Supporting information

The Effect of π-π Stacking Interaction of the indole ring with the Coordinated Phenoxyl Radical in a Nickel(II)-salen Type Complex. Comparison with the Corresponding Cu(II) Complex

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Table S1. Selected bond distances for $\mathbf{1}^{\mathbf{Indole}}$ and $\mathbf{2}^{\mathbf{Indole}}$

	$\mathbf{1}^{\mathbf{Indole}}$ [a]	$\mathbf{2}^{\mathbf{Indole}}$
M-O(1)	1.891(3)	1.837(7)
M-O(2)	1.8942(19)	1.852(5)
M-N(1)	1.944(3)	1.843(6)
M-N(2)	1.919(4)	1.827(8)

[a]Ref. 29 in main text.

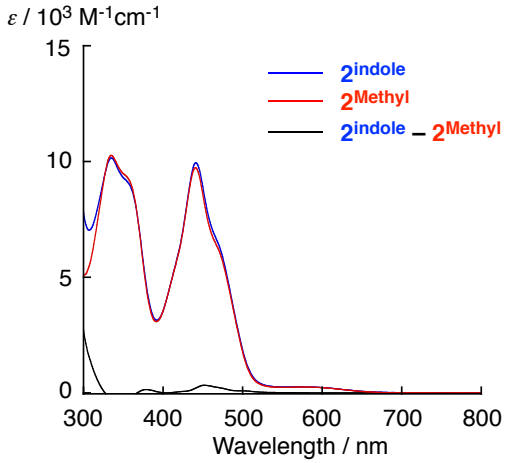

Figure S1. UV-vis spectra of Ni(II) complexes in CH_2Cl_2. The blue line is for $\mathbf{2}^{\mathbf{Indole}}$, the red line is for $\mathbf{2}^{\mathbf{Methyl}}$, and the black line is difference spectra of $\mathbf{2}^{\mathbf{Indole}} - \mathbf{2}^{\mathbf{Methyl}}$.

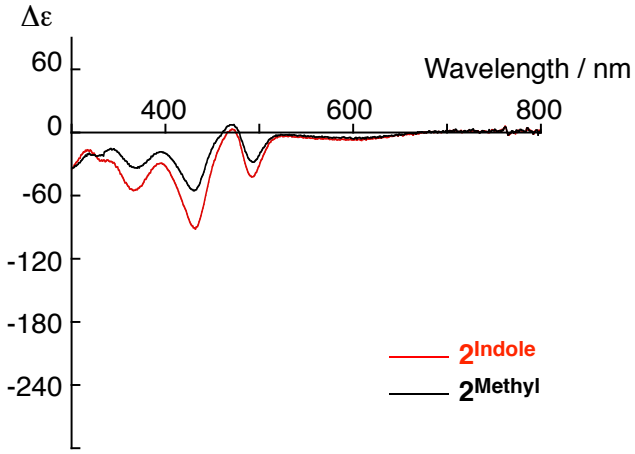

Figure S2. CD spectra of the neutral Ni complexes. The red line is for $\mathbf{2}^{\mathbf{Indole}}$, and the blue line is for $\mathbf{2}^{\mathbf{Methyl}}$.

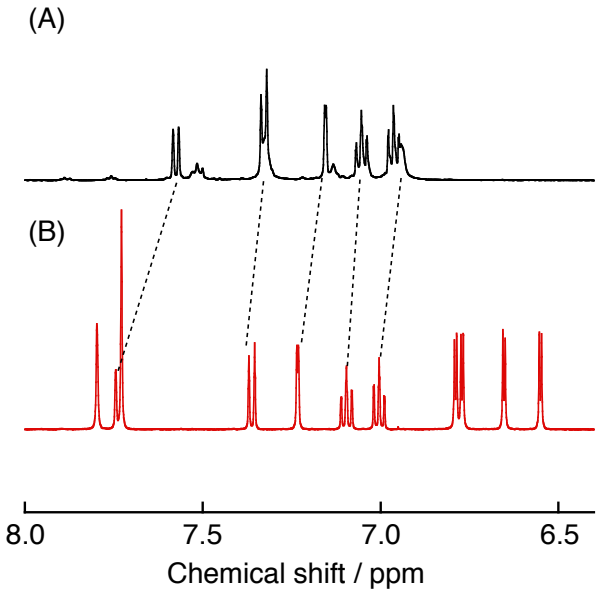

Figure S3. ^{1}H–NMR spectra of the Ni(II) complex of *S*-1,2-diamino-3-indol-3-ylpropane (A) and **2**$^{\mathbf{Indole}}$ (B). Dotted line in the spectra indicates the corresponding indole proton signals.

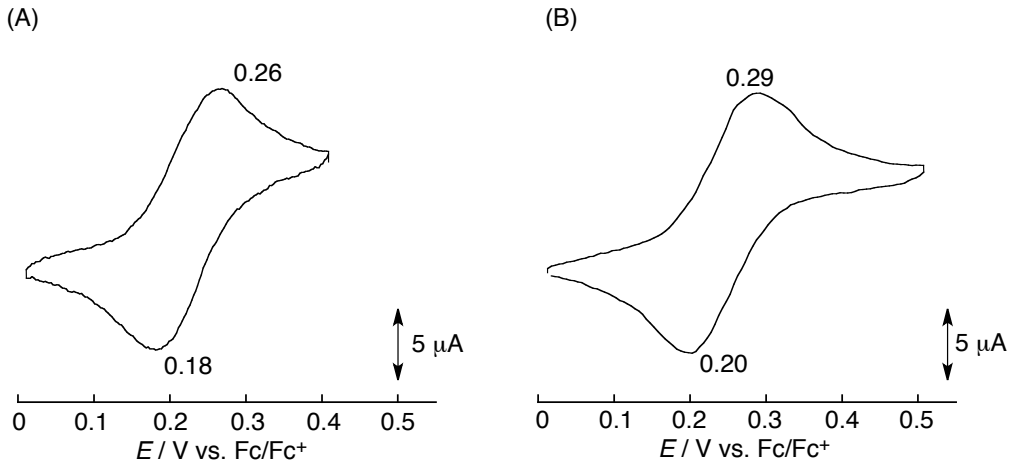

Figure S4. Cyclic voltammograms of complexes **2**$^{\mathbf{Indole}}$ (A), and **2**$^{\mathbf{Methyl}}$ (B).

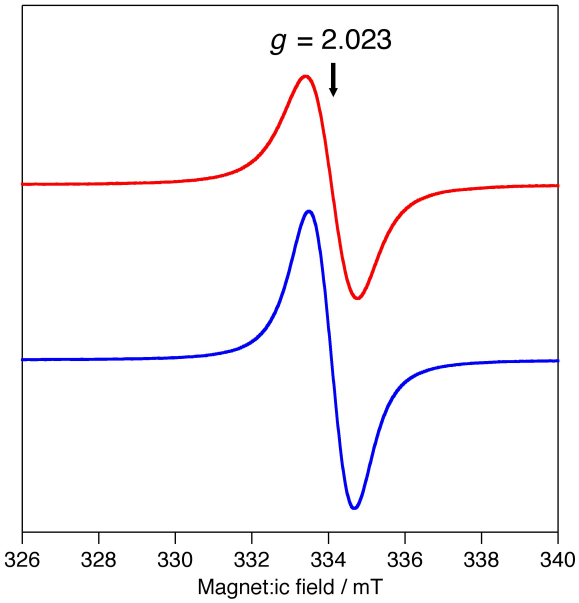

Figure S5. EPR spectra of one-electron oxidized Ni complexes having a side chain. Red line is $[\mathbf{2}^{\mathbf{Indole}}]^+$ and blue line is $[\mathbf{2}^{\mathbf{Methyl}}]^+$.

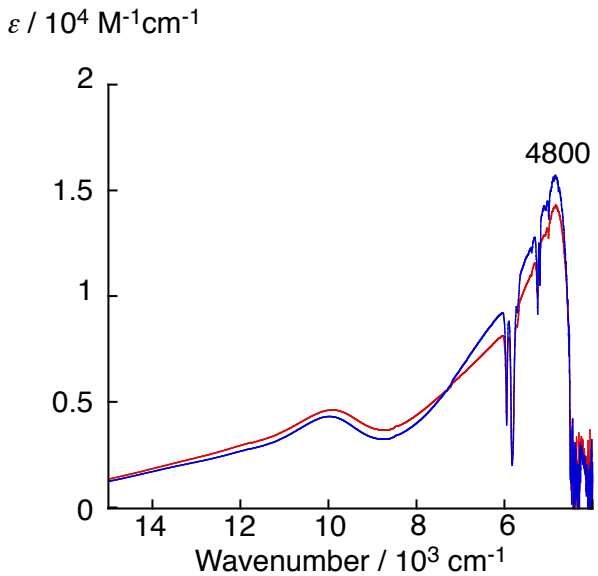

Figure S6. Comparison of UV-vis-NIR spectra of $[\mathbf{2}^{\mathbf{Indole}}]^+$ and $[\mathbf{2}^{\mathbf{Methyl}}]^+$ in CH_3CN solvents. The b red line is $[\mathbf{2}^{\mathbf{Indole}}]^+$ and the blue line is $[\mathbf{2}^{\mathbf{Methyl}}]^+$.

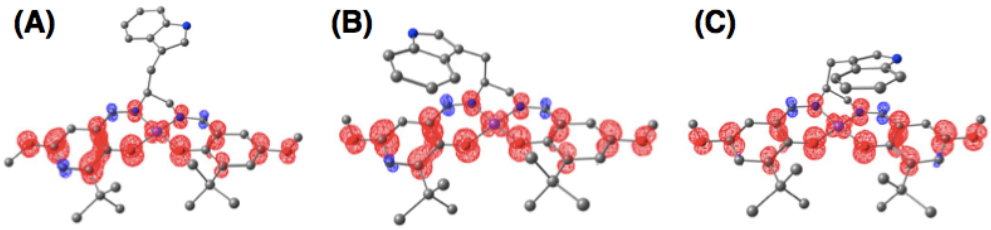

Figure S7. Mulliken spin density plots of complexes $[\mathbf{2}^{\mathbf{Indole}}]^+$ which were calculated at the B3LYP+D3/Def2SVP level. (A) is the open form, and (B) and (C) are the two isomers of the stacking species.

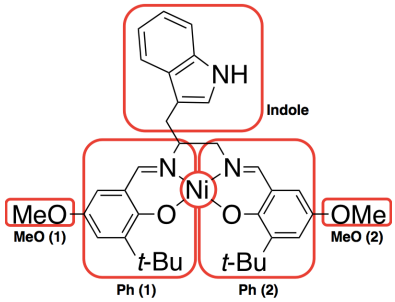

Figure S8. Separation of the oxidized complexes $[Ni(MeO\text{-}salen^{Indole})]^+$

Table S2. Mulliken spin densities of one-electron oxidized complex $[\mathbf{2}^{\mathbf{Indole}}]^+$ at the B3LYP+D3/Def2SVP level. Separation of the complexes is defined as shown in Figure S8.

Electronic structures in Figure S7	Ni	MeO(1)	Ph(1)	MeO(2)	Ph(2)	Indole
A	0.11	0.07	0.49	0.04	0.28	0.01
B	0.12	0.07	0.46	0.04	0.31	0.01
C	0.12	0.05	0.33	0.06	0.41	0.04

Table S3. Summary of the transitions for the calculated singlet $[2^{Indole}]^+$ electronic states predicted by TD-DFT calculations

Transition (MO number)[a]	Energy / cm^{-1}	Assignment
βHOMO (165) → βLUMO (166)	4859.7 cm^{-1}	LLCT
βHOMO-2 (163) → βLUMO (166)	9693.1 cm^{-1}	LLCT
βHOMO-4 (161) → βLUMO (166)	10686.0 cm-^{1}	MLCT

[a]TD-uB3LYP/Def2SVP level (75 states).

Table S4. Crystal data for complexes $\mathbf{2^{indole}}$ and $\mathbf{[2^{indole}]SbF_6}$.

	$\mathbf{2^{Indole}}$	$\mathbf{[2^{Indole}]SbF_6}$
Formula	$C_{35}H_{41}NiN_3O_4$	$C_{37}H_{43}NiN_3O_4SbF_6Cl_4$
Formula weight	626.43	1030.02
Color	green	brown
Crystal size /mm	0.1 x 0.1 x 0.1	0.380 x 0.100 x 0.030
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	11.9551(15)	10.7322(5)
b (Å)	6.9902(7)	38.488(2)
c (Å)	19.284(2)	11.7318(7)
α (°)	-	-
β (°)	108.879(3)	97.443(7)
γ (°)	-	-
V (Å^3)	1524.9(3)	4805.1(5)
Z	2	4
μ (Mo Kα) (cm^{-1})	6.80	12.35
F(000)	664.0	2076.0
D_{calc} (g/cm^3)	1.364	1.424
$2\theta_{max}$ (°)	54.97	55.0
No. reflections obsd.	14260	18710
No. reflections used.	6335	12365
No. variables	388	1010
R_1[a] (I>2σ(I))	0.0729	0.0703
R_w[b]	0.2136	0.2148

[a] $R_1 = \Sigma||F_o|-|F_c|| \,/\, \Sigma|F_o|$ for $I > 2\sigma(I)$ data. [b] $R_w = \{\Sigma\omega(|F_o|-|F_c|)^2 \,/\, \Sigma\omega F_o^2\}^{1/2}$; $\omega = 1/\sigma^2(F_o)$ $= \{\sigma^2_c(F_o) + p^2/4 \cdot F_o^2\}^{-1}$

Table S5. Cartesian coordinates of oxidized complex $[\mathbf{2}^{\mathbf{Indole}}]^{+}$.

Figure S7 (A)

Total electronic energy = -3330.46928432 a.u.

Gibbs Free energy = -3329.842018 a.u.

Ni	−0.441522	−0.001680	−0.298777
O	−0.564779	−6.292404	2.339794
O	0.833899	0.627837	−1.472125
O	1.530328	5.447487	−3.978691
O	0.434979	−1.635732	−0.335148
N	−1.455408	1.545704	−0.404265
N	−1.608224	−0.551838	1.045021
C	2.797038	−0.256314	−3.534768
H	3.611844	−0.994533	−3.604390
H	1.981221	−0.702708	−2.957845
C	2.183138	2.074707	−2.779742
C	0.932038	−3.939643	−0.096877
C	3.316596	1.039046	−2.869741
C	1.269291	4.310827	−3.300072
C	−0.013438	2.824159	−1.887613
C	0.673423	−5.104788	0.608835
C	0.135149	4.072135	−2.538459
H	−0.646643	4.822417	−2.423009
C	−1.657757	−1.711946	1.617213
H	−2.380347	−1.850724	2.433542
C	−0.843514	−2.847964	1.275727
C	−0.301772	−5.181347	1.636734
C	1.243308	−3.506090	−2.550543
H	0.753958	−2.528556	−2.465177
H	1.973889	−3.454026	−3.373021
H	0.483102	−4.258008	−2.816475
C	−1.062109	−4.050712	1.952745

H	−1.824090	−4.128982	2.730380
C	1.962021	−3.901948	−1.236993
C	2.624622	−5.274009	−1.458643
H	3.344363	−5.196602	−2.287437
H	3.180800	−5.613840	−0.570807
H	1.892527	−6.050409	−1.731028
C	0.180095	−2.747513	0.255870
C	0.158588	−7.493789	2.093336
H	−0.232838	−8.235223	2.800273
H	−0.001041	−7.853897	1.063468
H	1.237830	−7.355102	2.271433
C	−2.719159	1.426585	0.330265
H	−3.115073	2.411140	0.621030
H	−3.455649	0.928058	−0.320133
C	3.079259	−2.884844	−0.904074
H	3.594043	−3.165885	0.028772
H	3.825012	−2.875534	−1.714422
C	3.842212	0.742438	−1.444237
H	4.637124	−0.019010	−1.488335
H	4.267461	1.653477	−0.993281
H	3.045303	0.368719	−0.790085
C	2.274301	3.309135	−3.392689
H	3.147535	3.577005	−3.985585
C	−2.436743	0.555089	1.548507
H	−3.380195	0.161448	1.957538
C	4.500807	1.555122	−3.707891
H	5.288060	0.786069	−3.732591
H	4.211064	1.763670	−4.749849
H	4.945563	2.468182	−3.281899
C	0.581476	6.501798	−3.956272
H	0.995224	7.306920	−4.576303
h	0.421958	6.879517	−2.931357

C	0.981256	1.790803	−2.016249
C	−1.671938	1.309164	2.667184
H	−0.737786	1.707166	2.240260
H	−1.383788	0.563319	3.426471
C	−1.183461	2.614580	−1.090531
H	−1.912673	3.436055	−1.058306
C	−4.247808	1.103518	4.738096
C	−3.609214	2.227299	4.175844
C	−4.092380	3.531491	4.493456
C	−5.185852	3.731736	5.348602
C	−5.798813	2.601958	5.886679
C	−5.335061	1.300376	5.585661
C	−2.482468	2.399752	3.290177
C	−2.337256	3.760136	3.108037
N	−3.297026	4.436768	3.826519
H	−3.893336	0.092503	4.517956
H	−5.541695	4.737200	5.584646
H	−6.653902	2.724377	6.556241
H	−5.839425	0.438195	6.029162
H	−1.602126	4.300074	2.513299
H	−3.389942	5.443899	3.871150
H	1.232945	−6.003081	0.365234
H	2.437479	−0.049572	−4.555712
H	2.681277	−1.871132	−0.796419
H	−0.387156	6.180324	−4.377287

Figure S7 (B)

Total electronic energy = -3330.48040691 a.u.

Gibbs Free energy = -3329.849532 a.u.

Ni	−0.036508	−0.683578	−1.336490
O	−6.507000	0.581624	−3.244274

O	5.922530	0.193894	1.938018
O	−1.419909	0.532184	−1.228835
O	1.000627	0.529110	−0.392449
N	1.259398	−2.005422	−1.248197
N	2.439275	−4.476690	2.313337
H	3.172070	−4.979541	2.798234
N	−1.000103	−1.846404	−2.415319
C	1.803502	−4.911919	1.172110
H	2.095537	−5.847029	0.696741
C	1.903622	−3.269701	2.706886
C	2.245577	−2.419912	3.770011
H	3.042756	−2.682206	4.469506
C	−4.833408	1.465816	−1.872909
H	−5.585354	2.217238	−1.636929
C	0.874008	−2.941958	1.776838
C	2.953925	−0.781800	−0.004757
C	1.540394	−1.224660	3.891523
H	1.789449	−0.534687	4.701501
C	0.833744	−4.003163	0.796564
C	−3.577289	1.512939	−1.301574
C	2.423217	−1.930529	−0.677828
H	3.045491	−2.834068	−0.672364
C	4.742357	0.185516	1.299379
C	4.219501	−0.897350	0.596935
H	4.760068	−1.839480	0.515410
C	2.765602	1.574452	0.796465
C	0.507480	−0.887015	2.986235
H	−0.025295	0.058258	3.108028
C	2.827753	3.981277	1.628724
H	3.032401	3.692878	2.671627
H	3.787017	4.193815	1.131212
H	2.253317	4.919854	1.653600

C	-3.194050	2.587134	-0.270207
C	-3.069835	-0.574737	-2.555601
C	-2.836135	1.888947	1.064836
H	-2.007995	1.180565	0.941487
H	-2.536682	2.639695	1.813107
H	-3.708005	1.343025	1.459510
C	1.742604	3.436833	-0.549178
H	1.151369	2.726325	-1.138617
H	1.187574	4.386873	-0.498798
H	2.692140	3.625106	-1.075743
C	-2.627973	0.482036	-1.681957
C	-1.997164	3.418356	-0.787236
H	-2.254733	3.917283	-1.735474
H	-1.738252	4.197861	-0.053245
H	-1.113314	2.793030	-0.947083
C	-2.208077	-1.676030	-2.862037
H	-2.617484	-2.451810	-3.523947
C	0.164711	-1.735732	1.939091
H	-0.632807	-1.459347	1.246333
C	6.727918	-0.977922	1.945632
H	7.618214	-0.736939	2.539054
H	6.195390	-1.823809	2.412317
H	7.035667	-1.257506	0.923922
C	0.019174	-4.003556	-0.458257
H	-0.934307	-3.479699	-0.284833
H	-0.224223	-5.028348	-0.778898
C	4.008053	1.402305	1.368944
H	4.491950	2.209414	1.916336
C	-7.019914	-0.386664	-4.146032
H	-8.045265	-0.077443	-4.384338
H	-6.426791	-0.424490	-5.076142
H	-7.041082	-1.391124	-3.688770

C	−5.246909	0.453591	−2.782433
C	2.181578	0.434449	0.102779
C	0.739023	−3.312899	−1.659906
H	1.567165	−3.957038	−1.995133
C	−0.216020	−3.022523	−2.812108
H	−0.865691	−3.882429	−3.035842
H	0.359390	−2.772315	−3.718018
C	−4.371755	−0.572892	−3.108317
H	−4.662787	−1.383608	−3.775675
C	0.683970	2.707154	1.646024
H	0.042822	1.973184	1.148892
H	0.880539	2.364301	2.674127
H	0.134910	3.660064	1.703334
C	2.011967	2.910466	0.881555
C	−4.356679	3.558025	0.005511
H	−4.653959	4.114321	−0.897432
H	−5.244214	3.041215	0.402924
H	−4.039751	4.295576	0.758570

Figure S7 (C)

Total electronic energy = -3330.48334164 a.u.

Gibbs Free energy = -3329.851934 a.u.

O	−6.338246	−0.373024	−2.977128
O	1.213763	−0.539248	−0.224351
N	1.676363	1.755136	−1.540570
N	−0.801365	1.959873	−2.083947
N	2.165729	3.634703	1.543002
H	3.053117	3.785482	2.006628
C	−1.060323	2.098207	1.275263
H	−1.919873	2.180369	0.607424
C	4.513576	0.833844	0.579783

H	5.121046	1.704265	0.334456
C	-2.454504	-0.376867	-1.415205
C	2.394702	-0.433419	0.273780
C	0.086150	2.891793	1.067843
C	3.247209	0.693563	-0.023886
C	4.953304	-0.136513	1.471947
C	-0.074463	3.215192	-2.328109
C	1.193446	2.748761	1.955337
C	0.453240	3.891316	0.092758
C	-2.901542	0.735866	-2.218090
C	-4.206934	0.774011	-2.760769
H	-4.503127	1.632296	-3.363098
C	2.838562	1.687828	-0.970195
H	3.576045	2.460588	-1.223643
C	4.142932	-1.279496	1.724689
H	4.569156	-2.012205	2.408112
C	-5.076283	-0.278592	-2.515017
C	-2.999750	-2.626147	-0.226092
c	-1.074369	1.200563	2.337791
H	-1.956670	0.581214	2.508134
C	-2.039376	1.848845	-2.467046
H	-2.474760	2.690996	-3.022965
C	2.085301	-2.749874	1.415253
C	1.382360	2.797659	-2.526892
H	1.501860	2.361965	-3.531744
H	2.072936	3.648403	-2.428606
C	-3.392501	-1.454234	-1.139982
C	0.737860	-2.380173	2.073913
H	0.139192	-3.290663	2.234992
H	0.904175	-1.901565	3.051569
H	0.159613	-1.693269	1.449446
C	2.904041	-1.476890	1.152762

C	−1.745864	−3.341969	−0.778970
H	−1.474852	−4.181923	−0.119694
H	−1.943439	−3.749090	−1.783980
H	−0.889100	−2.663354	−0.835832
C	−0.270718	4.241220	−1.168672
H	0.087591	5.211644	−1.546654
H	−1.354558	4.345299	−0.997913
C	1.850832	−3.481338	0.071671
H	1.244665	−4.385643	0.239561
H	1.321492	−2.845752	−0.647765
H	2.810589	−3.790659	−0.372478
C	−4.125356	−3.670685	−0.112308
H	−3.794377	−4.485748	0.549341
H	−5.044480	−3.247776	0.322510
H	−4.375147	−4.116480	−1.088054
C	−2.721750	−2.068097	1.189041
H	−2.414830	−2.882655	1.863838
H	−1.921778	−1.320196	1.171491
H	−3.628936	−1.601570	1.605764
C	−6.863914	0.669910	−3.783915
H	−7.890448	0.378640	−4.038821
H	−6.883209	1.628986	−3.237932
H	−6.279908	0.793049	−4.712375
C	7.010032	0.983152	1.947942
H	7.880824	0.788833	2.586039
H	7.338410	1.060427	0.897471
H	6.539672	1.933681	2.253169
C	1.717594	4.325365	0.441126
H	2.348957	5.066716	−0.045929
C	−4.648689	−1.366779	−1.704469
H	−5.390791	−2.146733	−1.542201
C	2.820058	−3.721701	2.356491

H	2.198998	−4.618380	2.504308
H	3.785361	−4.052762	1.942214
h	3.000603	−3.279002	3.348657
C	0.040417	1.065341	3.195811
H	0.001768	0.340952	4.012366
C	1.187641	1.834688	3.018159
H	2.051681	1.730320	3.678079
H	−0.457840	3.679164	−3.250647