Supporting Information

Exploring the triplet excited state potential energy surfaces of a cyclometalated Pt(II) complex: Is there Non-Kasha emissive behavior?

Daniel Escudero,[a,*] Walter Thiel[a]

[a] Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Mülheim an der Ruhr, Germany.

Pt(II) complexes, phosphorescence, Kasha-rule, photodeactivation mechanisms, DFT, radiative rates.

Computational details

All calculations are based on density functional theory (DFT). The geometries of the singlet ground state (^{1}GS), the lowest triplet excited states (^{3}MLCT/^{3}LC$_{ppy}$, ^{3}MLCT/^{3}LC$_{acac}$, ^{3}MLCT/^{3}LLCT and ^{3}MC), and the transition states (TS_1 and TS_2) were optimized for complex **1** using the hybrid functional B3LYP[i,ii] in combination with the 6-31G* basis set for all atoms. Relativistic effects were included for the Pt atom by using the ECP-60-mwb Stuttgart/Dresden pseudopotential.[iii] The nature of the stationary points was confirmed by computing the Hessian at the same level of theory. In order to explore the triplet potential energy surfaces (PES) we preoptimized the first eight triplet excited states at the TD-B3LYP level of theory. These TD-DFT optimized geometries were used as initial guess for the final UDFT optimizations that led to the ^{3}MLCT/^{3}LC$_{ppy}$, ^{3}MLCT/^{3}LC$_{acac}$, ^{3}MLCT/^{3}LLCT and ^{3}MC optimized geometries. The minimum energy crossing point (MECP) between the S_0 and the ^{3}MC potential surfaces was optimized using Harvey´s algorithm,[iv] as implemented in the ORCA software;[v] in this case, the B3LYP functional was employed in combination with the def2-svp basis set and the ECP-60-mwb Stuttgart/Dresden pseudopotential for Pt. To get relative energies for the MECP, single-point calculations with the 6-31G* basis set were performed. All calculations apart from the MECP optimization were carried out with the Gaussian09 program package.[vi]

The phosphorescence emission spectra were simulated on the basis of ΔSCF-DFT calculations, which yield the energy difference between the triplet excited states at their optimized geometry and the closed-shell ground state at the same geometry in the gas phase. This approach is a simple but reliable way to determine emission energies. These calculations were also performed in solution using tetrahydrofuran as solvent with the polarization continuum model[vii,viii] and employing the same functional and basis set as in the optimizations. The phosphorescence radiative decay rates were computed using the QR TD-B3LYP approach, as implemented in the Dalton program, [ix] at the optimized geometries of the different emissive triplet states (T_{em}). Towards this aim, the TD-B3LYP excitations leading to ^{3}MLCT/^{3}LC$_{ppy}$, ^{3}MLCT/^{3}LC$_{acac}$, and ^{3}MLCT/^{3}LLCT states were first assigned. The rate constants (k_r) for phosphorescence radiative decay from one of the three spin sublevels (indexed by i) of the emissive states (T_m) can be expressed as

$$k_r^i = k_r\left(S_0, T_{em}^i\right) = \frac{4\alpha_0^3}{3t_0}\Delta E_{S-T}{}^3 \sum_{j\in\{x,y,z\}} \left|M_j^i\right|^2 \quad (1)$$

Here $\Delta E_{S\text{-}T}$ is the transition energy, $t_0 = (4\pi\varepsilon_0)^2/m_e e^4$, α_0 is the fine-structure constant, and M_j^i is the j axis projection of the electric dipole transition moment between the ground state and the ith sublevel of the triplet state T_{em}. The transition moment M_j^i can be expressed as

$$M_j^i = \sum_{n=0}^{\infty} \frac{\langle S_0|\hat{\mu}_j|S_n\rangle\langle S_n|\hat{H}_{SO}|T_{em}^i\rangle}{E(S_n) - E(T_{em})} + \sum_{n=0}^{\infty} \frac{\langle S_0|\hat{H}_{SO}|T_n\rangle\langle T_n|\hat{\mu}_j|T_{em}^i\rangle}{E(T_n) - E(S_0)}, j \in \{x, y, z\} \tag{2}$$

and calculated using the QR TD-B3LYP approach. The nonzero contributions to the $T_{em} \rightarrow S_0$ transition moment originate from matrix elements of the electronic spin-orbit coupling operator ($\hat{H}_{SO}$) including summations over intermediate triplet and singlet states. The $T_{em} \rightarrow S_0$ transition thus borrows intensity from the spin-allowed $S_n \rightarrow S_0$ and $T_{em} \rightarrow T_n$ transitions.

Note that individual phosphorescence rates for the three spin sublevels can only be observed experimentally in the limit of large fine-structure splittings and at low temperatures. In the high-temperature limit, spin relaxation is usually fast and the triplet levels are almost equally populated, and only weighted phosphorescence rates can be measured. Hence, phosphorescence rates are calculated according to (3).

$$k_r = \frac{1}{3}\sum_{i=1}^{3} k_r^i \tag{3}$$

From equations (1) and (3) we see that the phosphorescence rate is proportional to the cube of the emission energy and the square of the transition dipole moment. In our calculations, SOC matrix elements were evaluated at the B3LYP/def2-SV(P) level of theory (ECP-60-mwb Stuttgart/Dresden pseudopotential for Pt). These calculations were done for all possible emissive states at their optimized geometries. This computational approach has been found to provide radiative rates with maximum errors of ca. 15%.[x] The SOC operator applied in all our calculations makes use of a semi-empirical effective single-electron approximation, as suggested by Koseki et al.[xi]

Cartesian coordinates of the optimized geometries

^{1}GS

C	-0.521737	2.815112	-0.657295
H	-1.249173	2.250300	-0.085323
C	-0.842843	3.972657	-1.352651
H	-1.861545	4.344387	-1.338431
C	0.169681	4.631078	-2.056097
H	-0.045767	5.539545	-2.611327
C	1.459620	4.115120	-2.038497
H	2.258343	4.613756	-2.575799
C	1.739945	2.943942	-1.322396
C	3.034708	2.279569	-1.199696
C	4.216283	2.729857	-1.809839
H	4.217159	3.628702	-2.422034
C	5.400028	2.020706	-1.633391
H	6.316177	2.366008	-2.104316
C	5.402544	0.860321	-0.848997
H	6.328147	0.304814	-0.714764
C	4.230340	0.407546	-0.239121
H	4.243386	-0.497163	0.361473
Pt	1.250981	0.636433	0.363931
O	1.937789	-1.011958	1.342345
C	1.219657	-1.811351	2.052882
C	-0.151383	-1.692043	2.331557
H	-0.576336	-2.450683	2.973668
C	-1.032678	-0.695509	1.865360
O	-0.724154	0.264455	1.077372
C	3.026369	1.105731	-0.398349
N	0.728104	2.315900	-0.645277
C	-2.468636	-0.742870	2.285906
C	-3.450225	-0.242220	1.415600
C	-2.867076	-1.253172	3.531701
C	-4.796630	-0.270296	1.772256
H	-3.142816	0.153882	0.453432
C	-4.213784	-1.267451	3.893926
H	-2.120549	-1.610915	4.234102
C	-5.183085	-0.782235	3.013683
H	-4.505140	-1.653161	4.867172
C	1.985950	-2.954099	2.638436
C	3.347445	-2.781648	2.937183
C	1.391789	-4.202252	2.884422
C	4.088935	-3.824389	3.488291
H	3.808926	-1.819610	2.742051
C	2.139066	-5.248824	3.423650
H	0.350910	-4.367173	2.623676
C	3.487793	-5.061693	3.733181
H	5.138278	-3.672110	3.726402
H	1.668245	-6.212961	3.595778
H	4.068228	-5.876508	4.157669
H	-5.546185	0.107204	1.081713
H	-6.232683	-0.799031	3.294878

^{3}MLCT/^{3}LC$_{ppy}$

C	-0.532965	2.819026	-0.653127
H	-1.272046	2.271036	-0.078613
C	-0.850470	3.970639	-1.357578
H	-1.869141	4.341415	-1.340087
C	0.173503	4.645941	-2.090964
H	-0.056968	5.547328	-2.649800
C	1.446329	4.138620	-2.074320
H	2.244033	4.632196	-2.620274
C	1.754263	2.954023	-1.340943
C	2.997692	2.321402	-1.219003
C	4.224633	2.749746	-1.820095
H	4.250530	3.646359	-2.432403
C	5.369226	2.020462	-1.622699
H	6.296975	2.350406	-2.084328
C	5.380936	0.827689	-0.823056
H	6.309951	0.279878	-0.697226
C	4.209837	0.387634	-0.221073
H	4.206937	-0.514695	0.382761
Pt	1.260826	0.648034	0.367765
O	1.954492	-1.012459	1.359917
C	1.234028	-1.814013	2.061430
C	-0.140998	-1.695826	2.331468
H	-0.569311	-2.456456	2.968636
C	-1.018531	-0.697901	1.866365
O	-0.708671	0.266386	1.080194
C	3.006466	1.092317	-0.380585
N	0.706432	2.304342	-0.629526
C	-2.454964	-0.742239	2.281965
C	-3.429974	-0.221707	1.415551
C	-2.860909	-1.268791	3.518800
C	-4.777684	-0.247182	1.767049
H	-3.116552	0.188118	0.461273
C	-4.208814	-1.280040	3.875825
H	-2.119590	-1.640663	4.219300
C	-5.171650	-0.775577	2.999156
H	-4.506183	-1.678009	4.842229
C	1.994545	-2.958934	2.649367
C	3.354611	-2.789424	2.956533
C	1.396383	-4.206650	2.888696
C	4.091118	-3.834814	3.509063
H	3.818659	-1.827308	2.767915
C	2.139064	-5.256042	3.428539
H	0.356708	-4.369284	2.621975
C	3.486311	-5.071868	3.746330
H	5.139088	-3.684937	3.754398
H	1.665888	-6.219932	3.595131
H	4.062851	-5.888877	4.171819
H	-5.522177	0.146096	1.080003
H	-6.222318	-0.789762	3.276344

^{3}MLCT/^{3}LC$_{dbm}$

C	-0.667059	2.364657	-1.070318
H	-1.378906	1.660852	-0.654361
C	-1.046757	3.517468	-1.745794
H	-2.099393	3.742583	-1.876737
C	-0.048578	4.359645	-2.240419
H	-0.309323	5.269023	-2.774115
C	1.287703	4.027050	-2.043327
H	2.075114	4.670720	-2.418677
C	1.624763	2.856203	-1.355313
C	2.971970	2.365702	-1.061379
C	4.151359	3.018578	-1.445926
H	4.114307	3.953581	-1.999561
C	5.387455	2.465710	-1.118014
H	6.302713	2.969838	-1.415052
C	5.444194	1.261283	-0.408112
H	6.410109	0.829996	-0.155914
C	4.271305	0.607127	-0.021164
H	4.324897	-0.331352	0.521652
Pt	1.233730	0.378469	0.111364
O	1.948323	-1.269662	1.039499
C	1.317335	-1.958041	1.969178
C	-0.065444	-1.764409	2.275980
H	-0.446283	-2.376594	3.083153
C	-1.029485	-0.928178	1.635879
O	-0.729942	-0.271471	0.539247
C	3.017120	1.143536	-0.337020
N	0.626582	2.046875	-0.883671
C	-2.412728	-0.868805	2.116449
C	-3.420901	-0.355866	1.267782
C	-2.799481	-1.295023	3.408789
C	-4.744867	-0.287391	1.685185
H	-3.145593	-0.036009	0.268926
C	-4.126365	-1.220895	3.821385
H	-2.055871	-1.655570	4.113249
C	-5.111091	-0.720280	2.964619
H	-4.392048	-1.548009	4.823390
H	-5.500728	0.101712	1.007318
H	-6.146105	-0.664446	3.289848
C	2.111051	-2.955585	2.689293
C	3.522648	-2.920957	2.592479
C	1.536514	-3.981617	3.478494
C	4.311986	-3.846511	3.263154
H	3.982693	-2.146861	1.989920
C	2.333638	-4.904668	4.147564
H	0.458387	-4.085727	3.548550
C	3.726803	-4.845404	4.049933
H	5.394113	-3.788587	3.176258
H	1.862093	-5.683474	4.741412
H	4.346141	-5.568313	4.573324

^{3}MLCT/^{3}LLCT

C	2.1672240000	-2.6483050000	-0.0484850000
H	1.1405880000	-2.9955740000	-0.0690540000
C	3.2489800000	-3.5102240000	-0.0562160000
H	3.0771570000	-4.5807630000	-0.0808710000
C	4.5569060000	-2.9742540000	-0.0327910000
H	5.4231940000	-3.6278480000	-0.0361720000
C	4.7147300000	-1.5970990000	-0.0088300000
H	5.7080260000	-1.1598520000	0.0055260000
C	3.5975260000	-0.7490860000	-0.0039400000
C	3.5941250000	0.6915300000	0.0154730000
C	4.7315780000	1.5168430000	0.0295220000
H	5.7292220000	1.0867930000	0.0210730000
C	4.5838700000	2.9003390000	0.0579630000
H	5.4719180000	3.5273160000	0.0712640000
C	3.3063260000	3.5070410000	0.0719870000
H	3.2237230000	4.5896520000	0.0960350000
C	2.1690600000	2.7109420000	0.0549880000
H	1.1789020000	3.1552070000	0.0704220000
Pt	0.7964520000	0.0255790000	-0.0186540000
O	-0.6410560000	1.4640110000	-0.0290190000
C	-1.9255050000	1.2681320000	0.0266330000
C	-2.5506730000	-0.0073730000	0.0298170000
H	-3.6315120000	-0.0037370000	0.0417410000
C	-1.9433580000	-1.2628950000	0.0045660000
O	-0.6454810000	-1.4670510000	0.0358590000
C	2.2747760000	1.3030890000	0.0179180000
N	2.3199220000	-1.3068920000	-0.0190290000
C	-2.7680840000	-2.4962040000	-0.0251270000
C	-2.2343340000	-3.6944700000	0.4859220000
C	-4.0702320000	-2.5215820000	-0.5603100000
C	-2.9844950000	-4.8676880000	0.4843770000
H	-1.2323620000	-3.6852180000	0.9007720000
C	-4.8152200000	-3.6983490000	-0.5676500000
H	-4.4910910000	-1.6252880000	-1.0056470000
C	-4.2790770000	-4.8768990000	-0.0414400000
H	-5.8142170000	-3.6977780000	-0.9956700000
C	-2.7426310000	2.4973650000	0.0440500000
C	-2.1837080000	3.7075920000	-0.4190660000
C	-4.0707710000	2.5199740000	0.5205340000
C	-2.9274520000	4.8827790000	-0.4220460000
H	-1.1660550000	3.7025090000	-0.7928810000
C	-4.8080330000	3.7006990000	0.5231060000
H	-4.5202510000	1.6192790000	0.9260030000
C	-4.2446920000	4.8884690000	0.0480730000
H	-2.4797760000	5.8002600000	-0.7953990000
H	-5.8253390000	3.6951520000	0.9055790000
H	-4.8235000000	5.8079610000	0.0483100000
H	-2.5581860000	-5.7788890000	0.8961590000
H	-4.8618470000	-5.7939710000	-0.0478590000

^{3}MC

C	0.354940	-0.221169	-2.581743
H	0.216287	-1.257171	-2.286574
C	-0.157849	0.284153	-3.771367
H	-0.721358	-0.356583	-4.441111
C	0.077163	1.630378	-4.063358
H	-0.303515	2.067741	-4.982199
C	0.803339	2.412533	-3.172949
H	0.990905	3.456249	-3.396621
C	1.295594	1.849443	-1.983143
C	2.079078	2.559245	-0.956704
C	2.401718	3.922138	-1.069258
H	2.075889	4.500005	-1.930171
C	3.142321	4.555026	-0.075644
H	3.387318	5.609373	-0.169691
C	3.565018	3.827185	1.040754
H	4.144539	4.317239	1.819769
C	3.247299	2.471817	1.159061
H	3.585292	1.922620	2.034199
Pt	1.961966	-0.143361	0.217191
O	1.687266	-2.273161	0.245691
C	0.749724	-2.935025	0.811651
C	-0.401000	-2.390336	1.415365
H	-1.123429	-3.094014	1.802986
C	-0.712776	-1.026931	1.581492
O	0.010880	-0.022164	1.256515
C	2.505142	1.805417	0.171565
N	1.049814	0.539958	-1.730252
C	-2.014384	-0.658551	2.233059
C	-2.100169	0.556007	2.932807
C	-3.155560	-1.471936	2.146449
C	-3.289271	0.933688	3.552757
H	-1.222645	1.191413	2.984604
C	-4.348667	-1.086039	2.756832
H	-3.122585	-2.395115	1.576237
C	-4.417553	0.113961	3.467693
H	-5.226370	-1.721294	2.672036
H	-3.336761	1.870490	4.101595
H	-5.346479	0.411167	3.947207
C	0.921007	-4.424788	0.778330
C	0.319223	-5.277437	1.718185
C	1.736240	-4.987966	-0.217203
C	0.516313	-6.656407	1.654235
H	-0.278941	-4.863892	2.523884
C	1.922970	-6.366636	-0.287475
H	2.218045	-4.327393	-0.929834
C	1.312423	-7.206441	0.647494
H	0.053014	-7.300791	2.396588
H	2.549109	-6.786905	-1.070098
H	1.462477	-8.281641	0.596864

TS_1

C	-2.158576	2.661997	0.002269
H	-1.132984	3.013491	0.013457
C	-3.236586	3.533957	0.011884
H	-3.056824	4.602966	0.030772
C	-4.563582	3.003625	-0.003147
H	-5.420029	3.670173	0.004084
C	-4.733845	1.644180	-0.027006
H	-5.729936	1.213298	-0.039175
C	-3.611102	0.763948	-0.037044
C	-3.622161	-0.636164	-0.063141
C	-4.785155	-1.470662	-0.084696
H	-5.776910	-1.028206	-0.073515
C	-4.642696	-2.834274	-0.123625
H	-5.530580	-3.461965	-0.142165
C	-3.351471	-3.462307	-0.142898
H	-3.286513	-4.545600	-0.178153
C	-2.203269	-2.682594	-0.116724
H	-1.222049	-3.146879	-0.134160
Pt	-0.802405	-0.012678	-0.028089
O	0.629779	-1.481813	-0.028458
C	1.900014	-1.279984	-0.020411
C	2.563999	-0.041996	0.015208
H	3.639591	-0.100194	0.079546
C	1.983237	1.241501	0.024853
O	0.722490	1.475843	-0.002422
C	-2.282259	-1.281662	-0.071751
N	-2.304232	1.328263	-0.021100
C	2.856062	2.462371	0.070076
C	2.241082	3.726302	0.070071
C	4.260718	2.410903	0.111493
C	2.997371	4.894745	0.110199
H	1.159707	3.776319	0.037784
C	5.018519	3.579713	0.152683
H	4.781873	1.460387	0.112116
C	4.391343	4.827126	0.152236
H	6.102622	3.514029	0.185160
C	2.711587	-2.536090	-0.023471
C	2.188357	-3.689654	0.583205
C	3.975064	-2.604634	-0.632088
C	2.920651	-4.874628	0.599961
H	1.210241	-3.639222	1.049483
C	4.700479	-3.795482	-0.626623
H	4.378137	-1.734330	-1.140826
C	4.178786	-4.931982	-0.005240
H	2.509216	-5.755567	1.085313
H	5.670837	-3.836791	-1.113920
H	4.746864	-5.858343	0.002904
H	2.497879	5.859870	0.109000
H	4.984118	5.737319	0.184084

TS_2

C	-0.793300	3.041024	-0.928379
H	-1.530998	2.553180	-0.295934
C	-1.119789	4.130140	-1.735157
H	-2.131159	4.523422	-1.747376
C	-0.107813	4.684536	-2.519340
H	-0.313787	5.531325	-3.168288
C	1.173391	4.141712	-2.471514
H	1.958727	4.562659	-3.088715
C	1.434519	3.046004	-1.632552
C	2.755516	2.378963	-1.507877
C	3.892408	2.877154	-2.155429
H	3.842568	3.781220	-2.755512
C	5.122056	2.225554	-2.034771
H	5.993608	2.628307	-2.544164
C	5.232901	1.063539	-1.263284
H	6.192349	0.560061	-1.174024
C	4.109319	0.561186	-0.611209
H	4.191460	-0.338744	-0.007812
Pt	1.230748	0.565034	0.280825
O	2.025920	-1.423355	1.363978
C	1.354253	-2.133038	2.157154
C	-0.040439	-1.970479	2.436896
H	-0.488187	-2.701971	3.095628
C	-0.892204	-0.983436	1.943853
O	-0.559257	0.022079	1.196420
C	2.848972	1.197095	-0.703395
N	0.436392	2.528422	-0.883327
C	-2.343500	-1.022466	2.313827
C	-3.055760	0.183938	2.408971
C	-3.023867	-2.227351	2.552572
C	-4.404376	0.187279	2.759049
H	-2.532953	1.114772	2.216472
C	-4.376916	-2.224063	2.890269
H	-2.502125	-3.173345	2.443254
C	-5.070239	-1.016969	3.001154
H	-4.891561	-3.166174	3.059386
H	-6.123763	-1.015097	3.267944
H	-4.937864	1.130560	2.842980
C	2.082557	-3.262228	2.832699
C	1.701558	-3.769264	4.085098
C	3.206186	-3.810280	2.194055
C	2.423063	-4.804537	4.679817
H	0.858685	-3.335551	4.614510
C	3.916238	-4.855115	2.780521
H	3.504646	-3.406325	1.232409
C	3.526884	-5.355626	4.026116
H	2.124490	-5.177854	5.655799
H	4.775790	-5.279088	2.268057
H	4.083851	-6.167307	4.486750

^{1}GS/^{3}MC MECP

C	-0.02362427772026	-0.01451198911243	-2.43496031232036
H	-0.24272447598666	-1.04363010579706	-2.13473839826121
C	-0.62501085574156	0.56894038807038	-3.54891554228781
H	-1.33633667613711	0.00130761557447	-4.15169747658757
C	-0.28015939137564	1.88847263174865	-3.86243191840939
H	-0.72114486637515	2.38411526174615	-4.73123090589587
C	0.62710953860388	2.57249525673323	-3.05760772265972
H	0.91170520718850	3.59646688823427	-3.30116829423083
C	1.18468407834609	1.93559611017463	-1.93127713517476
C	2.13014152083391	2.55099067715438	-0.97970458258230
C	2.55197211078672	3.88854742273496	-1.09935359515638
H	2.18591641001918	4.51886790352125	-1.91378086072714
C	3.43837749607820	4.43368218823986	-0.17219343551371
H	3.77050956672822	5.46971569265554	-0.27754544800054
C	3.90057290379219	3.64739320305519	0.89071805947651
H	4.59261941546861	4.07299453809261	1.62386198845083
C	3.48205562255922	2.31832205955390	1.01683398032248
H	3.85995657256691	1.72099829694036	1.85127226015218
Pt	1.93438820182536	-0.18097435089105	0.13997344443340
O	1.64007482971881	-2.31250979608672	0.20767043763315
C	0.73068275449988	-2.99408500514277	0.77837345888145
C	-0.44429456223336	-2.45462685272265	1.34947175441424
H	-1.17501793813137	-3.15157206417756	1.74956029647385
C	-0.74188580359361	-1.08418871344785	1.50435523434760
O	0.00851731524281	-0.09857406682687	1.20793672916184
C	2.59999684944740	1.73586731478333	0.08823684772617
N	0.84194765745474	0.65307121379176	-1.66862664799817
C	-2.06050356403423	-0.69749005263158	2.11514917571937
C	-2.13943083086462	0.48334271265839	2.87511128146594
C	-3.22593665544402	-1.46099623659730	1.92557902688207
C	-3.34801166715848	0.87794035871395	3.45070557147805
H	-1.23621794451154	1.08079574080192	3.01127207728543
C	-4.43965411599400	-1.05358889222301	2.48527908767491
H	-3.19081232214250	-2.36681591943387	1.31603001179599
C	-4.50304273613377	0.11232893248893	3.25564177753533
H	-5.34034491239647	-1.64881710061851	2.31165588653605
H	-3.39237161644025	1.79126036964336	4.05004533752294
H	-5.45017782050866	0.42974105681858	3.70055275992225
C	0.97150138115701	-4.47843155464049	0.81668989772092
C	0.21818946517324	-5.35931318376242	1.61490932473722
C	2.03063083213925	-5.00327030159076	0.05237696091555
C	0.52276058372036	-6.72189893519173	1.65269168180252
H	-0.59978649444522	-4.98330462780584	2.23165159943990
C	2.32887765076798	-6.36605089161447	0.08235729514229
H	2.61942482353480	-4.31411038679232	-0.55396960864825
C	1.57933268399112	-7.22910196087228	0.88897122710208
H	-0.06415744575506	-7.38982383681942	2.28852470383545
H	3.15551702068290	-6.75750408965592	-0.51711685124704
H	1.82618548079619	-8.29396091947517	0.93055755971307

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