SO_2-Binding Properties of Cationic η^6,η^1-NCN-Pincer Arene Ruthenium Platinum Complexes: Spectroscopic and Theoretical Studies.

Supplementary Information

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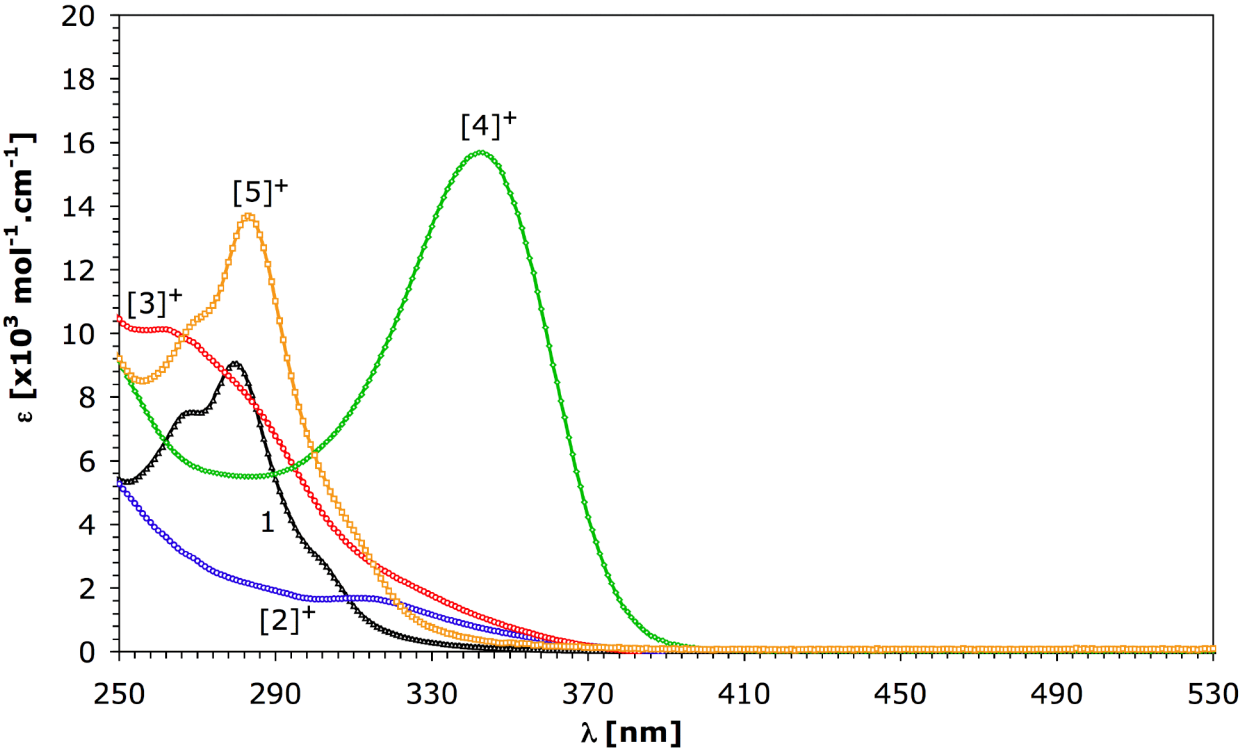
Figure S1. UV-vis spectra of CH_2Cl_2 solutions of complex **1** and $[\mathbf{2}]^+$-$[\mathbf{5}]^+$ (C = 10^{-4} M).



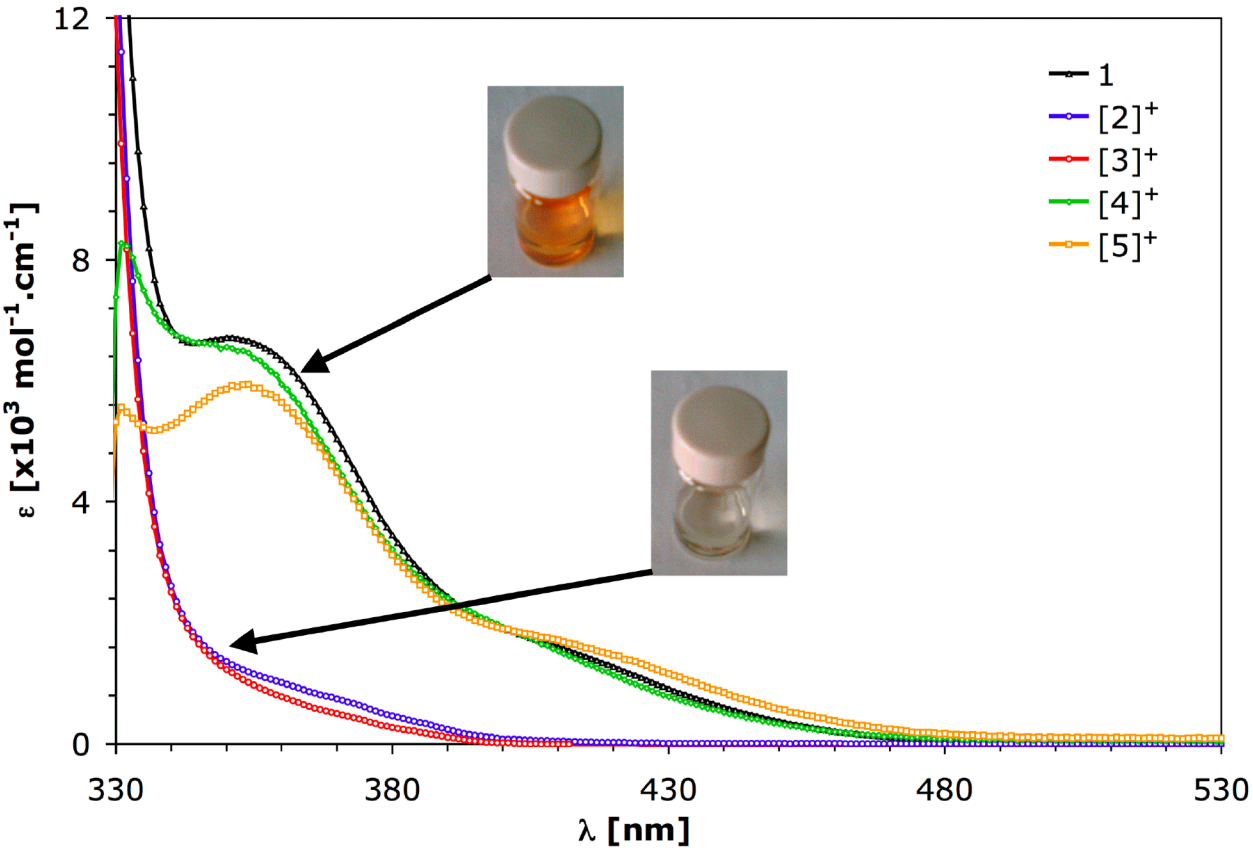


Figure S2. UV-vis spectra of dichloromethane solutions of complexes **1** and $[\mathbf{2}]^+$-$[\mathbf{5}]^+$ after saturation with SO_2 gas. Inlets show optical photographs of solutions of $[\mathbf{2}]^+$ (colorless) and $[\mathbf{4}]^+$ (orange) after SO_2-bubbling.

Table S1. Structural parameters for MP2-minimized complexes [**1**], [**2**]Cl and [**4**]Cl.

Parameter (Type)	[**1**] (MP2)	[**2**]Cl (MP2)	[**4**]Cl (MP2)
Pt-Cl	2.424	2.404	2.414
Pt-C_{ipso}	1.916	1.899	1.909
Pt-N	2.089	2.102	2.089
Cl-Pt-C_{ipso}	180.00	179.34	179.88
N-Pt-C_{ipso}	81.69	81.81	81.77
C_{ortho}-C_{ispo}-Pt-N	11.49	12.84	10.94

Table S2. Electronic parameters for MP2-minimized complexes [**1**], [**2**]Cl and [**4**]Cl.

Parameter	[**1**]	[**2**]Cl	[**4**]Cl
Q(Pt)	0.515	0.545	0.528
q^1(Pt)	0.169	0.679	0.201
Q(Cl)	-0.681	-0.655	-0.669
q^1(Cl)	0.596	0.634	0.619
Q(C_{ipso})	-0.186	-0.177	-0.181
q^1(C_{ipso})	0.791	0.580	0.750
BI(Pt-C_{ipso})	0.859	0.924	0.862
BI(Pt-Cl)	0.879	0.936	0.891

Table S3. Experimental and calculated electronic transitions for complexes **1**, [**2**]Cl, and [**4**]Cl. Only the most intense transition ($f > 0.01$) with $\lambda > 250$ nm are given.

Complex	**Calculated transitions**		
	E (eV)	**λ (nm)**	**f**
1	4.37	284	0.0115
	4.51	275	0.1049
	4.54	274	0.0145
	4.56	272	0.0224
	4.95	251	0.0219
[**2**]Cl	3.96	314	0.0124
[**4**]Cl	3.16	393	0.0149
	3.85	323	0.3758
	3.86	322	0.0455

Table S4. Atomic coordinates (in atomic units) of the MP2-minimized structures (without Counterpoise for **1**, [**2**]Cl and [**4**]Cl, and with Counterpoise for [**1**(SO_2)], [**2**(SO_2)]Cl, and [**4**(SO_2)]Cl.

[1]

X	Y	Z	e-	symbol
0	0	0	6	c
0	0	2.643426	6	c
2.254349	0	4.023865	6	c
4.563703	-0.019797	2.740127	6	c
4.563765	-0.000003	0.086583	6	c
2.300729	0.019802	-1.299043	6	c
-3.159362	0	4.413478	78	pt
-7.155131	0.000008	6.652155	17	cl
1.819553	0.217227	6.825647	6	c
-0.790195	-0.777998	7.474448	7	n
-0.651161	-3.570863	7.771864	6	c
-2.616455	-0.217227	-1.092335	6	c
-4.532612	0.777997	0.794478	7	n
-4.713679	3.570864	0.520628	6	c
-1.624948	0.352853	9.902315	6	c
-7.03905	-0.352854	0.238496	6	c
6.353418	-0.028993	3.759631	1	h
2.365876	0.028983	-3.357739	1	h
6.35716	-0.000011	-0.918159	1	h
-2.877033	0.776525	-2.900058	1	h
-3.089185	-2.211723	-1.388717	1	h
3.225125	-0.776525	7.991893	1	h
1.825445	2.211723	7.383573	1	h
-7.584722	0.085557	-1.715371	1	h
-6.918454	-2.391653	0.507413	1	h
-8.409237	0.408603	1.571839	1	h
-5.45113	4.036434	-1.364337	1	h
-5.979621	4.294011	1.976863	1	h
-2.837621	4.386391	0.765979	1	h
-0.243622	-0.085558	11.388013	1	h
-1.791317	2.391653	9.659071	1	h
-3.477576	-0.408604	10.374537	1	h
0.571264	-4.036418	9.385125	1	h
-2.554142	-4.294047	8.090974	1	h
0.119318	-4.386371	6.043806	1	h

[2]Cl

X	Y	Z	e-	symbol
0	0	0	6	c
0	0	2.703399	6	c
2.381341	0	3.994586	6	c
4.738467	-0.119502	2.643675	6	c
4.690502	-0.156447	-0.061836	6	c
2.331114	0.036827	-1.348414	6	c
2.264889	-3.146145	1.404405	44	ru
4.25131	-6.711785	1.069618	6	c

2.226274	-6.653334	-0.742423	6	c
-0.10924	-6.416532	0.626872	6	c
0.466007	-6.341394	3.272951	6	c
3.156105	-6.528073	3.55418	6	c
6.907388	-0.403777	-1.842441	6	c
6.179094	0.580866	-4.429448	7	n
6.62962	3.359617	-4.506608	6	c
2.278207	0.029177	-4.936761	78	pt
-1.60303	-0.378369	-4.39927	7	n
-3.094482	1.341369	-6.057141	6	c
-2.286358	0.196184	-1.656608	6	c
2.26356	0.016615	-9.480371	17	cl
-2.34749	-3.030462	-4.990672	6	c
7.804173	-0.655467	-6.356691	6	c
-5.220007	-3.597815	2.524277	17	cl
6.504359	-0.264691	3.691038	1	h
-1.779071	-0.224404	3.719338	1	h
2.404478	-0.100895	6.047938	1	h
-3.814284	-1.039776	-0.980339	1	h
-2.942331	2.161615	-1.598435	1	h
7.411407	-2.393673	-2.083702	1	h
8.596157	0.613827	-1.183832	1	h
9.802073	-0.310363	-5.914891	1	h
7.319814	0.11149	-8.203866	1	h
7.409169	-2.677979	-6.358004	1	h
5.556852	4.258184	-2.993044	1	h
5.982278	4.077304	-6.326824	1	h
8.65646	3.742381	-4.265976	1	h
-2.509172	3.283869	-5.696194	1	h
-5.112006	1.11168	-5.640701	1	h
-2.691873	0.870113	-8.019976	1	h
-1.335332	-4.283871	-3.716294	1	h
-4.387531	-3.258775	-4.708746	1	h
-1.825791	-3.43583	-6.943802	1	h
-2.028179	-6.213598	-0.067017	1	h
-0.958299	-6.075912	4.722767	1	h
4.1915	-6.520882	5.322989	1	h
6.248343	-6.909681	0.650142	1	h
2.441142	-6.764609	-2.777814	1	h

[4]Cl

X	Y	Z	e-	symbol
5.521598	0.297418	3.79535	6	c
6.201848	2.644823	2.579965	6	c
8.841436	2.529763	1.897206	6	c
9.811476	0.109466	2.703285	6	c
7.760742	-1.268405	3.879377	6	c
6.779067	-0.511915	-0.003972	44	ru
4.701296	-3.733275	-1.450374	6	c
3.470334	-1.459165	-2.29027	6	c
4.963345	0.394473	-3.605998	6	c
7.60513	0.02382	-4.003039	6	c
8.797534	-2.243375	-3.15976	6	c

7.33507	-4.125807	-1.903886	6	c
0.757948	-1.058972	-1.788796	6	c
-0.153982	1.397762	-1.272681	6	c
-2.711517	1.756578	-0.752309	6	c
-4.354821	-0.318636	-0.768877	6	c
-3.475484	-2.752375	-1.315724	6	c
-0.913592	-3.138533	-1.81429	6	c
-7.856407	0.188306	-0.061605	78	pt
-7.819849	-3.757652	0.062875	7	n
-10.156563	-4.964529	-0.920807	6	c
-3.992566	4.155751	0.081816	6	c
-6.804873	3.975802	-0.440542	7	n
-8.167443	5.736566	1.269582	6	c
-5.582963	-4.654299	-1.491699	6	c
4.565858	4.942875	2.373879	6	c
10.386165	4.603692	0.764443	6	c
12.51084	-0.694548	2.483535	6	c
7.97484	-3.782982	5.156546	6	c
3.00398	-0.305924	4.938559	6	c
-12.282204	0.829015	0.842311	17	cl
-7.286778	4.741047	-3.105872	6	c
-7.447469	-4.543782	2.737703	6	c
-5.063568	-6.571807	-0.879805	1	h
-6.251336	-4.769143	-3.44851	1	h
-8.987208	-3.772983	3.869685	1	h
-5.650734	-3.791386	3.410148	1	h
-7.440618	-6.616826	2.857084	1	h
-9.951569	-7.028484	-0.864024	1	h
-10.465286	-4.328567	-2.855684	1	h
-11.743865	-4.352723	0.237145	1	h
5.010412	6.248228	3.922412	1	h
2.566412	4.450312	2.506434	1	h
4.889483	5.937831	0.592951	1	h
11.445963	5.561845	2.268769	1	h
9.178093	6.000052	-0.162507	1	h
11.718076	3.843493	-0.632518	1	h
13.306511	-0.062765	0.675443	1	h
12.686091	-2.749978	2.601223	1	h
13.60139	0.136725	4.039866	1	h
9.466571	-4.921958	4.297082	1	h
6.203086	-4.838419	5.035058	1	h
8.437925	-3.524755	7.160448	1	h
2.73885	-2.348572	5.094658	1	h
1.464232	0.439373	3.777625	1	h
2.856669	0.512471	6.838077	1	h
1.170494	2.972439	-1.244766	1	h
-0.200107	-5.005589	-2.314763	1	h
-3.804041	4.369224	2.13395	1	h
-3.249892	5.87985	-0.81163	1	h
-6.767203	6.735305	-3.358731	1	h
-9.288427	4.471942	-3.514507	1	h
-6.159545	3.553378	-4.356714	1	h
-7.873228	5.129021	3.215994	1	h
-10.177975	5.634261	0.843046	1	h

-7.451711	7.665229	0.998815	1	h
4.080291	2.138911	-4.241282	1	h
8.821356	1.464173	-4.826899	1	h
10.845298	-2.343105	-3.363563	1	h
8.253272	-5.803781	-1.148953	1	h
3.644917	-5.104766	-0.34116	1	h
13.766743	1.251242	-3.812159	17	cl

[1(SO_2)]

X	Y	Z	e-	symbol
0	0	0	6	c
0	0	2.650683	6	c
2.32419	0	3.927308	6	c
4.645791	0.095078	2.649486	6	c
4.644425	0.095253	-0.001202	6	c
2.322466	0.018154	-1.299861	6	c
-2.22583	0.263804	4.406689	6	c
-1.565507	-0.892981	6.937059	7	n
-1.928313	-3.689107	6.773594	6	c
2.334004	-0.430874	7.552902	78	pt
2.364503	-1.861313	11.903801	17	cl
6.859877	0.449293	4.404437	6	c
6.248562	-0.734886	6.934435	7	n
7.922943	0.335486	8.919022	6	c
2.235199	4.429947	8.400211	16	s
4.604467	5.354298	7.191312	8	o
-0.175532	5.255153	7.20158	8	o
6.723512	-3.514013	6.768455	6	c
-3.280194	0.110919	8.921924	6	c
6.410996	0.170698	-1.067011	1	h
-1.768743	0.003087	-1.064872	1	h
2.322204	0.004244	-3.360944	1	h
-2.56028	2.282984	4.772188	1	h
-3.990922	-0.592207	3.705089	1	h
8.658137	-0.333536	3.701603	1	h
7.111642	2.48032	4.770637	1	h
-3.947186	-4.099665	6.470603	1	h
-0.826657	-4.424229	5.183873	1	h
-1.287941	-4.550806	8.541225	1	h
-5.247579	-0.355373	8.431587	1	h
-2.759335	-0.753466	10.726043	1	h
-3.041191	2.159216	9.026972	1	h
9.907161	-0.050175	8.426463	1	h
7.60121	2.372259	9.026781	1	h
7.439203	-0.551458	10.722531	1	h
8.756942	-3.842743	6.463008	1	h
6.120276	-4.40211	8.536079	1	h
5.650604	-4.291739	5.179329	1	h

[2(SO_2)]Cl

X	Y	Z	e-	symbol
0	0	0	6	c
0	0	2.699581	6	c
2.363452	0	4.009341	6	c
4.716776	-0.085348	2.673792	6	c
4.702449	-0.099791	-0.033525	6	c
2.344438	0.01971	-1.317819	6	c
2.300293	-3.152717	1.402637	44	ru
3.442188	-6.309992	3.751383	6	c
4.29376	-6.736076	1.204989	6	c
2.101228	-6.854213	-0.398787	6	c
-0.084045	-6.488497	1.18022	6	c
0.735823	-6.155358	3.745979	6	c
6.932399	0.153327	-1.769782	6	c
6.231921	-0.670028	-4.421984	7	n
7.852593	0.695702	-6.276882	6	c
2.317475	-0.233757	-4.930824	78	pt
2.451282	5.060263	-4.947772	16	s
4.899857	5.559352	-3.636968	8	o
-2.243727	0.326561	-1.703698	6	c
-1.604551	-0.473534	-4.382756	7	n
-3.171216	1.011748	-6.192707	6	c
2.27871	-1.088355	-9.39474	17	cl
-2.246212	-3.200847	-4.704789	6	c
6.728237	-3.432993	-4.688682	6	c
0.097875	5.681544	-3.523708	8	o
-1.717844	-2.495068	8.041564	17	cl
6.478361	-0.216801	3.729179	1	h
-1.686719	-0.202284	3.871163	1	h
2.259618	-0.215315	6.055173	1	h
-3.940323	-0.684784	-1.069626	1	h
-2.665393	2.353747	-1.769109	1	h
8.614862	-0.894594	-1.153049	1	h
7.402208	2.168195	-1.878256	1	h
8.764493	-3.782226	-4.494216	1	h
6.078446	-4.040509	-6.548387	1	h
5.695058	-4.419897	-3.207089	1	h
7.516069	2.716179	-6.093339	1	h
7.334817	0.061668	-8.166684	1	h
9.844104	0.269205	-5.886922	1	h
-2.734289	3.008721	-5.968792	1	h
-5.177212	0.677213	-5.789724	1	h
-2.704997	0.393307	-8.101154	1	h
-1.235802	-4.273784	-3.269698	1	h
-4.29223	-3.45332	-4.473902	1	h
-1.662917	-3.795501	-6.590345	1	h
2.099987	-7.235816	-2.412997	1	h
-2.038957	-6.475376	0.565974	1	h
-0.426079	-5.590704	5.369543	1	h
4.627817	-6.092269	5.409046	1	h
6.240799	-6.986627	0.616218	1	h

[4(SO_2)]Cl

X	Y	Z	e-	symbol
6.075732	2.372228	2.897317	6	c
6.755143	3.596833	0.554245	6	c
9.399125	3.123906	0.0695	6	c
10.371651	1.614164	2.124534	6	c
8.31864	1.151624	3.872838	6	c
7.351605	-0.46772	0.258099	44	ru
5.290764	-3.945453	0.922772	6	c
4.062017	-2.566641	-1.073139	6	c
5.552977	-1.807642	-3.217215	6	c
8.196505	-2.329482	-3.320744	6	c
9.39044	-3.691102	-1.322315	6	c
7.926467	-4.517158	0.782925	6	c
1.352662	-1.937158	-0.87866	6	c
0.449532	0.370793	-1.871628	6	c
-2.09259	1.006542	-1.598194	6	c
-3.700467	-0.65561	-0.316174	6	c
-2.862107	-2.99258	0.587518	6	c
-0.319993	-3.64345	0.306678	6	c
-7.099574	0.407209	0.426124	78	pt
-7.107552	-2.975287	2.490096	7	n
-9.519364	-4.420918	2.479901	6	c
-3.467645	3.216616	-2.734887	6	c
-5.788843	3.795566	-1.162682	7	n
-5.027365	5.387562	1.035557	6	c
-4.985536	-4.634761	1.517456	6	c
5.114173	5.350001	-0.940502	6	c
10.944471	4.176752	-2.045481	6	c
13.074415	0.846355	2.416771	6	c
8.533018	-0.169618	6.364489	6	c
3.55609	2.526395	4.177088	6	c
-11.086361	2.014881	1.961263	17	cl
-7.645733	5.232787	-2.709703	6	c
-6.528451	-2.215267	5.142814	6	c
-4.451605	-5.979482	3.007601	1	h
-5.765966	-5.69115	-0.0841	1	h
-7.982683	-0.904468	5.787167	1	h
-4.680488	-1.300797	5.192924	1	h
-6.507236	-3.905262	6.345934	1	h
-9.321451	-6.0904	3.694135	1	h
-9.931493	-4.997193	0.548707	1	h
-11.010808	-3.186622	3.182446	1	h
5.542188	7.310482	-0.418096	1	h
3.114792	5.007088	-0.560651	1	h
5.449807	5.146474	-2.96838	1	h
11.994607	5.830347	-1.362186	1	h
9.738412	4.780438	-3.610503	1	h
12.285199	2.757437	-2.746834	1	h
13.878006	0.321327	0.578122	1	h
13.255988	-0.761115	3.70214	1	h
14.153044	2.43141	3.208294	1	h
10.029443	-1.59076	6.319393	1	h
6.763601	-1.108823	6.869623	1	h

8.989449	1.196062	7.855561	1	h
3.286574	0.931729	5.462578	1	h
2.020327	2.485502	2.793174	1	h
3.410288	4.277289	5.278761	1	h
1.761192	1.636563	-2.824759	1	h
0.374767	-5.48181	0.923418	1	h
-2.329514	4.946133	-2.912336	1	h
-4.159202	2.680962	-4.61223	1	h
-6.775888	7.00155	-3.354591	1	h
-9.294479	5.620593	-1.538165	1	h
-8.184804	4.080308	-4.326142	1	h
-3.53906	4.418431	2.084912	1	h
-6.670948	5.674783	2.245905	1	h
-4.323585	7.212721	0.343565	1	h
4.670384	-0.754273	-4.746122	1	h
9.413048	-1.621755	-4.821335	1	h
11.439606	-3.879403	-1.426685	1	h
8.844528	-5.453328	2.366963	1	h
4.232162	-4.434852	2.616103	1	h
14.352919	-1.181453	-3.832918	17	cl
-8.780612	-1.627629	-3.950703	16	s
-8.116832	-4.358936	-3.645096	8	o
-7.317714	-0.182466	-5.891559	8	o