++G(3df,3p)// B3LYP-6-31+G(d)			M06-2X/6-311++G(3df,3p)// B3LYP-6-31+G(d)		
Pubname	Electronic energy [Hartree]	dE Etot+ZPE [KJ/mol]	RSE Etot+cH [KJ/mol]	[Hartree]	dE Etot+ZPE [KJ/mol]	RSE Etot+cH [KJ/mol]
1a	-769.7679067	0.0		-771.0892815	0.0	
1b	-769.7657426	6.8		-771.0867597	7.8	
3	-769.1124231	0.0	-49.0	-770.4472803	0.0	-86.2
4	-769.0496581	160.0		-770.3903890	144.6	
5	-769.0691923	110.4		-770.4039967	110.5	
6	-769.0534670	149.3		-770.3919301	139.8	
7	-769.0337559	199.5		-770.3748222	183.2	
8	-769.0663607	116.6	70.3	-770.3978573	125.4	41.9
9	-769.0313360	206.1		-770.3707673	194.1	
10	-769.0892941	55.0	-24.3	-770.4167629	74.4	-43.1
(10-H)	-769.7633666	10.4		-771.0808282	20.7	
11	-769.0863712	61.3		-770.4119943	85.6	
12	-769.0915344	48.8		-770.4336819	29.7	
1aHcis	-770.3039732	6.6		-771.6292950	6.1	
3Hcis	-769.6751414	0.0	-117.2	-771.0083368	0.0	-139.6
10Hcis	-769.6359739	96.3	-22.4	-770.9633002	111.8	-30.3
(10H-H)cis	-770.3103347	-11.7		-771.6318025	-2.0	
4Hcis	-769.6067704	173.0		-770.9438884	162.7	
5Hcis	-769.6099247	166.6		-770.9470691	156.2	
6Hcis	-769.6042619	178.7		-770.9394536	173.5	
(10H-H)trans	-770.3103347	-11.7		-771.6318025	-2.0	
1aHtrans	-770.3065977	0.0		-771.6317370	0	
3Htrans	-769.6761920	-2.6	-113.0	-771.0083278	0.2	-133.2
10Htrans	-769.6356773	96.7	-16.8	-770.9623967	113.7	-23.6

4Htrans	-769.6065698	173.5		-770.9430853	164.8	
5Htrans	-769.6031981	184.2		-770.9462451	158.3	
6Htrans	-769.6031987	181.1		-770.9385992	175.3	
7Htrans	-769.5581783	298.2		-770.9060296	259.7	
13	-567.6529513	0.0	-42.0	-568.6469482	0.0	-81.1
(13-H)	-568.3108820	0.0		-569.2906999	0.0	
14	-567.6204216	81.2		-568.6095722	93.9	
15	-567.6510697	3.0		-568.6306809	40.8	
16	--					
17	-567.6412398	28.7	6.8	-568.6270738	50.1	-24.7
(17-H)	-568.3193667	-19.5		-569.293901	-8.4	
13H	-568.2037459	0.0	-68.4	-569.2011612	0.0	-110.6
(13-H)H	-568.8510326	0.0		-569.8330564	0.0	
14H	-568.1578720	110.8		-569.1484625	128.7	
15H	-568.1759784	65.9		-569.1581628	105.9	
16H	-568.1745628	67.9		-569.1567092	107.9	
17H	-568.1723173	77.1	-6.6	-569.1599936	102.6	-26.4
(17-H)H	-568.8528764	-3.5		-569.830149	9.0	
1Mg4H2O	-1274.7013346	0.0		-1276.8523835	0.0	
3Mg4H2O	-1274.0332833	0.0	-16.3	-1276.1883456	0.0	-28.6
4Mg4H2O	-1274.0016510	76.4		-1276.1587206	71.2	
5Mg4H2O	-1274.0103088	55.8		-1276.1659933	54.2	
6Mg4H2O	-1274.0041468	69.5		-1276.1616392	63.1	
10Mg4H2O	-1274.0345215	-9.6	-20.6	-1276.1869873	-2.8	-27.3
(10-H)Mg4H2O	-1274.7095077	-26.3		-1276.8565391	-15.7	
1Mg3H2O	-1198.3484795	0.0		-1200.3932758	0.0	
(10-H)Mg3H2O	-1198.3583853	-30.0		-1200.4005109	-23.0	
3Mg3H2O	-1197.6810138	0.0	-17.3	-1199.731274	0.0	-33.4
4Mg3H2O	-1197.6495265	75.5		-1199.7026908	67.9	
5Mg3H2O	-1197.6596528	51.5		-1199.7109152	48.9	
6Mg3H2O	-1197.6527105	67.2		-1199.705897	59.5	
10Mg3H2O	-1197.6824160	-10.2	-17.7	-1199.729804	-2.7	-24.0
11Mg3H2O	-1197.612543	170.8		-1199.675433	137.6	
12Mg3H2O	-1197.630574	124.0		-1199.701312	70.2	39.3
1HMg4H2O				-1277.1410783	0.0	
(10-H)HMg4H2O				-1277.1282543	24.94	
3HMg4H2O				-1276.4834532	0.0	-45.3
10HMg4H2O				-1276.4586681	57.05	-30.7

1Mg2H2OOH	-1197.9420448	0.0		-1199.9856596	0	
(10-H)Mg2H2OOH	-1197.9467226	-18.8		-1199.9860073	-7.4	
3Mg2H2OOH	-1197.2746164	0.0	-17.0	-1199.3245129	0	-35.3
4Mg2H2OOH	-1197.2384010	86.0		-1199.2902867	80.8	
5Mg2H2OOH	-1197.2464749	66.6		-1199.3005095	55.7	
6Mg2H2OOH	-1197.2467842	63.0		-1199.2936046	71.1	
10Mg2H2OOH	-1197.2730735	-5.3	-23.9	-1199.3181662	7.3	-37.9
13Mg4H2O	-1072.568111	0.0	-30.8	-1074.38742	0	-64.8
(13-H)Mg4H2O	-1073.230314	0.0		-1075.037349	0.0	
14Mg4H2O	-1072.543978	53.4		-1074.357199	69.4	
15Mg4H2O	-1072.558507	18.6		-1074.365812	50.2	
16Mg4H2O	-1072.527744	97.0		-1074.345768	100.3	
17Mg4H2O	-1072.558505	22.7	-30.0	-1074.36677	51.7	-25.8
(17-H)Mg4H2O	-1073.230314			-1075.037349		
3Ca4H2O	-1751.4486181	0.0	-23.1	-1753.740891	0.0	-37.6
4Ca4H2O	-1751.4178947	73.7		-1753.708345	78.4	
5Ca4H2O	-1751.4272356	50.7		-1753.715128	62.2	
6Ca4H2O	-1751.418792	70.4		-1753.710426	72.1	
10Ca4H2O	-1751.447020	-3.4	-21.3	-1753.735356	7.0	-28.2
1Ca4H2O	-1752.113543	0.0		-1754.400989	0.0	
(10-H)Ca4H2O	-1752.121754	-23.7		-1754.404585	-11.6	
3Mn4H2O	-2224.288002	0.0	-10.7	-2227.043245	0.0	-25.1
4Mn4H2O	-2224.256598	75.6		-2227.011184	77.3	
6Mn4H2O	-2224.256849	74.8		-2227.013201	71.8	
10Mn4H2O	-2224.288529	-9.0	-20.4	-2227.039516	2.2	-27.1
1Mn4H2O	-2224.958272	0.0		-2227.708744	0.0	
(10-H)Mn4H2O	-2224.963569	-21.3		-2227.709133	-8.4	
3Na3H2O	-1160.0472697	0.0	-62.7	-1162.081272	0.0	-81.0
4Na3H2O	-1159.9895805	144.8		-1162.032379	121.7	
5Na3H2O	-1159.9987020	123.2		-1162.042567	97.3	
6Na3H2O	-1159.9959596	129.1		-1162.035958	113.4	
10Na3H2O	-1160.0269533	48.6	-25.0	-1162.060581	49.6	-32.6
1Na3H2O	-1160.6974552	0.0		-1162.725197	0.0	
(10-H)Na3H2O	-1160.7001973	-9.9		-1162.728063	-10.2	
3K4H2O	-1673.9211341	0.0	-104.1	-1676.190428	0.0	-119.5
4K4H2O	-1673.8620048	150.1		-1676.138299	131.7	
5K4H2O	-1673.8746251	118.0		-1676.149664	102.9	

6K4H2O	-1673.8689159	128.6		-1676.144128	114.7		
10NK4H2O	-1673.9014484	46.1	-24.1	-1676.165247	60.5	-31.8	
1K4H2O	-1674.5549344	0.0		-1676.819029	0.0		
(10-H)K4H2O	-1674.5750984	-52.2		-1676.833108	-36.2		
AdoH	-887.6437597		-11.5				
AdoR	-888.3157534						

Table S4. Important interatomic distances. Units in Ångstrom.

		C4a-C6	C4a-N5	C6-N5	C-O	C6-C9	C-Oa1	C-Oa2	N8-C7	M-CO	M-COO
1a	B3LYP/6-31+G(d)	2.462	1.386	1.461	1.238	1.575	1.258	1.257			
	BMK/6-31+G(2df,p)	2.446	1.384	1.452	1.223	1.575	1.243	1.243			
1b	B3LYP/6-31+G(d)	2.409	1.405	1.472	1.240	1.584	1.256	1.260			
	BMK/6-31+G(2df,p)	2.390	1.405	1.465	1.224	1.582	1.242	1.246			
3	B3LYP/6-31+G(d)	2.413	1.377	1.363	1.240	1.501	1.268	1.265			
	BMK/6-31+G(2df,p)	2.399	1.371	1.359	1.224	1.508	1.251	1.249			
4	B3LYP/6-31+G(d)	1.801	1.456	1.440	1.232	1.528	1.258	1.262			
	BMK/6-31+G(2df,p)	1.830	1.446	1.438	1.217	1.531	1.244	1.247			
5	B3LYP/6-31+G(d)	1.524	1.512	1.460	1.227	1.559	1.253	1.258			
	BMK/6-31+G(2df,p)	1.534	1.508	1.461	1.212	1.561	1.238	1.242			
6	B3LYP/6-31+G(d)	1.503	1.787	1.449	1.228	1.572	1.252	1.258			
	BMK/6-31+G(2df,p)	1.502	1.800	1.444	1.213	1.573	1.238	1.243			
7	B3LYP/6-31+G(d)	2.781	2.057	1.284	1.225	1.553	1.247	1.249			
	BMK/6-31+G(2df,p)	2.765	2.041	1.277	1.223	1.560	1.239	1.243			
8	B3LYP/6-31+G(d)			1.277	1.235	1.561	1.256	1.256			
	BMK/6-31+G(2df,p)			1.269	1.220	1.567	1.240	1.240			
9	B3LYP/6-31+G(d)	2.235	2.894	1.303	1.231	1.588	1.249	1.258			
	BMK/6-31+G(2df,p)	2.218	2.854	1.294	1.216	1.586	1.235	1.244			
10	B3LYP/6-31+G(d)	1.519	2.542	1.389	1.234	1.789	1.232	1.240			
	BMK/6-31+G(2df,p)	1.527	2.518	1.402	1.218	1.688	1.226	1.233			
11	BMK/6-31+G(2df,p)	2.417	1.392	1.327	1.228	1.554	1.243	1.238	2.125		
12	BMK/6-31+G(2df,p)	2.569	1.357	1.376	1.220	1.575	1.248	1.234	2.996		
1aHcis	B3LYP/6-31+G(d)	2.445	1.404	1.451	1.235	1.521	1.353	1.212			
	BMK/6-31+G(2df,p)	2.427	1.400	1.444	1.219	1.524	1.335	1.200			
3Hcis	B3LYP/6-31+G(d)	2.410	1.390	1.365	1.234	1.425	1.380	1.233			
	BMK/6-31+G(2df,p)	2.395	1.386	1.356	1.219	1.432	1.359	1.219			
4Hcis	B3LYP/6-31+G(d)	1.673	1.463	1.455	1.229	1.464	1.361	1.225			

	BMK/6-31+G(2df,p)	1.658	1.457	1.450	1.213	1.474	1.340	1.209		
5Hcis	B3LYP/6-31+G(d)	1.541	1.499	1.464	1.230	1.488	1.353	1.218		
	BMK/6-31+G(2df,p)	1.551	1.495	1.465	1.214	1.491	1.334	1.204		
6Hcis	B3LYP/6-31+G(d)	1.497	1.736	1.454	1.231	1.508	1.348	1.217		
	BMK/6-31+G(2df,p)	1.493	1.731	1.450	1.215	1.511	1.330	1.201		
10Hcis	B3LYP/6-31+G(d)	1.523	2.406	1.449	1.231	1.544	1.348	1.212		
	BMK/6-31+G(2df,p)	1.522	2.395	1.442	1.217	1.544	1.330	1.199		
1Htrans	B3LYP/6-31+G(d)	2.442	1.404	1.447	1.234	1.519	1.212	1.355		
	BMK/6-31+G(2df,p)	2.424	1.401	1.440	1.218	1.521	1.198	1.337		
3Htrans	B3LYP/6-31+G(d)	2.410	1.388	1.363	1.232	1.428	1.234	1.376		
	BMK/6-31+G(2df,p)	2.394	1.383	1.354	1.217	1.434	1.219	1.356		
4Htrans	B3LYP/6-31+G(d)	1.672	1.462	1.451	1.227	1.464	1.221	1.369		
	BMK/6-31+G(2df,p)	1.659	1.456	1.446	1.211	1.472	1.205	1.348		
5Htrans	B3LYP/6-31+G(d)	1.539	1.500	1.460	1.228	1.488	1.214	1.361		
	BMK/6-31+G(2df,p)	1.552	1.494	1.460	1.212	1.491	1.200	1.342		
6Htrans	B3LYP/6-31+G(d)	1.494	1.735	1.449	1.230	1.508	1.210	1.357		
	BMK/6-31+G(2df,p)	1.491	1.733	1.445	1.214	1.510	1.197	1.339		
7Htrans	B3LYP/6-31+G(d)	2.781	2.057	1.284	1.225	1.553	1.247	1.249		
	BMK/6-31+G(2df,p)	2.813	2.224	1.272	1.214	1.511	1.199	1.338		
10Htrans	B3LYP/6-31+G(d)	1.521	2.388	1.449	1.230	1.536	1.210	1.355		
	BMK/6-31+G(2df,p)	1.520	2.381	1.442	1.216	1.537	1.197	1.337		
(10-H)trans	B3LYP/6-31+G(d)	1.514	2.447	1.466	1.232	1.547	1.214	1.353		
	BMK/6-31+G(2df,p)	1.507	2.447	1.458	1.219	1.543	1.200	1.336		
13Hcis	BMK/6-31+G(2df,p)	2.500	1.373	1.361	1.214	1.452	1.356	1.215		
(13-H)H	BMK/6-31+G(2df,p)	2.460	1.369	1.442	1.214	1.524	1.338	1.199		
14H	BMK/6-31+G(2df,p)	1.511	1.877	1.433	1.214	1.529	1.331	1.199		
15H	BMK/6-31+G(2df,p)	1.561	1.477	1.446	1.214	1.518	1.333	1.199		
16H	BMK/6-31+G(2df,p)	1.522	1.488	1.458	1.214	1.518	1.332	1.200		
17H	BMK/6-31+G(2df,p)	1.535	2.397	1.452	1.216	1.543	1.331	1.200		
(17-H)H	BMK/6-31+G(2df,p)	1.535	2.491	1.461	1.216	1.539	1.328	1.203		
13Mg4H2O	BMK/6-31+G(2df,p)	2.436	1.409	1.399	1.239	1.468	1.299	1.241	2.039	1.969
(13-H)Mg4H2O	BMK/6-31+G(2df,p)	2.517	1.397	1.486	1.241	1.542	1.280	1.233	2.032	1.969
14Mg4H2O	BMK/6-31+G(2df,p)	1.864	1.448	1.419	1.245	1.510	1.279	1.235	2.017	1.970
15Mg4H2O	BMK/6-31+G(2df,p)	1.591	1.472	1.440	1.243	1.527	1.275	1.231	2.011	1.973
16Mg4H2O	BMK/6-31+G(2df,p)									
17Mg4H2O	BMK/6-31+G(2df,p)	1.526	2.404	1.443	1.238	1.596	1.270	1.218	2.030	1.995
(17-H)Mg4H2O	BMK/6-31+G(2df,p)	1.526	2.426	1.483	1.236	1.566	1.271	1.226		
1Mg4H2O	B3LYP/6-31+G(d)	2.385	1.442	1.487	1.272	1.562	1.300	1.225	2.067	2.006
	BMK/6-31+G(2df,p)	2.366	1.435	1.479	1.257	1.563	1.284	1.212	2.032	1.961
3Mg4H2O	BMK/6-31+G(2df,p)	2.305	1.418	1.400	1.271	1.484	1.294	1.231	2.066	1.972

4Mg4H2O	BMK/6-31+G(2df,p)	1.735	1.451	1.440	1.270	1.483	1.286	1.234		2.002	1.966
5Mg4H2O	BMK/6-31+G(2df,p)	1.528	1.526	1.466	1.272	1.512	1.276	1.229		1.991	1.984
6Mg4H2O	BMK/6-31+G(2df,p)	1.501	1.699	1.452	1.271	1.523	1.275	1.228		1.996	1.986
10Mg4H2O	BMK/6-31+G(2df,p)	1.534	2.389	1.441	1.266	1.555	1.276	1.225		2.001	1.976
(10-H)Mg4H2O	BMK/6-31+G(2df,p)	1.528	2.444	1.463	1.269	1.551	1.278	1.228		1.998	1.974
11Mg3H2O	BMK/6-31+G(2df,p)	2.404	1.400	1.409	1.291	1.496	1.304	1.241	2.185	2.025	1.979
12Mg3H2O	BMK/6-31+G(2df,p)	2.514	1.357	1.420	1.265	1.528	1.290	1.221	3.089	1.985	1.948

Table S5. Mulliken atomic Spin densities >0.1

		C6	C7	N8	C8a	N1	C2	N3	C4	O-C4	C4a	N5	O-COOMg
3		0.635			0.110		0.153						
4		0.414			0.250		0.242						
5				0.099	0.331		0.435						
6			0.269						0.225			0.442	
10		0.129							0.111			0.746	
3Htrans		0.510			0.114							0.190	0.105
3Hcis		0.454			0.214								
4Htrans					0.096							0.951	
4Hcis					0.127							0.946	
5Htrans					0.340		0.369						
3Mg3H2O	0.789										0.086		
3Mg4H2O	0.780			0.101						0.083	0.083		
4Mg4H2O	0.384		0.063	0.098		0.136		0.242	0.074				
5Mg4H2O	0.078		0.072	0.135		0.194		0.430	0.106	-0.088	0.118		
6Mg4H2O				0.139		0.132		0.346	0.098		0.346		
10Mg4H2O								0.101			0.959		
11Mg4H2O	0.302		0.267							0.149	0.218		
12Mg4H2O			0.149					0.119		0.384	0.240		
3Na3H2O	0.643										0.139		0.096
4Na3H2O	0.412		0.083	0.201		0.213		0.090					
5Na3H2O			0.108	0.252		0.366		0.178	0.089		0.088		
6Na3H2O				0.233		0.216		0.146			0.359		
10Na3H2O				0.106							0.955		
3Ca4H2O	0.740										0.110		0.123
4Ca4H2O	0.385			0.108		0.151		0.204			0.056		

5Ca4H2O	0.078		0.156	0.228	0.371	0.102	0.114		
6Ca4H2O			0.164	0.154	0.295	0.095	0.340		
10Ca4H2O					0.107		0.954		
13	0.552		0.575						
13Mg4H2O	0.702						0.104		
15Mg4H2O	0.130		1.104						
17H			0.112				0.975		
3	0.656		0.108	0.113					
5			0.378	0.448					
10							0.827		
3Hcis	0.483						0.217		0.162
5Hcis	0.122		0.384	0.321					
6Hcis			0.323	0.199			0.359		
10Hcis							0.927		
3Htrans	0.484						0.223		
5Htrans	0.135		0.394	0.318					
10Htrans							0.935		
3Mg4H2O	0.779					0.120			
5Mg4H2O			0.149	0.193	0.398		0.153		
10Mg4H2O							0.945		
11Mg4H2O									
12Mg4H2O									
3Mg3H2O	0.786					0.123			0.116
5Mg3H2O	0.106		0.136	0.171	0.437		0.152		
10Mg3H2O							0.946		
3Mg2H2OOH	0.818					0.118			
5Mg2H2OOH		0.100	0.259	0.327	0.209		0.122		
10Mg2H2OOH							0.939		
13	0.563		0.523						
15	0.158		1.008						
17							0.931		
13H	0.545		0.303				0.111		
15H	0.130		1.117						
17H			0.112				0.975		
13Mg4H2O	0.694					0.104	0.102		0.126
15Mg4H2O	0.169					0.998			
17Mg4H2O							0.932		

Table S6. Detailed results of *ab initio* and DFT calculations. G3B3 results.

	G3B3				
Name	Enthalp	Energy (0K)	dE Etot+ZPE [KJ/mol]	RSE Etot+cH [KJ/mol]	nimag
1a	-770.642442	-770.656823	0.0		0
3	-770.010631	-770.024792	0.0	-86.9	0
1aHtrans	-771.172803	-771.187029	0.0		0
3Htrans	-770.553838	-770.568119	0.0	-120.7	0
10Htrans	-770.518173	-770.532871	92.5	-20.9	0
4Htrans	-770.493756	-770.507487	159.2		1
5Htrans	-770.496355	-770.510492	151.3		0
6Htrans	-770.496353	-770.510491	151.3		0
13H	-568.847307	-568.860211	0	-100.8	0
(13-H)H	-569.473844	-569.474788			0
14H	-568.800441	-568.813332	123.1		1
15H	-568.807177	-568.820278	104.8		0
16H	-568.806786	-568.8195	106.9		1
17H	-568.816851	-568.817795	111.4	-20.8	0

Table S7. Calculated relative energies for the radical rearrangements of **3** complexed to different ions

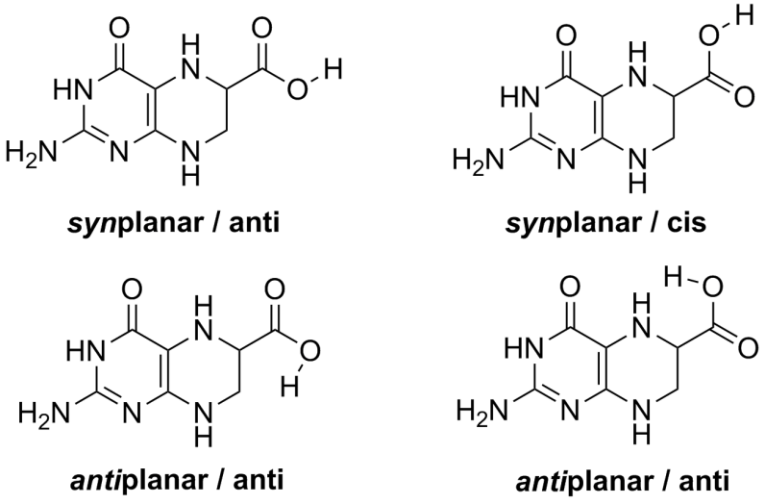
	B3LYP/ 6-31+G(d)[a]	MP2[b]	M06-2X[b]
3Ca$_{4H2O}$	0.0	0.0	0.0
4Ca$_{4H2O}$‡	85.5	73.3	78.4
5Ca$_{4H2O}$	74.0	50.7	62.2
6Ca$_{4H2O}$‡	77.2	70.4	72.1
10Ca$_{4H2O}$	9.1	-3.4	7.0
3Mn$_{4H2O}$	0.0	0.0	0.0
4Mn$_{4H2O}$‡	79.4	75.6	77.3
6Mn$_{4H2O}$‡	74.7	74.8	71.8
10Mn$_{4H2O}$	0.5	-9.0	2.2
3K$_{4H2O}$	0.0	0.0	0.0
4K$_{4H2O}$‡	142.9	150.1	131.7
5K$_{4H2O}$	124.5	118.0	102.9

6K$_{4H2O}$‡	131.0	128.6	114.7
10k$_{4H2O}$	66.6	46.1	60.5
3Na$_{3H2O}$	0.0	0.0	0.0
4Na$_{3H2O}$‡	130.5	144.8	121.7
5Na$_{3H2O}$	122.6	123.2	97.3
6Na$_{3H2O}$‡	128.7	129.1	113.4
10Na$_{3H2O}$	62.7	48.6	49.6

Table S8. Calculated radical stabilization enthalpies the rearrangement of **3** complexed to different ions at 298.15 K.

	B3LYP/ 6-31+G(d)[a]	MP2[b]	M06-2X[b]
3Ca$_{4H2O}$	-64.3	-23.1	-37.6
10Ca$_{4H2O}$	-35.5	-21.3	-28.2
3Mn$_{4H2O}$	-49.9	-10.7	-25.1
10Mn$_{4H2O}$	-33.7	-20.4	-27.1
3K$_{4H2O}$	-136.8	-104.1	-119.5
10K$_{4H2O}$	-36.9	-24.1	-31.8
3Na$_{3H2O}$	-96.6	-62.7	-81.0
10Na$_{3H2O}$	-39.1	-25.0	-32.6

[a] All radical energies are given in kJ mol-1; absolute energies are given in the supporting information; B3LYP, ROMP2, M06-2X energies are corrected with B3LYP/6-31+G(d) enthalpy corrections (BMK values with BMK/6-31+G(2df,p) enthalpy corrections respectively).[b] basis set 6-311++G(3df,3p).



Scheme S1. Conformer nomenclature of CPH4.