Electronic Supplementary Information: Theoretical study on aquation reaction of *cis*-platin complex: RISM-SCF-SEDD, a hybrid approach of accurate quantum chemical method and statistical mechanics

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1 Total energy

	in gas phase		in aqueous phase	
1	-1303.67137	(0.0)	-1303.737224	(0.0)
TS$_{1-2}$	-1303.63613	(22.1)	-1303.700119	(23.3)
2'	-1303.66510	(3.9)	-1303.726604	(6.7)
2	-1303.49278	(112.1)	-1303.725303	(7.5)
TS$_{2-3}$	-1303.45147	(138.0)	-1303.687690	(31.1)
3'	-1303.47083	(125.8)	-1303.709231	(17.6)
3	-1303.15903	(321.5)	-1303.702362	(21.9)

given in a.u. and kcal/mol^{-1}

2 The functional check

	B3LYP	M06
1	(0.00)	(0.00)
TS$_{1-2}$	(9.77)	(9.09)
2'	(-8.31)	(-8.48)
2	(106.78)	(106.59)
TS$_{2-3}$	(120.36)	(119.68)
3'	(109.75)	(109.40)
3	(312.50)	(312.28)

The geometry was optimized with DFT, followed by CCSD(T) computation in gas phase. All the values are given in kcal/mol^{-1}

3 Estimation of the reaction free energy related to the chloride concentration

Under physiological conditions, the concentration of chloride anion is regulated at a specific finite value. As an analogy with K_a, the following concentration-dependent expression may become adequate in the comparison with experimental values for the dissociation process, i.e., **2'**→**2** and **3'**→**3**, in the presence of the excess anion.

pCl	pK_1	pK_2
0.99	2.75	7.82
2.40	1.34	6.41

$$\mathrm{p}K_{a'} = \frac{\Delta_r G^0_{a'}}{2.303RT} - \log c_w - \mathrm{pCl}, \quad (1)$$

Evaluated $\mathrm{p}K'_1$ and $\mathrm{p}K'_2$ are given in the table.

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4 Radial distribution functions

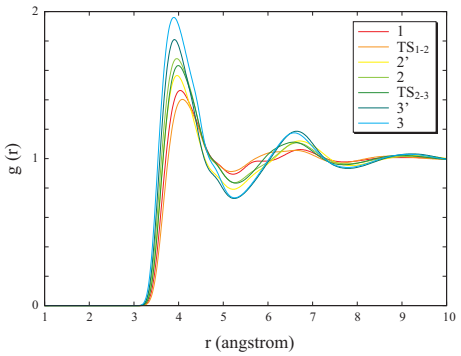

Fig. 1 RDFs between platinum and solvent water oxygen

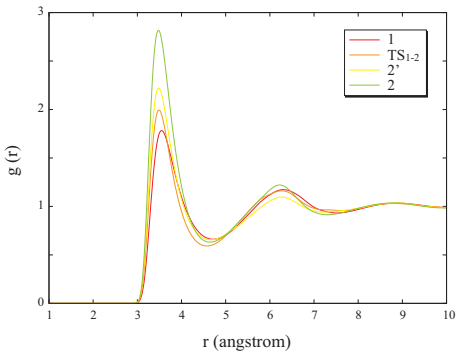

Fig. 2 RDFs between chloride and solvent water oxygen

5 Cartesian coordinates of optimized structure in the gas phase

1

Pt	78	0.000778	0.000897	0.000835
Cl	17	2.326352	-0.001786	0.002711
Cl	17	-0.229577	-2.287394	0.343527
N	7	0.264084	2.066881	-0.317969
N	7	-2.104467	-0.055790	0.011170
H	1	1.289903	2.166682	-0.283971
H	1	-0.048904	2.405234	-1.232349
H	1	-0.133772	2.681579	0.397527
H	1	-2.305482	-1.062751	0.109810
H	1	-2.542955	0.424209	0.802404
H	1	-2.561403	0.270258	-0.845122

TS_{1-2}

Pt	78	0.007600	-0.007199	0.003170
N	7	2.085802	0.006591	0.008072
N	7	-0.307093	1.768344	1.070081
O	8	-2.088077	0.284601	-1.165056
H	1	0.446951	2.133917	1.655491
H	1	-1.092412	1.465043	1.678964
H	1	-0.641465	2.528605	0.470589
H	1	2.336988	-0.811886	-0.564391
H	1	2.492337	-0.130032	0.937719
H	1	2.521031	0.830916	-0.414869
H	1	-2.090394	-0.449036	-1.799959
H	1	-2.585779	-0.042591	-0.377345
Cl	17	0.244286	-1.976875	-1.223405
Cl	17	-2.177306	-0.502501	1.648758

2'

Pt	78	0.114831	-0.051344	-0.192478
N	7	2.136526	-0.035649	0.203139
N	7	-0.378164	1.487797	1.146063
O	8	-1.886094	-0.120427	-0.677791
H	1	0.252309	1.628274	1.939487
H	1	-1.330558	1.239933	1.542145
H	1	-0.481773	2.394823	0.680001
H	1	2.526929	-0.806262	-0.356362
H	1	2.374835	-0.213421	1.183699
H	1	2.610875	0.825485	-0.085736
H	1	-2.074914	-0.989572	-1.064428
H	1	-2.478720	-0.000130	0.175464
Cl	17	0.569788	-1.786754	-1.677100
Cl	17	-3.197620	0.465849	1.792425

2

Pt	78	0.002690	-0.007206	-0.002704
O	8	2.113556	-0.013632	-0.007274
N	7	0.099520	1.937098	0.849660
N	7	-2.036298	-0.127910	-0.063034
H	1	-0.414824	2.041492	1.731259
H	1	-0.231439	2.683023	0.226622
H	1	1.076945	2.166920	1.066573
H	1	-2.492204	-0.086065	0.855671
H	1	-2.256063	-1.051766	-0.464596
H	1	-2.479263	0.574365	-0.666205
H	1	2.416158	-0.805639	0.472255
H	1	2.433368	-0.136569	-0.919076
Cl	17	0.036677	-2.111269	-0.926990

TS_{2-3}

Pt	78	-0.043296	-0.005029	-0.054608
O	8	-0.650587	-1.824917	0.767907
O	8	1.725716	0.537816	1.374268
N	7	-1.918007	0.096460	-0.958923
N	7	0.748453	1.643968	-0.977741
H	1	-2.504224	0.879905	-0.649209
H	1	-2.423556	-0.765421	-0.718917
H	1	-1.881962	0.127066	-1.984179
H	1	0.103976	2.368337	-1.310052
H	1	1.392737	2.091951	-0.311713
H	1	1.318196	1.347401	-1.780920
H	1	0.220017	-2.306213	0.566403
H	1	-0.769835	-1.830013	1.731628
H	1	1.612118	0.542496	2.336677
H	1	2.256314	-0.265389	1.131561
Cl	17	2.020630	-1.851243	-0.230424

3'

Pt	78	-0.033183	0.133710	-0.111268
O	8	-0.328626	-1.791525	0.559714
O	8	1.874230	0.207867	0.672884
N	7	-1.896619	-0.085015	-0.979348
N	7	0.399212	2.017165	-0.845171
H	1	-1.932238	0.123095	-1.983938
H	1	-2.636037	0.468801	-0.531472
H	1	-2.162937	-1.074066	-0.879815
H	1	-0.147848	2.775541	-0.421477
H	1	1.387766	2.205776	-0.629787
H	1	0.305899	2.108667	-1.863323
H	1	0.637331	-2.259349	0.471763
H	1	-0.577259	-1.860935	1.496250
H	1	1.904019	0.378121	1.628868
H	1	2.259183	-0.787567	0.544781
Cl	17	2.371450	-2.540485	0.326668

3

Pt	78	0.002564	-0.003174	0.003768
O	8	2.112609	-0.023934	-0.031500
O	8	-0.224540	-1.883675	-0.925945
N	7	0.196900	1.832237	0.896689
N	7	-2.046302	0.039402	0.040713
H	1	2.604745	-0.652230	0.525799
H	1	2.585316	0.060276	-0.878143
H	1	0.020575	-1.999617	-1.860856
H	1	0.026247	-2.693123	-0.447301
H	1	-0.327061	1.934137	1.777019
H	1	-0.087412	2.611884	0.285892
H	1	1.184998	2.002019	1.134625
H	1	-2.456738	0.838236	-0.463728
H	1	-2.425270	-0.805533	-0.411756
H	1	-2.439010	0.052012	0.992828