Electronic Supplementary Information

Ligand Rigidity and Electronic Effect on the Complexation of Hexavalent Plutonyl with Three Dicarboxylic Acids: A Combined Spectrophotometric and Computational Study

Lei Xu[§], Ning Pu[§], Jianhua Yuan, Pingping Wei, Xue Dong, Yingcai Wang, Jing Chen, Chao Xu*

Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

Contents

1. The supplementary data of Pu(VI) speciation diagrams during the titration process.

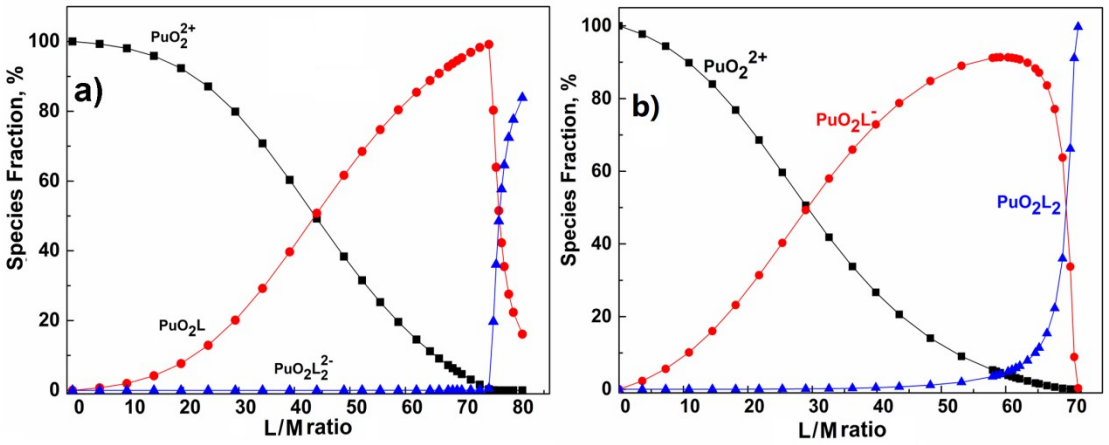

Fig. S1 Species fractions for the titrations of Pu(VI) with IDA a) and MIDA b) in I = 1.0 mol/L $NaClO_4$ solution at 298K.

2. The supplementary structure of the 1:1 Pu(VI)/IDA complex.

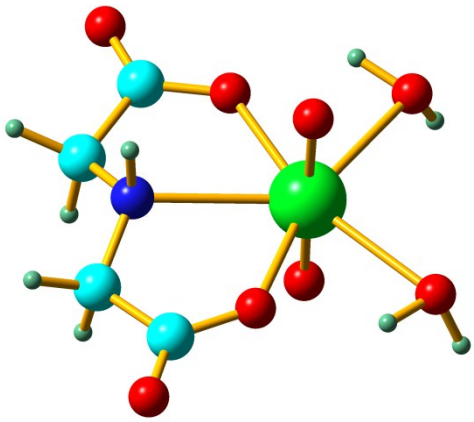

Fig. S2 The optimized structure of the 1:1 Pu(VI)/IDA complex with two coordinated water molecules. Grey-green, cyan, blue, red and green colors denote H, C, N, O and Pu atoms, respectively.

3. The coordinates of the optimized structures of the three ligands with DFT methods.

IDA^{2-}

C	-2.505922287	1.708847334	0.11168394
C	-1.225507745	2.591101862	-0.108084603
O	-2.315053422	0.531014862	0.511241545
C	1.2259383	2.590914817	-0.108109126
C	2.506224518	1.708465191	0.111617372
O	3.601353229	2.306954683	-0.086050838
O	2.315186325	0.530645785	0.51113169
H	-1.432956393	3.285466439	-0.938762166
H	-1.144575002	3.246719012	0.795084555
H	1.145127719	3.246533123	0.795070286
H	1.433469229	3.285258171	-0.938783873
O	-3.600965825	2.307515043	-0.085914898
N	0.000156467	1.851723816	-0.354219458
H	9.55072E-05	1.001590874	0.207829245

$MIDA^{2-}$

C	-2.632611155	1.948812321	-0.000446228
C	-1.204042814	2.585624495	-0.212320198
O	-2.752394521	0.90000357	0.683171191
C	1.204476135	2.585421275	-0.212351799
C	2.632952728	1.948368794	-0.000566807
O	3.541714232	2.618901287	-0.566292923
O	2.752598846	0.899491955	0.682969712
H	-1.109809048	2.747882639	-1.294664326
H	-1.258988031	3.611879301	0.226246485
H	1.259614488	3.611661558	0.226225207
H	1.110226071	2.747711981	-1.294689554
O	-3.541279069	2.619389806	-0.566270693
N	0.000162205	1.886013198	0.24398547
C	0.000147865	1.708716199	1.6876605
H	0.000232393	2.688052765	2.232226566
H	-0.905588053	1.162668618	1.960248494
H	0.905785179	1.16250814	1.960250013

DPA^{2-}

C	0.12681	5.72995	-1.46317
C	-0.00549	7.10901	-1.70814
C	-1.28815	7.6395	-1.85789

C	-2.38564	6.78248	-1.75907
C	-2.15144	5.41731	-1.51206
N	-0.92084	4.88869	-1.36479
H	-1.43097	8.71216	-2.05119
H	0.8841	7.74778	-1.77848
H	-3.41074	7.15814	-1.87048
C	1.51661	5.08976	-1.28941
C	-3.32331	4.42526	-1.39306
O	1.6184	3.81228	-1.06343
O	2.58518	5.82813	-1.36907
O	-3.08643	3.16631	-1.16433
O	-4.54702	4.84881	-1.52158

4. The coordinates of the optimized structures of Pu(VI) complexes using DFT methods.

$PuO_2(IDA)(H_2O)_2$

C	-2.44254	1.57463	-0.01182
C	-1.2534	2.53913	-0.1866
O	-2.06684	0.32344	0.18717
C	1.25345	2.53912	-0.18661
C	2.44257	1.57456	-0.01201
O	3.58652	1.96853	-0.0949
O	2.06684	0.3234	0.1871
H	-1.13359	2.71676	-1.2614
H	-1.48565	3.50151	0.28315
H	1.48575	3.50147	0.28318
H	1.1336	2.71681	-1.26138
O	-0.00002	-0.47572	-1.72255
O	0.	-0.87871	1.8064
O	-3.58648	1.96857	-0.09501
O	1.94803	-2.32382	-0.2432
H	2.60434	-1.63718	0.00919
H	2.13763	-2.51542	-1.17717
O	-1.94807	-2.32379	-0.2432
H	-2.13765	-2.51538	-1.17718
H	-2.60437	-1.63711	0.00911
N	0.00002	1.93858	0.32075
H	0.00003	2.01069	1.33985
Pu	-0.00001	-0.62752	0.05256

$PuO_2(MIDA)(H_2O)_2$

C	-2.40499	1.62326	-0.02024
C	-1.21878	2.59993	-0.04984
O	-2.04581	0.35687	-0.01787
C	1.21922	2.59976	-0.04984
C	2.40526	1.62289	-0.02035
O	3.53987	2.05082	0.00127
O	2.04587	0.35656	-0.01816
H	-1.30648	3.2633	-0.91836
H	-1.227	3.20974	0.86229
H	1.22758	3.20952	0.86233
H	1.307	3.26316	-0.91833
O	-0.00019	-0.89314	-1.73705
O	0.00006	-0.599	1.79395
O	-3.53953	2.05138	0.00126
O	1.93737	-2.35155	0.04861
H	2.61227	-1.66448	0.23518
H	2.13861	-2.6544	-0.85334
O	-1.93774	-2.35129	0.04846
H	-2.1389	-2.65384	-0.85361
H	-2.61256	-1.66418	0.23514
N	0.00017	1.85098	-0.12469
C	0.0002	2.26787	1.28496
H	0.00028	3.33641	1.34088
H	-0.87348	1.8854	1.77003
H	0.87382	1.88526	1.77003
Pu	-0.00006	-0.63866	0.02417

$PuO_2(DPA)(H_2O)_2$

C	-2.153491774	1.14688375	-0.075636617
C	-3.551836893	1.175877947	-0.042498284
C	-4.243124214	-0.036542168	0.019907333
C	-3.523040731	-1.236174666	0.055370992
C	-2.127293208	-1.182651093	-0.010457121
N	-1.477234637	-0.012182192	-0.08406932
H	-5.335744067	-0.045646644	.047344176
H	-4.054561028	2.138294525	-0.05882155
H	-4.004644096	-2.204645079	0.129610508
C	-1.28724458	2.392232681	-0.070346389
C	-1.233476033	-2.40955609	0.005616522
O	-0.008102798	2.102993577	-0.073689377
O	-1.781780524	3.506254183	-0.055780988
O	0.027932456	-2.102591503	-0.175681347
O	-1.698976366	-3.524239844	0.167516739

O	2.52520499	2.001068289	0.457867875
H	3.307949565	2.225581376	-0.05168103
H	1.838513227	2.682167312	0.284337573
O	2.585629545	-2.006479176	-0.004187583
H	1.850171625	-2.643328004	-0.106846913
H	3.290261003	-2.234987425	-0.593763157
Pu	0.986165864	0.010776526	-0.007900814
O	0.794338278	-0.072337482	1.720221859
O	1.239023118	0.10213492	-1.737611737

$[PuO_2(IDA)_2]^{2-}$

C	2.51834	-2.4401	-0.15877
C	3.46426	-1.23921	0.0853
O	1.27913	-2.11054	-0.25798
C	3.45986	1.24793	0.09242
C	2.50929	2.44669	-0.14401
O	2.99543	3.57993	-0.19308
O	1.27136	2.11282	-0.24484
H	3.61969	-1.15406	1.16851
H	4.44553	-1.43871	-0.3741
H	4.44016	1.45382	-0.36625
H	3.61615	1.15695	1.17502
O	0.67482	-0.00556	1.80151
O	-0.11769	0.00306	-1.70118
O	3.00888	-3.57115	-0.21466
N	2.84288	0.00457	-0.36855
H	2.78738	0.00738	-1.38642
C	-2.82975	1.79408	0.35062
C	-3.63376	1.23727	-0.86044
O	-1.59596	1.42071	0.46245
C	-3.65122	-1.23438	-0.831
C	-2.83049	-1.79332	0.36774
O	-3.39572	-2.60925	1.09902
O	-1.59033	-1.43469	0.45226
H	-4.68233	1.17717	-0.54363
H	-3.59151	2.04144	-1.61285
H	-3.65044	-2.05273	-1.56944
H	-4.68938	-1.14036	-0.48943
O	-3.39908	2.62045	1.06687
N	-3.26676	-0.00919	-1.5166
H	-2.27125	-0.01854	-1.73035
Pu	0.17236	-0.00174	0.0799

$[PuO_2(MIDA)_2]^{2-}$

C	0.08443	2.41361	-2.39122
C	0.66238	3.27649	-1.24056
O	-0.42313	1.2986	-1.99163
C	0.66276	3.27628	1.24028
C	0.08471	2.41365	2.39103
O	0.14971	2.84127	3.54656
O	-0.4244	1.29943	1.99126
H	1.72146	3.0193	-1.12327
H	0.59699	4.34513	-1.5139
H	0.59785	4.34495	1.51362
H	1.72171	3.01866	1.12278
O	1.73916	0.42519	0.0004
O	-1.73916	-0.42519	-0.0004
O	0.14938	2.84114	-3.54678
N	-0.02767	2.95244	-0.00008
C	-0.08471	-2.41365	-2.39103
C	-0.66276	-3.27628	-1.24028
O	0.4244	-1.29943	-1.99126
C	-0.66238	-3.27649	1.24056
C	-0.08443	-2.41361	2.39122
O	-0.14938	-2.84114	3.54678
O	0.42313	-1.2986	1.99163
H	-1.72171	-3.01866	-1.12278
H	-0.59785	-4.34495	-1.51362
H	-0.59699	-4.34513	1.5139
H	-1.72146	-3.0193	1.12327
O	-0.14971	-2.84127	-3.54656
N	0.02767	-2.95244	0.00008
C	-1.39631	3.46444	0.00015
H	-1.41781	4.57303	0.00108
H	-1.92084	3.10134	-0.88694
H	-1.92106	3.09971	0.88642
C	1.39631	-3.46444	-0.00015
H	1.41781	-4.57303	-0.00108
H	1.92106	-3.09971	-0.88642
H	1.92084	-3.10134	0.88694
Pu	0.	0.	0.

$[PuO_2(PDA)_2]^{2-}$

C	-0.08329	5.72045	-1.30305
C	-0.21559	7.0995	-1.54802

C	-1.49824	7.62999	-1.69776
C	-2.59574	6.77297	-1.59894
C	-2.36153	5.40781	-1.35193
N	-1.13094	4.87919	-1.20467
H	-1.64107	8.70266	-1.89107
H	0.674	7.73827	-1.61836
H	-3.62084	7.14864	-1.71035
C	1.30651	5.08025	-1.12929
C	-3.5334	4.41576	-1.23293
O	1.4083	3.80278	-0.9033
O	2.37508	5.81863	-1.20895
O	-3.29652	3.15681	-1.0042
O	-4.75712	4.83931	-1.36146
Pu	-0.92296	2.21227	-0.66493
O	-1.32008	2.73133	1.12977
O	-0.52584	1.69322	-2.45964
C	0.61608	-1.30573	0.00627
C	0.80946	-2.69031	0.16394
C	-0.31347	-3.51739	0.22704
C	-1.5804	-2.93899	0.13166
C	-1.67148	-1.54368	-0.02448
N	-0.59871	-0.73087	-0.08746
H	-0.20188	-4.60396	0.35072
H	1.82334	-3.1043	0.2348
H	-2.48913	-3.55262	0.17668
C	1.81757	-0.34539	-0.06974
C	-3.04223	-0.85058	-0.13526
O	1.61824	0.93223	-0.21575
O	3.02867	-0.81432	0.01225
O	-3.10591	0.44115	-0.2793
O	-4.13284	-1.55865	-0.08452