Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Stepwise dissociation of ion pairs by water molecules: cation-dependant separation mechanisms between carboxylate and alkali-earth metal ions

Jeremy Donon,[a] Jean-Xavier Bardaud,[a] Valérie Brenner,[a] Shun-ichi Ishiuchi,[b,*] Masaaki Fujii,[b,*] Eric Gloaguen[a,*]

S1. Experimental methods

The experimental setup was reported previously (see Figure S1 and ref.[1] and its Supporting Information). Briefly, a 10^{-4} M solution of $Ca(AcO)_2 \cdot H_2O$ in methanol was electrosprayed to generate complexes of carboxylate and alkali-earth metal ions. These complex ions were introduced into vacuum via a glass capillary heated to 60°C. The ions were guided into a clustering linear ion trap in which water molecules were introduced by a pulsed valve and micro-hydrate the ions. The clustering trap was cooled down to 180 K by a closed cycle refrigerator. Hydrated complex ions of interest were mass-selected by a quadrupole mass filter, and then introduced into a cryogenic quadrupole ion trap (QIT). The QIT was cooled to 4 K by a closed cycle He refrigerator. A 1:4 mixture of hydrogen and helium buffer gas was introduced to the QIT via a pulsed nozzle and cooled down by collisions with the QIT's gold-coated copper electrodes.[2] The complex ions were trapped and cooled to ~10 K by collisions with helium gas. Hydrogen molecules were condensed onto the cold ions, forming a variety of weakly-bound hydrogen cluster ions. The cluster ions were then irradiated with a tunable IR laser. Absorption of a photon resulted in the dissociation of the clusters, yielding the parent complex ion as a charged fragment. An IR absorption spectrum of the trapped ions was then generated by monitoring the fragment yield, recorded by a time-of-flight mass spectrometer as a function of the wavenumber of the dissociating laser light. IR spectra were obtained from the H_2-loss of the following $(Ca^{2+}, AcO^-)(H_2O)_n(H_2)_m$ clusters: (n=0, m=8), (n=1, m=7), (n=2, m=4), and m=1 for $3 \leq n \leq 8$, *m* being chosen for each *n* in order to get a signal-to-noise ratio compatible with IR spectra recording. $(Ba^{2+}, AcO^-)(H_2O)_n(H_2)$ clusters for $0 \leq n \leq 5$ were investigated similarly.

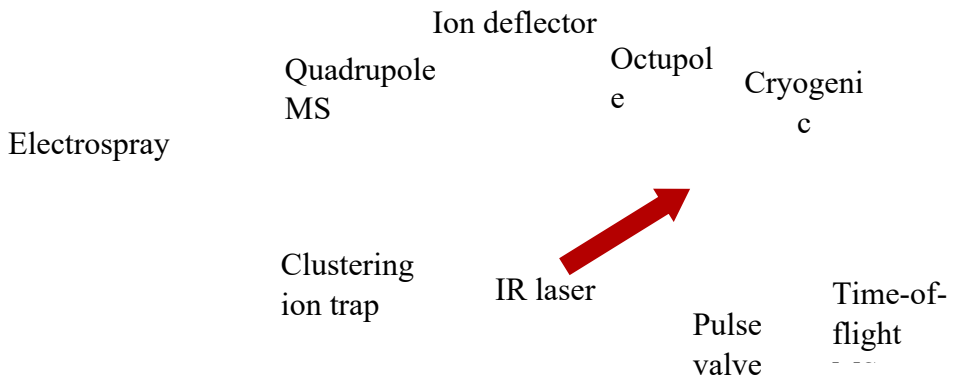

Figure S1 Experimental setup

S2. Theoretical methods

H_2-tagged (Ca^{2+}, AcO^-)$(H_2O)_{n=0-8}$ and (Ba^{2+}, AcO^-)$(H_2O)_{n=0-5}$ clusters were explored manually, taking into account that H_2-tags are added in the last stage of cluster formation and must be located on the outer layers. These tags are therefore considered innocuous to the inner cluster structure and are often omitted in the calculations reported in the literature. However, as they may shift theoretical IR frequencies[3] by typically several cm^{-1} and sometimes up to ~15 cm^{-1} for clusters with several tags, they are included in our calculations, but not shown on figures for clarity purposes.

As experimental spectra are specific to that of bidentate ion pairs,[4, 5] only this type of structures was considered. The respective number of computed structures as a function of the cluster size were respectively 1, 5, 21, 14, 15, 31, 11, 4, 4 for Ca^{2+} and 8, 6, 12, 17, 10, 29 for Ba^{2+}. While these numbers ensure a rather complete exploration of the clusters up to n=5, the weak number of (Ca^{2+}, AcO^-)$(H_2O)_{n=6-8}$ structures cannot guarantee that other structures may also fit the IR spectra as well as those assigned in this study. Geometry optimization and frequency calculations have been conducted at the RI-B97-D3/dhf-TZVPP[6-8] level using the TURBOMOLE package.[9] A vibrational mode analysis was further conducted, in particular to assign the $\nu_s(CO_2^-)$ and $\nu_a(CO_2^-)$ modes. Potential energy contributions V_{ij}^n were calculated according to the following equation:[9]

$$V_{ij}^n = \frac{L_i^n L_j^n F_{ij}}{\omega^n}$$

where n designates the nth normal mode, i and j are respectively the ith and jth internal coordinates, L_i^n and L_j^n are respectively the ith and jth elements of the nth normal mode vector expressed in the internal coordinate basis, F_{ij} are the elements of the force constant matrix expressed in the internal coordinate basis, and ω^n is the eigenvalue associated to the nth normal mode and depends on the harmonic frequency and the reduced mass. Coupling between the CO stretches, CO(1) and CO(2) was estimated by calculating the product of the following normalized coefficients : $\sum_i V_{iCO(1)}^n \times \sum_i V_{iCO(2)}^n$ for each mode n in the 1200-1600 cm^{-1} range. CO stretches were considered coupled if this product was higher than the arbitrary chosen value 0.01. Furthermore, the sign of the off-diagonal contributions $V_{CO(1)CO(2)}^n$ was used to determine the symmetric or antisymmetric nature of the coupling. Harmonic frequencies f_0 were then scaled with a scaling procedure specific to the mode in order to determine the theoretical frequencies f that can be compared to experiment:

- For $\nu_s(CO_2^-)$: $f = 1.1431 \times f_0 - 164.3\ cm^{-1}$
- For $\nu_a(CO_2^-)$: $f = 0.9272 \times f_0 + 137.9\ cm^{-1}$
- For $\delta(H_2O)$: $f = 0.81037 \times f_0 + 293.3\ cm^{-1}$
- For other modes ($\delta(CH_3)$, $\nu(CO)$ and their combinations) : $f = 1.018 \times f_0\ cm^{-1}$

The scaling functions of $\nu_s(CO_2^-)$ and $\nu_a(CO_2^-)$ are available in the literature.[4] That of $\delta(H_2O)$ has been determined by comparing frequencies resulting from dedicated RI-B97-D3/dhf-TZVPP calculations with experimental transitions of several clusters available in the literature.[10-15] Finally, a single scaling factor has been applied to the $\delta(CH_3)$ / $\nu(CO)$ modes, and has been chosen in order to fit the corresponding experimental transitions of the H_2-tagged (Ca^{2+}, AcO^-) and (Ba^{2+}, AcO^-) clusters.

The calculated intensities used to scale the experimental spectra (Fig. 1 and 2) are shown in Fig. S2.

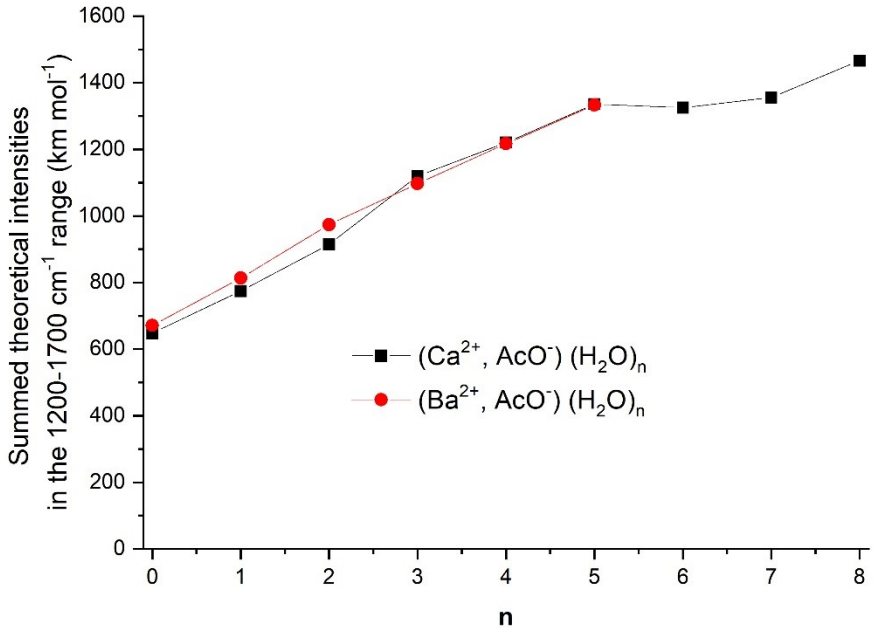

Figure S2 Summed theoretical intensities in the 1200-1700 cm^{-1} range.

3. Structures

$(Ca^{2+}, AcO^{-})(H_2)_8$

C	-3.47520	-0.79647	0.50697
C	-2.04078	-0.42314	0.28905
Ca	0.41912	0.15448	-0.04756
O	-1.46765	-0.65558	-0.83969
O	-1.35619	0.11350	1.23862
H	-3.94461	-0.10924	1.21410
H	-3.50122	-1.80069	0.95015
H	-4.01377	-0.82820	-0.44178
H	-0.40274	2.69011	0.97120
H	0.18793	3.01346	0.64284
H	-0.85509	1.63139	-2.10880
H	-0.39635	2.20947	-1.97907
H	0.74053	-0.99631	2.54774
H	1.47295	-1.09154	2.42394
H	0.63963	-1.04181	-2.62182
H	1.35656	-0.82585	-2.63809
H	2.18092	1.54617	1.86037
H	2.70390	1.45296	1.33397
H	2.11355	1.70918	-1.81360
H	2.60529	1.65569	-1.25199
H	0.17447	-2.67339	-0.22382
H	0.79733	-2.75914	0.18324
H	3.11651	-0.92363	0.22734
H	2.94491	-1.25142	-0.42330

$(Ca^{2+}, AcO^{-})(H_2O)(H_2)_7$

C	-3.75430	-0.17839	-0.27017
C	-2.29129	0.15649	-0.27058
Ca	0.21554	0.70698	-0.26745
O	-1.56726	-0.12409	-1.29505
O	-1.74817	0.70692	0.75743
H	-4.28078	0.37746	0.50692
H	-3.85992	-1.25245	-0.07082
H	-4.18382	0.01167	-1.25712
O	2.44712	0.04671	0.45036
H	3.22422	-0.17724	-0.07805
H	2.67477	-0.18910	1.35963
H	-1.11505	2.46651	-2.06773
H	-0.76370	3.04477	-1.74821
H	-0.41646	-1.49185	1.54314
H	0.15230	-1.87876	1.24990
H	0.41913	-1.88976	-1.62447
H	1.13306	-1.95255	-1.41159
H	-0.37358	3.22806	1.01443
H	0.28503	3.48981	0.77438
H	1.27322	0.79133	-3.04974
H	0.61484	0.44507	-3.13002
H	0.93189	1.23990	2.65567
H	0.25401	0.92646	2.68605
H	2.31520	2.66415	-0.95236
H	1.86901	2.85190	-1.52256

$(Ca^{2+}, AcO^{-})(H_2O)_2(H_2)_4$

H	-2.73650	-1.36780	-2.86065
H	-2.21775	-1.85404	-2.62683
H	0.14623	1.31132	2.75095
H	-0.14312	1.64183	3.35822
H	1.80039	1.72427	-0.96224
H	2.01699	2.18181	-1.51492
H	-4.04280	-1.72795	0.08213
H	-3.47601	-2.19952	0.21115
O	-0.90589	1.44698	-2.12987
H	-1.18947	1.80734	-2.97835
H	0.01356	1.73097	-2.00370
O	-2.52404	0.99761	1.52462
H	-1.83590	1.23255	2.16745
H	-3.36975	1.17911	1.95140
C	1.74633	-1.85746	0.81303
C	0.47824	-1.18767	0.36198
O	-0.47220	-1.88566	-0.13764
O	0.35228	0.09123	0.45832
Ca	-1.69121	-0.04215	-0.44795
H	2.37446	-2.03274	-0.06960
H	1.52203	-2.83229	1.25262
H	2.29613	-1.22374	1.51089

$(Ca^{2+}, AcO^{-})(H_2O)_3(H_2)$

H	2.10566	1.36014	2.77921
H	2.22092	1.97138	3.19710
H	0.73620	2.53939	1.79875
O	0.03426	2.81155	1.18516
H	0.13133	0.05118	-2.80366
O	-0.08657	0.96610	-2.57075
O	-2.70750	-0.08409	0.12428
H	-3.60848	0.02311	0.44971
H	-2.56932	-1.03114	-0.02696
H	0.06922	1.50410	-3.35527
H	-0.14766	3.73964	1.37178
C	0.79349	-1.15769	0.27799
C	1.63183	-2.36714	0.59797
H	2.67713	-2.15088	0.34935
O	1.00102	-0.06203	0.91081
O	-0.11700	-1.21662	-0.62379
Ca	-0.61481	1.00058	-0.24569
H	1.59618	-2.56048	1.67493
H	1.29209	-3.24111	0.04109

$(Ca^{2+}, AcO^{-})(H_2O)_4(H_2)$

C	3.46589	-1.74897	0.88344
C	2.05124	-1.26548	0.68375
Ca	-0.45448	-0.44499	0.34057
H	3.44970	-2.56526	1.61644
O	1.61746	-0.26094	1.34738
H	3.86794	-2.15073	-0.04979
O	1.28192	-1.87780	-0.13622
H	4.09894	-0.94971	1.27329
H	-1.94464	-2.00739	-2.12626
O	-0.60894	1.36990	-1.26534
H	-2.18333	-1.34682	2.67084
H	-1.08068	1.91717	2.58210
O	-0.62421	1.15986	2.20036
H	-0.65653	1.20716	-2.21550
H	-2.36630	-2.52039	1.68510
H	0.28452	1.16920	2.53979
O	-1.18208	-1.73806	-1.60325
H	-0.29256	2.27583	-1.16473
O	-2.04506	-1.61327	1.75344
H	-0.45975	-2.34747	-1.82377
H	0.94066	-3.81108	-2.73676
H	1.26228	-3.51878	-2.12687

$(Ca^{2+}, AcO^{-})(H_2O)_5(H_2)$

H	2.78442	1.71230	-0.19091
H	2.96599	2.19649	-0.73275
O	-2.23917	-0.92885	-1.10429
H	-2.29972	-0.45759	-1.95626
H	-2.79903	-1.71024	-1.16902
O	0.04987	1.04757	-1.24978
H	-0.39777	1.16354	-2.10457
H	0.89542	1.51250	-1.28250
O	-0.69969	0.76748	2.40105
H	0.20057	0.94719	2.71165
H	-1.30173	1.28776	2.94303
O	-1.13457	-2.72656	1.39420
H	-1.64494	-3.08752	2.12704
H	-0.32852	-3.26118	1.31886
O	-1.85053	0.76625	-3.37907
H	-2.47098	1.47876	-3.58068
H	-1.59645	0.39466	-4.23381
C	3.61511	-1.63187	1.12535
C	2.17600	-1.24934	0.87167
O	1.39235	-2.08180	0.29671
O	1.75165	-0.10144	1.24588
Ca	-0.38245	-0.59938	0.43032
H	3.95346	-2.36951	0.39475
H	3.68304	-2.08504	2.12250
H	4.25468	-0.74618	1.11763

$(Ca^{2+}, AcO^{-})(H_2O)_6(H_2)$

C	2.25409	-2.32433	-0.05566
C	1.20987	-1.23604	-0.06641
O	-0.02981	-1.53723	-0.01514
O	1.56423	-0.00932	-0.10134
Ca	-0.68688	0.74363	-0.00392
H	3.16389	-1.99321	-0.56068
H	1.86554	-3.23840	-0.50985
H	2.50572	-2.54987	0.98844
H	-3.69173	-5.11798	-1.35895
H	-3.50329	-5.01557	-2.07402
O	2.35262	2.32465	0.99163
H	2.45949	1.42107	0.62247
H	3.23129	2.66560	1.19077
O	-1.73073	0.27915	-2.13472
H	-1.46195	0.44150	-3.04501
H	-2.11667	-0.62005	-2.10213
O	-2.79751	-0.09552	0.80409
H	-3.00332	-0.93146	0.33529
H	-3.61504	0.22617	1.19659
O	0.22582	2.85319	-0.71838
H	1.08742	2.99541	-0.27368
H	-0.04723	3.69274	-1.10088
O	-2.46380	-2.17366	-1.00883
H	-2.86072	-3.02462	-1.22904
H	-1.55042	-2.34443	-0.69500
O	-0.09927	1.63465	2.16554
H	-0.25833	1.32775	3.06423
H	0.81372	1.98417	2.13461

$(Ca^{2+}, AcO^{-})(H_2O)_7(H_2)$

C	2.49368	-1.79776	-0.24126
C	1.31981	-0.88924	0.02592
O	0.12930	-1.31365	-0.22986
O	1.49123	0.26427	0.52142
Ca	-0.84796	0.78538	0.53493
H	3.43833	-1.25721	-0.16739
H	2.39343	-2.27010	-1.22298
H	2.48501	-2.60086	0.50596
H	4.79145	4.31352	-0.88578
H	4.79395	4.37524	-0.14183
O	1.98824	2.82559	-0.34902
H	2.21676	1.92557	-0.04197
H	2.81282	3.32202	-0.41505
O	-0.37975	1.73400	-1.63724
H	0.46817	2.20012	-1.71069
H	-0.46669	1.13661	-2.39628
O	-2.83609	0.11531	-0.62538
H	-2.60494	-0.29739	-1.48370
H	-3.73540	-0.14369	-0.40271
O	-0.20760	2.96511	1.29082
H	0.62574	3.20884	0.82602
H	-0.60694	3.77725	1.61740
O	-1.59186	-0.22153	2.55106
H	-1.45830	-1.20708	2.50113
H	-1.50743	0.02789	3.47712
O	-0.93573	-2.73696	1.96961
H	-1.48460	-3.52623	1.90626
H	-0.56849	-2.56978	1.08102
O	-1.21020	-0.85401	-2.63771
H	-1.28350	-1.43983	-3.39922
H	-0.63845	-1.30039	-1.98060

$(Ca^{2+}, AcO^{-})(H_2O)_8(H_2)$

C	2.30609	-2.28698	-0.34209
C	1.32515	-1.14491	-0.23433
O	0.09136	-1.36067	-0.04162
O	1.75419	0.06227	-0.34602
H	2.68979	-2.33048	-1.36822
H	1.83409	-3.23791	-0.09149
H	3.16309	-2.10402	0.31376
Ca	-0.48245	0.98052	-0.16550
H	-4.16035	-4.74939	-0.34223
H	-4.01800	-4.78081	-1.07425
O	2.74691	1.92945	1.68975
H	2.69079	1.12017	1.15425
H	3.16692	2.56294	1.09210
O	-1.96124	0.30163	-1.94052
H	-2.04952	0.45536	-2.88575
H	-2.37884	-0.55962	-1.73182
O	-2.43262	0.43053	1.12613
H	-2.80959	-0.43571	0.89629
H	-2.44014	0.52296	2.09411
O	0.05981	2.12210	1.82371
H	-0.36916	1.97430	2.68029
H	1.03829	2.19778	1.96057
O	0.38309	2.75498	-1.52902
H	0.11641	3.67054	-1.65968
H	1.37104	2.72782	-1.60091
O	-2.57240	-1.95740	-0.46428
H	-3.03001	-2.79970	-0.56830
H	-1.62903	-2.15632	-0.30625
O	3.04007	2.24122	-1.38067
H	2.88214	1.29274	-1.19742
H	3.68711	2.28535	-2.09383
O	-1.89385	1.26226	3.84113
H	-2.48113	1.93194	4.21419
H	-1.67199	0.67802	4.57692

$(Ba^{2+}, AcO^{-})(H_2)$

H	-1.34909	0.14410	-3.12143
H	-1.22489	-0.47931	-2.72541
C	1.51903	-1.92116	0.67566
C	0.53729	-0.81948	0.40367
O	-0.71973	-1.08388	0.31429
O	0.94427	0.39468	0.27885
Ba	-1.31356	1.25076	-0.07574
H	1.17164	-2.85848	0.23565
H	1.57668	-2.06427	1.76263
H	2.51237	-1.64996	0.31383

$(Ba^{2+}, AcO^{-})(H_2O)(H_2)$

C	-0.04193	-3.56390	0.13501
C	0.01753	-2.06604	0.01009
O	-0.46889	-1.50036	-1.03444
O	0.54442	-1.35634	0.94247
Ba	0.09243	0.78651	-0.27962
H	0.34800	-4.02175	-0.77941
H	-1.09176	-3.86883	0.21893
H	0.51427	-3.90880	1.00734
H	-1.92339	1.12962	-2.87526
H	-1.86402	0.38701	-2.80216
O	-0.52419	0.89112	2.34842
H	-0.30783	0.00769	2.68638
H	-0.85651	1.40386	3.09512

$(Ba^{2+}, AcO^{-})(H_2O)_2(H_2)$

H	-3.42794	-0.23147	1.73028
H	-2.97151	-0.71395	1.38549
O	0.83220	3.13944	0.88243
H	1.41800	2.48319	1.29213
H	1.27130	3.99452	0.95854
H	-1.05637	-0.10965	-2.47602
H	-1.54068	0.98448	-3.47008
O	-1.36250	0.80925	-2.53882
C	1.20757	-1.94493	0.79635
C	0.35552	-0.72449	0.55865
O	-0.57481	-0.77250	-0.32283
O	0.55492	0.34368	1.23527
Ba	-1.28643	1.64297	0.04873
H	0.56344	-2.77537	1.10570
H	1.96516	-1.75583	1.55765
H	1.68113	-2.24534	-0.14447

$(Ba^{2+}, AcO^{-})(H_2O)_3(H_2)$

C	1.58047	-1.80866	-0.10319
C	0.56370	-0.69871	-0.22330
O	-0.50114	-0.75057	0.48094
O	0.76837	0.26856	-1.03855
Ba	-1.52125	1.41748	-0.44932
H	1.17464	-2.70695	-0.58426
H	1.74251	-2.05531	0.94998
H	2.51973	-1.53762	-0.58771
H	-3.41729	-1.23526	-1.37074
H	-2.88653	-1.50544	-0.91938
O	0.70146	2.96413	-0.07716
H	1.12432	3.76525	0.25217
H	1.40989	2.35994	-0.35092
O	-2.57401	0.52402	1.94139
H	-3.20807	0.59770	2.66349
H	-2.04716	-0.27241	2.11137
O	-1.07521	0.94801	-3.11934
H	-1.35726	0.95277	-4.04097
H	-0.20016	0.52907	-3.09250

$(Ba^{2+}, AcO^{-})(H_2O)_4(H_2)$

C	2.10431	-1.94779	1.00927
C	1.12167	-0.93428	0.46637
O	0.00587	-1.33510	-0.01070
O	1.41471	0.30864	0.51774
Ba	-0.90660	1.11150	-0.52194
H	1.95336	-2.92499	0.54612
H	1.93111	-2.05206	2.08802
H	3.13127	-1.60169	0.87126
H	-3.22030	1.77487	-2.84878
H	-3.07441	2.50104	-2.75383
O	1.39673	2.20428	-1.61731
H	1.86402	2.74733	-2.26134
H	2.07056	1.74786	-1.08933
O	-0.09581	2.33750	1.82884
H	0.74213	1.87255	1.98093
H	-0.22290	2.93928	2.57032
O	-2.61836	-0.60183	0.83078
H	-3.43118	-0.79115	1.31204
H	-2.05953	-1.39213	0.89695
O	-1.04474	-0.73309	-2.59501
H	-0.64727	-1.50560	-2.16321
H	-1.14066	-0.95214	-3.52821

$(Ba^{2+}, AcO^{-})(H_2O)_5(H_2)$

C	1.48077	-1.36805	0.20386
C	2.39507	-2.54887	0.45642
H	2.18514	-2.93907	1.46060
H	2.19815	-3.35090	-0.25871
H	3.44347	-2.24452	0.42601
Ba	-0.41273	1.07029	-0.21991
O	1.88672	-0.19303	0.49732
O	0.31539	-1.57599	-0.27353
H	-3.51056	1.56938	-1.69979
H	-3.75666	1.34905	-1.03120
H	0.63404	1.94999	3.19349
H	-0.39692	-1.21525	-2.26940
H	-2.86902	-1.11375	1.44724
H	-2.64738	3.81704	-0.57477
H	-0.99594	-0.48640	-3.50785
O	-0.75358	-0.36760	-2.58362
H	2.52897	2.57917	-1.81193
O	-2.12548	-0.82152	0.90972
H	-1.57411	-1.60286	0.73532
O	0.67004	1.60766	2.29421
O	-1.73310	3.63817	-0.32276
O	2.00508	2.07806	-1.17815
H	2.59335	1.41202	-0.78587
H	-1.35915	4.49930	-0.09816
H	1.43544	1.01168	2.24546

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