

**Elucidation of complexation multi-equilibrium with Mg^{II} and a
multisite ligand. A combined electronic spectroscopies and DFT
investigation.**

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Table S1: Centres, widths, scale coefficient and linear combination coefficients obtained for each Gaussian function from the analysis of the spectra obtained by variation of temperature (centres given in nm and eV, widths in cm^{-1} and eV, x_5 and η_i without unit).

	μ_3	σ_3	$\mu_{5,1}$	$\sigma_{5,1}$	$\mu_{5,2}$	$\sigma_{5,2}$	x_5		
	429 (2.89)	1104 (0.14)	399 (3.11)	1357 (0.17)	331 (3.75)	1920 (0.24)	2.52*		
T	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C	50°C
η_3	1157	1224	1289	1333	1371	1402	1429	1456	1474
η_5	1858	1805	1751	1708	1668	1623	1594	1554	1520

* This scale coefficient cannot be directly compared with the experimental data due to the presence of the normalisation coefficient of the Gaussian functions that includes their widths.

Table S2: Main geometrical parameters in the fundamental state for Q, C3 and C5 and in the first excited state for C3 and C5 (angle in ° and bond lengths in Å).

	Q	S ₀ C3	S ₁ C3	S ₀ C5	S ₁ C5
C2-C1'	1.458	1.455	1.417	1.458	1.426
Dihedral angle	4.4	0.8	0.3	0.3	0.1
C9-O1	1.349	1.340	1.360	1.352	1.345
O1-C2	1.360	1.365	1.378	1.354	1.381
C2-C3	1.367	1.387	1.426	1.365	1.404
C3-C4	1.441	1.446	1.445	1.442	1.401
C4-C10	1.427	1.418	1.411	1.418	1.449
C10-C9	1.401	1.404	1.407	1.413	1.381
C9-C8	1.385	1.388	1.376	1.380	1.405
C8-C7	1.392	1.389	1.408	1.395	1.404
C7-C6	1.401	1.404	1.390	1.390	1.376
C6-C5	1.382	1.380	1.391	1.405	1.433
C5-C10	1.417	1.422	1.422	1.449	1.446
C3-O3	1.349	1.305	1.285	1.349	1.347
C4-O4	1.256	1.279	1.310	1.272	1.306
C5-O5	1.337	1.338	1.338	1.285	1.269
O3-Mg	–	2.010	2.062	–	–
O4-Mg	–	2.082	2.038	2.030	1.989
O5-Mg	–	–	–	1.985	2.041

The variations are illustrated on Figures S1 and S2.

Figure S1: Main bond variations occurring upon the complexation of Q with Mg^{II}. Only variations above 1 pm are reported, green is for lengthening whereas red is for shortening. (a) Formation of C3; (b) formation of C5.

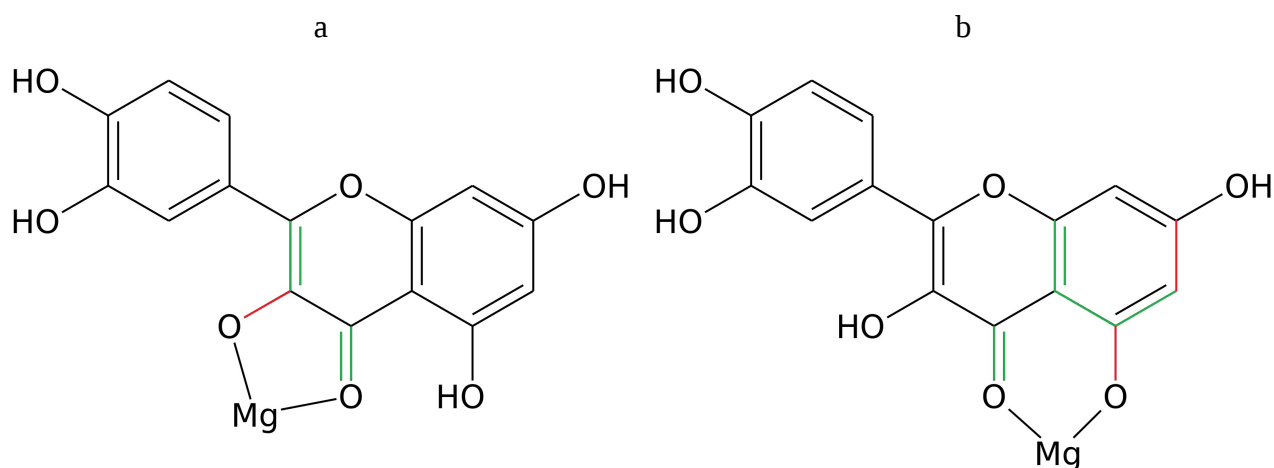
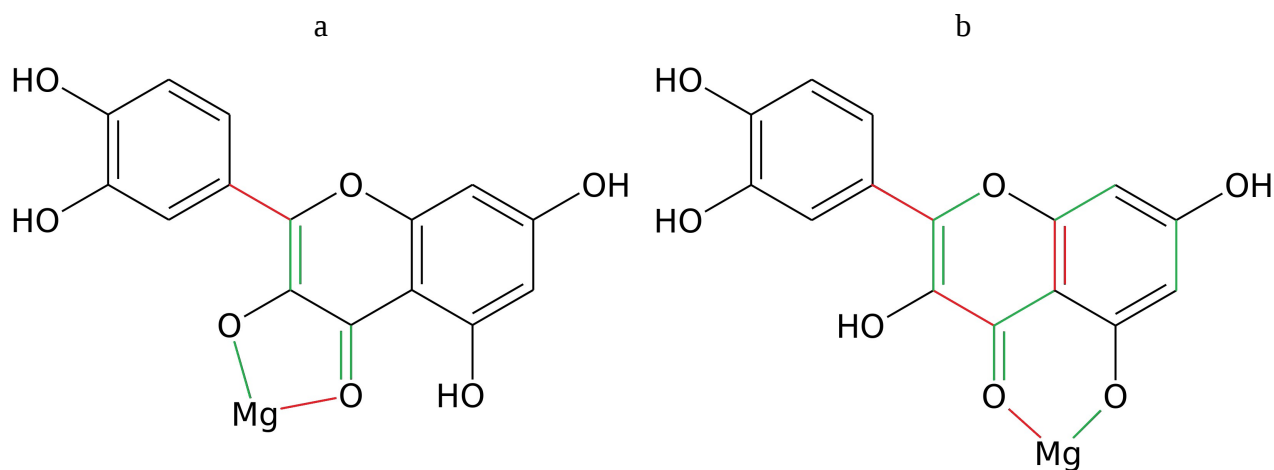


Figure S2: Main bond variations occurring upon the S1 ← S0 transition for C3 (a) and C5 (b) complexes. Only variations above 2.5 pm are reported, green is for lengthening whereas red is for shortening.



Cartesian coordinates for 3HF

C	-3.6337265478	-2.0693725353	-0.1142159094
C	-4.3420688146	-0.857408373	-0.0897323663
C	-3.657880287	0.3374807585	-0.0501783446
C	-2.2535697759	0.3477870356	-0.0342481373
C	-1.5682660508	-0.8694982996	-0.0596665857
C	-2.2537282837	-2.0850411959	-0.0995768461
H	-5.4260674817	-0.8661259956	-0.1019708545
H	-1.6919881603	-3.0118297718	-0.1183496792
C	0.5548947927	0.1821293574	-0.0084182195
C	-0.0386922529	1.4119158383	0.020053829
C	-1.4802371096	1.5705635585	0.0086569902
O	-1.9467029502	2.7172115472	0.0369011672
C	1.98339541	-0.1372712337	-0.0010517646
C	2.3885847095	-1.4817226281	-0.0131253951
C	2.9703996784	0.8608094459	0.01664406
C	3.7346488831	-1.8148011468	-0.0069102568
H	1.6430919579	-2.2665856155	-0.0270824335
C	4.3156590183	0.516620924	0.0220591814
H	2.686259749	1.9033381934	0.0254862532
C	4.7058271563	-0.8180683615	0.0107267835
O	0.6447463255	2.5699488886	0.0617342281
H	-0.0536831271	3.2529694074	0.0744194565
O	-0.2210591659	-0.9310241028	-0.0473148825
H	4.0262884917	-2.8597860032	-0.0159514889
H	-4.1750847799	-3.0087709061	-0.1452799209
H	5.7585775142	-1.0803805515	0.0153821425
H	5.0640997375	1.3019924519	0.0352360247
H	-4.1796010167	1.2878529939	-0.0305396212

Cartesian coordinates for 5HF

C	3.177416326	2.1056334187	-0.855332616
C	3.9581517334	0.9883361993	-0.5713450931
C	3.3447992672	-0.2066464365	-0.2158586735
C	1.9326699947	-0.2751308666	-0.1469215114
C	1.188741768	0.8726472992	-0.4398913827
C	1.7907266726	2.0704712031	-0.7960116773
H	5.039864548	1.0333820974	-0.6226649614
H	1.1831554219	2.9390421915	-1.017517662
C	-0.8310051412	-0.2683586736	-0.0427387923
C	-0.180928885	-1.4197052509	0.268766563
C	1.2501001152	-1.5008946103	0.2240515568
C	-2.2862408132	-0.0787527563	-0.0286302751
C	-2.8268755676	1.2100258882	0.0478730998
C	-3.1494522507	-1.1788774636	-0.0872580101
C	-4.2028368548	1.3904780343	0.0810673308
H	-2.1664508755	2.067750764	0.0917836722
C	-4.5234294231	-0.9922096935	-0.0574562531
H	-2.7517595552	-2.1833325232	-0.1770988556
C	-5.0545299841	0.2918243175	0.0294056062
O	-0.1703010668	0.8506167594	-0.389876614
H	-4.6106680861	2.3933154052	0.1482631865
H	3.6681343546	3.0328224204	-1.1317985649
H	-6.1296818032	0.4348464089	0.0521832409
H	-5.1823583024	-1.8520513837	-0.1105690266
H	-0.7375069349	-2.2951083116	0.5744956579
O	1.8822045976	-2.5437863478	0.4939644049
O	4.0811063672	-1.2872138235	0.0605342833
H	3.4357984975	-2.0088851861	0.2854654468

Cartesian coordinates for 3'4'diHF

C	-4.3411239618	-1.8020544978	-0.5946966136
C	-5.0026499014	-0.5828375902	-0.4013378084
C	-4.272727679	0.5658432272	-0.168279915
C	-2.8735929409	0.5240290081	-0.1241769373
C	-2.2380487801	-0.702421513	-0.3200565516
C	-2.9607918694	-1.8703187107	-0.5553767713
H	-6.0857341682	-0.5444032402	-0.4349768866
H	-2.4306672973	-2.8042073494	-0.7034276914
C	-0.1086392958	0.2577776765	-0.0701754446
C	-0.6426745311	1.4890076179	0.1448509631
C	-2.0632342005	1.7260727951	0.1247075607
O	-2.5671295619	2.8362829839	0.3089225423
C	1.3173699895	-0.072286315	-0.0719407484
C	1.7365006728	-1.4008096952	0.0403749209
C	2.2832065549	0.9394298098	-0.1811045954
C	3.0876116435	-1.7160016404	0.0584557353
H	1.0031318409	-2.1926073632	0.1247003906
C	3.6265102268	0.6232003942	-0.1659093374
H	1.9915375679	1.9775508728	-0.2998890088
C	4.0400337854	-0.7131698322	-0.0437082868
O	5.3528620443	-1.0198549081	-0.0317586883
O	-0.8836035521	-0.8212488423	-0.2983752372
H	5.8603427994	-0.202203108	-0.1136112721
H	3.4179662751	-2.7444722183	0.1527462746
O	4.638669488	1.5231209547	-0.2751789481
H	4.3018839146	2.4207547809	-0.3521194955
H	-4.9134471482	-2.7051158283	-0.7776970106
H	-4.7587512051	1.5229895168	-0.0139651673
H	0.0064945895	2.3285004044	0.3555617283

Cartesian coordinates for 3HF-Mg^{II}

C	-1.7119400063	4.363945558	0.0751530381
C	-2.8947985011	3.602324408	0.0551943582
C	-2.82818564	2.2291667597	0.0209474191
C	-1.5781338623	1.5795891529	0.0056600438
C	-0.4147584816	2.3567338731	0.026194559
C	-0.4761463237	3.753334875	0.0610712533
H	-3.8566999416	4.1025212718	0.0667388956
H	0.4446600948	4.3251074355	0.0761813504
C	0.9849942336	0.4474685691	-0.0206798245
C	-0.1000211855	-0.4193478107	-0.0470841169
C	-1.439023251	0.1514685068	-0.0315878797
O	-2.4238331527	-0.6349890361	-0.0522395659
C	2.3994437683	0.0893825021	-0.0234354719
C	3.3807081145	1.0969692048	0.0024083634
C	2.8210100246	-1.2513981646	-0.0490136055
C	4.7290385982	0.7739218237	0.0031654834
H	3.08052936	2.1372551525	0.022215809
C	4.1746301799	-1.5629803636	-0.0475870158
H	2.0731209473	-2.032114876	-0.0694193434
C	5.1355692065	-0.5578552205	-0.0213642563
O	-0.024345243	-1.7176451891	-0.0826849505
O	0.8016283786	1.79580376	0.0136731169
H	5.4682289956	1.5682241509	0.0233305605
H	-1.7701383349	5.4467477652	0.1019508936
H	6.1914678621	-0.8077479056	-0.0202568904
H	4.4798235192	-2.6044268085	-0.0670118351
H	-3.7246565848	1.6197209314	0.0047439569
Mg	-1.8210284973	-2.6194704814	-0.1178300618
O	-3.8425895495	-3.1398938997	-0.1361734557
H	-4.2205973474	-4.0194757037	-0.0528978334
O	-1.3113856903	-4.6451599351	-0.209999204
H	-0.9700902898	-5.0474018229	-1.0136825108
H	-4.5532492066	-2.5062169277	-0.0037598885
H	-0.9315247242	-5.1188389748	0.5352913659
O	-1.8292541348	-2.7926956976	-2.2366467142
H	-2.6479686114	-2.7833777043	-2.7413093308
O	-1.7333388192	-2.9455328358	1.979791823
H	-2.4945840238	-2.9541438088	2.567327089
H	-1.1815553149	-2.3043162787	-2.7534130326
H	-1.0214965657	-2.508043255	2.4566514087

Cartesian coordinates for 5HF-Mg^{II}

C	1.4072471564	3.0104480426	-2.1963972713
C	2.4789998163	2.2530679652	-1.7621764394
C	2.3132729256	1.1665931993	-0.8733261636
C	0.9665181418	0.8780677697	-0.435620641
C	-0.0875930934	1.6873058624	-0.9138037791
C	0.1036530302	2.7445975647	-1.7829321092
H	3.486835326	2.4753159925	-2.0964332153
H	-0.7430181193	3.3300841169	-2.1184321622
C	-1.6990390405	0.4724864561	0.3030472658
C	-0.7456080021	-0.3428754755	0.818166272
C	0.6369689095	-0.1940070906	0.4710713647
C	-3.1366705678	0.4081160486	0.5909268435
C	-3.9563497357	1.5104231054	0.3227885544
C	-3.7053464435	-0.7482066251	1.13717337
C	-5.313671226	1.4595016321	0.6095216744
H	-3.5251072092	2.4089076603	-0.1021846602
C	-5.062709892	-0.7946207481	1.4187217382
H	-3.093709067	-1.6232479852	1.3256715759
C	-5.8706569432	0.3090144041	1.1583717145
O	-1.3810178128	1.4611944336	-0.5417037621
H	-5.938022661	2.3223838586	0.4040147038
H	1.5834145399	3.8359252377	-2.8794415194
H	-6.9320811042	0.2698582437	1.3792843425
H	-5.493090699	-1.6986088018	1.8358766698
H	-1.0082758358	-1.1204009357	1.5222298084
O	1.4781905188	-0.9885591829	0.9736244638
O	3.3320725449	0.4824968538	-0.4875164595
Mg	3.4788201585	-1.0750272735	0.7290007645
O	5.5343251108	-0.9541173432	0.3740233904
H	6.2223547981	-1.6092676762	0.5162375002
O	3.8373853247	-2.7259178817	1.9776898123
H	3.7814517329	-2.6497902699	2.934385956
H	5.8362221731	-0.35430246	-0.3145684572
H	3.5453031331	-3.6103100557	1.739951652
O	3.8127597929	-0.0099496306	2.5491917765
H	4.6263304453	0.4927301511	2.6530864503
O	3.2554672773	-2.6202114692	-0.7333041296
H	2.4008243129	-2.7263930444	-1.1617656433
H	3.9174623467	-2.77625153	-1.4134144044
H	3.112275937	0.5253108809	2.9335531529

Cartesian coordinates for 3'4'diHF-Mg^{II}

C	-5.8899910951	-1.6492011893	-0.1592311038
C	-6.4677812391	-0.3737820207	-0.1647001824
C	-5.6594882614	0.7465234501	-0.1731270321
C	-4.2654560266	0.619170385	-0.1767461805
C	-3.7134707632	-0.6618520929	-0.1715342894
C	-4.5153544291	-1.8014312639	-0.1624027829
H	-7.5470598157	-0.2690461361	-0.1622773938
H	-4.0497174084	-2.7804104023	-0.1585258418
C	-1.5142394204	0.179157781	-0.185226066
C	-1.9727395373	1.4647003156	-0.1855966418
C	-3.3709794956	1.7881473002	-0.1842570253
O	-3.8033659051	2.9458171604	-0.1872108749
C	-0.1223656615	-0.2425327694	-0.1928839175
C	0.2198879892	-1.6012898433	-0.1338322503
C	0.9208574609	0.7033732218	-0.2626352417
C	1.5398758005	-2.018082128	-0.1412910283
H	-0.5672871567	-2.3435553773	-0.0795731376
C	2.2211358336	0.2753088843	-0.269751006
H	0.7110878439	1.7666195806	-0.318174115
C	2.5992358831	-1.0947915439	-0.2119712116
O	3.8555101204	-1.411020595	-0.2295084874
O	-2.3699329712	-0.8658526148	-0.1767394618
H	1.7829797153	-3.074675957	-0.0945923793
O	3.3127473104	1.1252643538	-0.3400584732
Mg	5.175223708	0.0793873018	-0.3618456948
H	3.061283422	2.0525251232	-0.3898263409
O	6.3474584139	1.7821288663	-0.5174617804
O	6.8095294171	-1.1912943944	-0.3686891399
H	7.7425292011	-0.9638202571	-0.4038903574
H	6.7473466741	-2.1484366055	-0.3021179284
H	6.6540707901	2.3254012346	0.2134312101
H	6.5838800611	2.221094169	-1.3389635562
H	-6.522880576	-2.5301496069	-0.152536128
H	-6.0784294303	1.7469351405	-0.1771075154
H	-1.2707348118	2.287660519	-0.1847193347
O	5.4329084213	0.4264602746	1.7165409408
H	5.9557983632	-0.1878025502	2.2409588538
O	5.2411947132	0.1946083223	-2.482883252
H	5.7163021509	-0.4779523691	-2.9806076469
H	4.6999472708	0.7007466861	2.2760396615
H	4.4581148003	0.407558057	-2.9995392165

Cartesian coordinates for Q

C	3.8888199803	-1.7817615935	0.0371531883
C	4.526969761	-0.5344437379	0.0211932704
C	3.7643453104	0.6181218163	0.0003385361
C	2.3500695645	0.530135129	-0.0043008148
C	1.7541792833	-0.7373936716	0.0114957176
C	2.5024388054	-1.9022184004	0.0323761288
H	5.6094104702	-0.4622885102	0.0238511625
H	2.0264652898	-2.8741196316	0.0451135214
C	-0.4272646251	0.21001415	-0.0121416835
C	0.095724366	1.4724003137	-0.0303496305
C	1.5200954	1.6904374043	-0.0257399626
O	1.9544039361	2.868438611	-0.0442432691
C	-1.8306353889	-0.1867903653	-0.0177217183
C	-2.1700637383	-1.5449312278	-0.0962953822
C	-2.8653011055	0.7625228132	0.059591261
C	-3.4966168165	-1.9457959132	-0.1015959805
H	-1.39118129	-2.29352897	-0.1555858809
C	-4.1847907366	0.3547020786	0.0572476926
H	-2.6383677933	1.8188236266	0.1252068412
C	-4.5138307506	-1.0051527781	-0.0250635292
O	-5.8046766271	-1.3983914855	-0.029666569
O	4.5942618532	-2.9294014777	0.0578259871
O	4.3567326611	1.8163589477	-0.0160052423
O	-0.6558130969	2.5919720771	-0.0575315758
H	3.6371760722	2.4924180053	-0.0304380956
H	-0.0108781541	3.3220152491	-0.0674589874
O	0.411265203	-0.8606710955	0.0080337448
H	5.5383771676	-2.741889324	0.0598195165
H	-6.3643598584	-0.6139006876	0.0330457474
H	-3.7582222003	-2.9963349354	-0.1648081269
O	-5.2520554169	1.1951386159	0.1327467853
H	-4.9677015257	2.1114229677	0.1988813476

Cartesian coordinates for C3

C	-5.7776464592	-2.769528629	1.4012754895
C	-5.7248060663	-1.7765438773	0.410747297
C	-4.6504890576	-0.9118910975	0.3697142318
C	-3.605596427	-1.0298870725	1.3265176977
C	-3.7001713752	-2.0387756141	2.297786073
C	-4.7746726213	-2.9154213153	2.350631181
H	-6.5187125718	-1.680076275	-0.3221238651
H	-4.829648848	-3.6860144853	3.1087043877
C	-1.6327674494	-1.3762699863	3.2681032456
C	-1.4565053623	-0.3507611815	2.3506762189
C	-2.4773651988	-0.171704395	1.3416812564
O	-2.3236461529	0.7678736151	0.4871414234
C	-0.740150008	-1.743414851	4.3563438361
C	-1.0499097364	-2.8252353057	5.1959270024
C	0.4492510247	-1.0296985813	4.5937181983
C	-0.2052295801	-3.1826171548	6.2349424277
H	-1.9581323959	-3.3911391406	5.0349540567
C	1.2841726809	-1.3932917471	5.6327506102
H	0.6987558682	-0.1937620078	3.9505069903
C	0.9658938443	-2.4734880475	6.4648412243
O	1.7863849687	-2.8248617657	7.4809220109
O	-6.8132356791	-3.6299330069	1.4725406803
O	-4.5924972453	0.0383343599	-0.570554673
O	-0.4445601263	0.4716502121	2.3140742841
H	-3.7557883899	0.5374661844	-0.4206218782
O	-2.7345995816	-2.1796124193	3.2159277782
H	-7.4550699133	-3.4387649264	0.7811249362
H	2.5375556984	-2.2184686996	7.4891965022
H	-0.4460001001	-4.0185875347	6.8828488052
O	2.4531373647	-0.7612895458	5.9362799441
H	2.605913428	-0.0221082263	5.3405484741
Mg	-0.5513551115	1.8091677641	0.817938164
O	1.2159092547	2.8999364595	1.0622545206
H	1.3510303322	3.5216843805	1.7829212886
O	-0.9913155337	3.0276054804	-0.8179247402
H	-0.4429646992	3.7503245506	-1.1351125806
H	-1.7770629317	2.9968160182	-1.3705868357
H	2.0733822711	2.5285977945	0.8359485136
O	0.6594279553	0.6089676186	-0.4479187448
H	0.8402896105	-0.2987351561	-0.1859603977
H	0.5776727547	0.6086813199	-1.4061160918
O	-1.3738564623	3.2760000673	2.1112411817
H	-1.9868230853	3.9590096474	1.8239850443
H	-1.6676772171	2.988940733	2.9810851912

Cartesian coordinates for C5

C	-2.238819	3.402623	0.016231
C	-3.234603	2.432387	0.001885
C	-2.924892	1.061791	-0.004337
C	-1.521667	0.70224	0.004076
C	-0.555081	1.73244	0.017761
C	-0.882908	3.073279	0.024153
H	-4.281822	2.719471	-0.004178
H	-0.116591	3.837086	0.034883
C	1.252648	0.183309	0.02074
C	0.371327	-0.858372	0.008224
C	-1.053131	-0.635762	-0.001204
O	-1.764296	-1.690373	-0.014646
C	2.710287	0.142303	0.029102
C	3.439329	1.339932	0.033975
C	3.415262	-1.074408	0.032122
C	4.825157	1.327816	0.041217
H	2.918546	2.28834	0.031816
C	4.79649	-1.078009	0.039477
H	2.883564	-2.017073	0.028776
C	5.516128	0.124487	0.043895
O	6.865828	0.115522	0.050624
O	-2.534227	4.720864	0.023119
O	-3.854893	0.175301	-0.016698
O	0.750911	-2.152843	0.002282
H	-0.090763	-2.646173	-0.006805
Mg	-3.790489	-1.808412	-0.024879
O	-5.876286	-1.776188	0.003143
H	-6.356737	-0.951643	-0.113615
O	-3.902167	-3.903872	-0.033508
H	-3.69935	-4.427172	0.746951
H	-6.486544	-2.498454	-0.16689
H	-3.670793	-4.429615	-0.804234
H	7.166194	-0.802208	0.05079
H	-3.489118	4.841993	0.018271
O	0.766692	1.446852	0.025448
H	5.387764	2.254954	0.044656
O	5.563948	-2.201638	0.043021
H	5.018156	-2.993473	0.037152
O	-3.831825	-2.099708	2.087304
H	-4.637505	-1.890817	2.569827
O	-3.773937	-2.081454	-2.14161
H	-4.5327	-1.846157	-2.683999
H	-2.995174	-1.806143	-2.634748
H	-3.102363	-1.787687	2.63109