Effect of hydration of room temperature ionic liquid on the Cation-Cation Interaction of UO_2^{2+} and NpO_2^{+} ion

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Discussion about peak at 1002

Carrying forward from the discussion in the main manuscript, that Dong et al.[1], have assigned peak in the 990-1010 nm region due to the Np-hydroxo or carbonato complexes[1]. Initially, we have also assumed similar situation in present studies but later our studies for CCI interaction of Np(V) with U(VI) contradicts this peak assignments. We have added ~300 times U(VI) during the titration of Np(V) with U(VI) for elucidating CCI interaction of the Np(V) with U(VI). During the titration studies we have observed no change either in the position or intensity of the peak at 1002 nm. If these peak are arising from the hydroxo[2] or carbonato[3] complexes of the Np(V) , the addition of U(VI) with more effective charge on central metal ion must have caused dissociation of these Np-hydroxo or carbonato complexes and we should get spectra changes in 1002 nm peak. This lead to the conclusion that these peaks are not from the Np(V)-hydroxo or carbonato complex of Np(V).

To elucidate further on the present hypothesis, we have plotted Np(V) speciation in the with pH in carbonate containing media. The concentration of carbonate in the pH variation diagram was assumed similar to the aqueous system (~$10^{-3.4}$ M). The speciation diagram clearly suggest that the Np-carbonto species formation starts in alkaline region, which is not the case with the either of ionic liquid used in the present studies.Two inherent question that can arise when comparing aqueous and RTIL phase for Np(V) speciation firstly, CO_2(g) dissolution in RTIL and secondly pK_a value of carbonic acid (assuming dissolved CO_2(g) form H_2CO_3 with dissolved water in RTIL) in RTIL. Although we have not studied these things specifically, but as we know pK_a value reflect the concentration of carbonate available at given pH for metal complexation in any media. We have plotted Np(V) speciation as a function of carbonate concentration and the **Fig. S1(a)** shows that the Np-monocarboato species

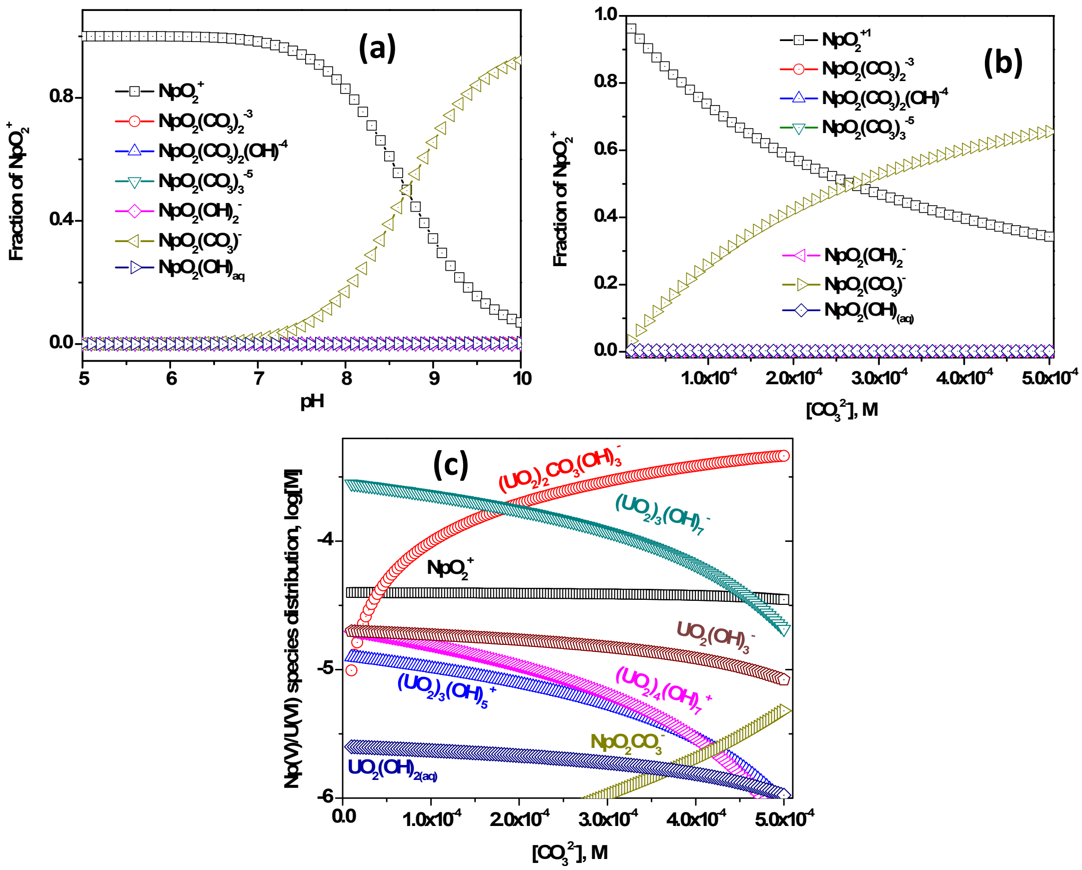

Figure S1. Neptunium speciation in aqueous solution, [Np(V)]: 5×10^{-5} M; [CO_3^{2-}]:5×10^{-4} M; Np(V) speciation in the b) absence and (c) presence of U(VI) as function of carbonate concentration at pH 9; [U(VI)] : 1×10^{-3} M at 298 K.

dominates as the carbonate concentration increase in absence of any U(VI) **(Fig. S1(b))**. To understand the effect of U(VI) addition on the Np(V) speciation, we have again plotted Np(V) speciation in presence of U(VI) **(Fig. S1(c))**. The concentration of Np(V) was kept same as during the CCI titration. The U(VI) concentration was kept as was used 10 time lower than the final titration point. There can be difference in the logβ value of the Np-carbonated complexation in the RTIL, even if so, the complexation constant for UO_2^{2+} must be higher than for NpO_2^{+} under similar conditions. Assuming, the Np(V)-carbonate/hydroxo and U(VI)-carbonate/hydroxo complexation constant value of aqueous media, we have of plotted Np(V) and U(VI) species distribution as a function of carbonate concentration (as the exact amount of carbonate in the RTIL is not known). The figures clearly shows that, if the peak at 1002 belongs to the Np-hydroxo/carbonato species the addition of U(VI) must decomplex the Np-carbonato/hydroxo complex and make U(VI)-carbonato/hydroxo species and Np(V) must remains as free ions, which is not observed in present studies.

The origin of the 1002 peak in the Np-RTIL system can be due to the CCI of Np(V) with the Np(IV). Since we have only Np in the system and the redox chemistry of Np is not well understood in the these media, we propose that the either Np(V) get either reduced or disproportioned to Np(IV) and Np(VI). Since the epsilon of the Np(IV) and Np(VI) are poor compared to Np(V), they are not detected in the vis-NIR spectra but the CCI between Np(V) and Np(IV) are prominent compred to Np(V)-Np(VI) CCI due to strong electrostatic interaction between Np(V) and Np(IV).

Our titration data suggest no change in the 1002 paeak after U(VI) addition. This can only be possible if the interaction governing 1002 peak is stronger than Np(V)-U(VI) interaction and Np(V)-Np(IV) interaction can definitely fulfill this condition.

To verify it experimentally, we have recorded vis-NIR spectra of Np(V) in dry C_4mim.NTf_2 and later to the same solution $HNTf_2$ was added to facilitate Np(V) disproportion. We have observed quick decrease in the 971 peak with rise in the 1002 peak. The signature of the Np(IV) at 727 nm was also seen in the vis-NIR spectra, However, Np(VI) could not be observed possibly due to its very low molar absorbance. This clearly suggest that the 1002 peak comes mainly due to the interaction between Np(IV) and Np(V).

References

[1] X. Dong, Z. Wang, Q. Yan, H. Liu, Y. Guo, H. Cao, J. Chen, C. Xu, *Chinese Chemical Letters* **2022**, *33*, 3531-3533.

[2] L. Rao, T. G. Srinivasan, A. Y. Garnov, P. Zanonato, P. Di Bernardo, A. Bismondo, *Geochimica et cosmochimica acta* **2004**, *68*, 4821-4830.

[3] S. Yang, Y. Zhao, G. Tian, *Dalton Transactions* **2016**, *45*, 2681-2685.

Figures

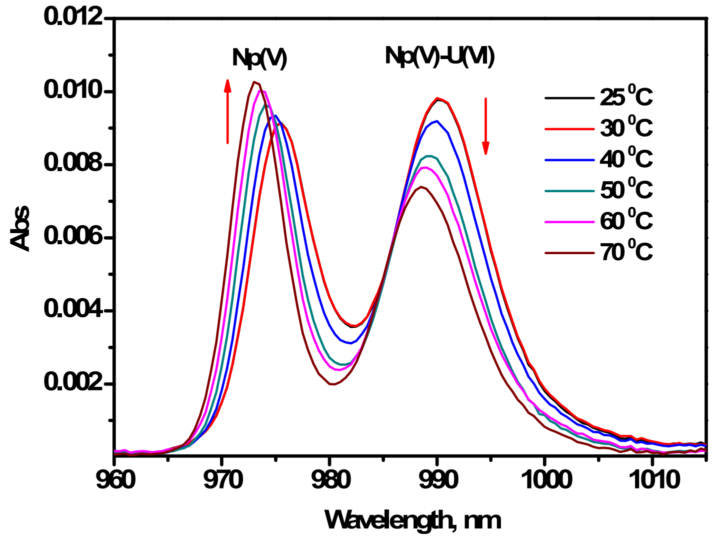

Figure S2. The effect of temperature on the Np(V)-U(VI) CCI in wet RTIL.

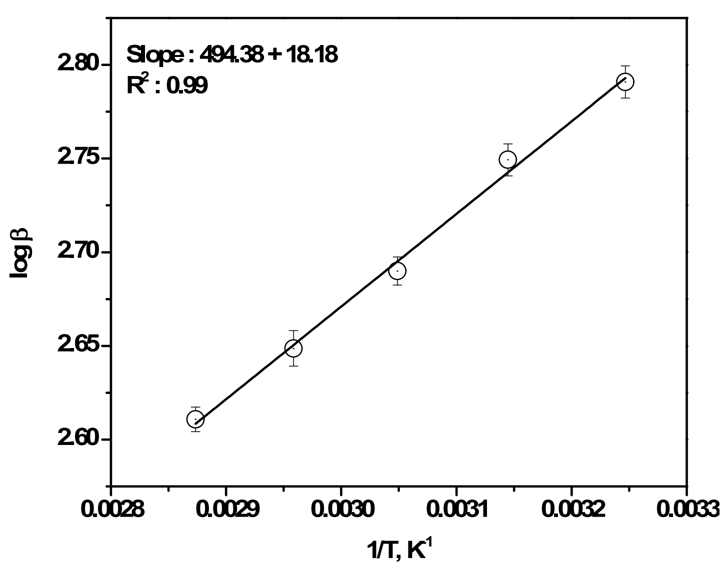

Figure S3. The effect of temperature on the stability constant of the Np(V)-U(VI) CCI in wet RTIL.

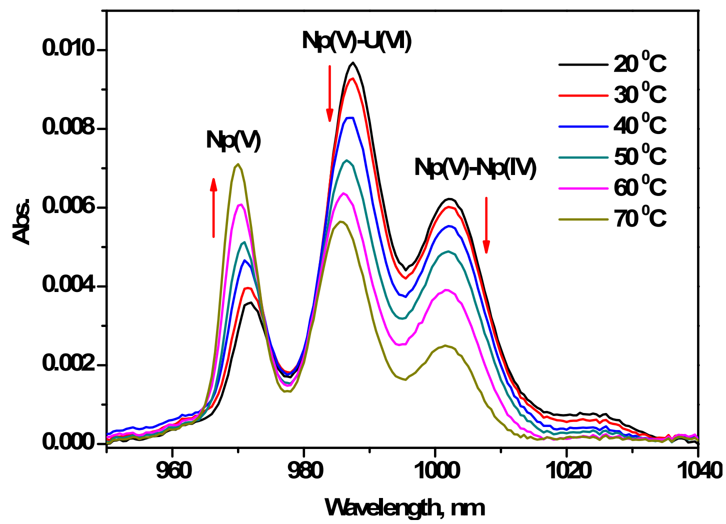

Figure S4. The effect of temperature on the Np(V)-U(VI) and Np(V)-Np(IV) CCI in dry RTIL.

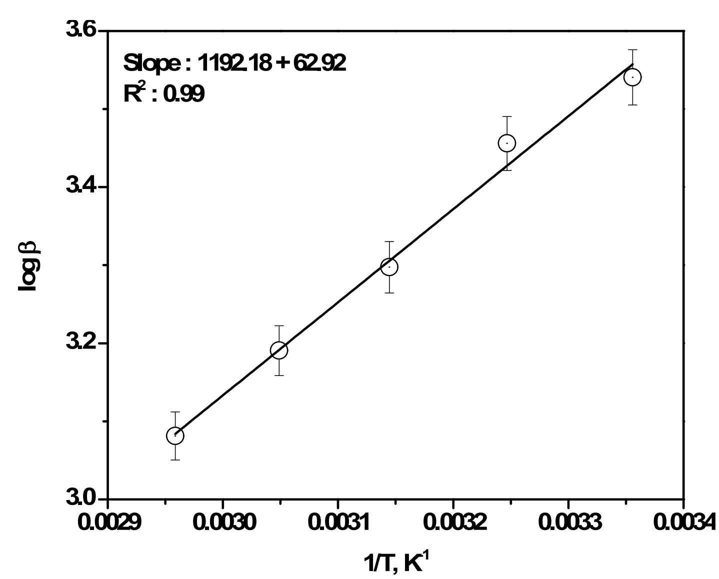

Figure S5. The effect of temperature on the stability constants of the Np(V)-U(VI) CCI in dry RTIL.

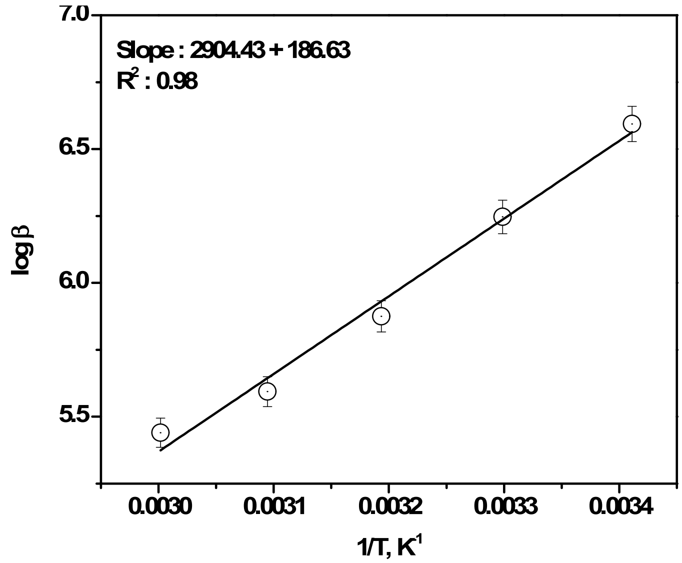

Figure S6. The effect of temperature on the stability constants of the Np(V)-Np(IV) CCI in dry RTIL.

Table S1: Cartesian coordinates of the Np(V), U(VI) species and their CCI complexes considered in aqueous and RTIL media

$NpO_2(H_2O)_5^+$

Np	0.8523969	0.0294560	-1.0717098
O	1.2051562	-1.0015090	0.3677148
O	0.4982590	1.0597048	-2.5094323
O	-0.0737201	1.8744774	0.4442310
O	2.9658291	-0.8704984	-2.2022373
O	-1.6482399	-0.4040776	-0.7335490
O	0.2368914	-2.1232280	-2.3114012
O	2.8092484	1.5279361	-0.3880171
H	0.2286072	1.8894105	1.3798693
H	0.0612702	2.7851315	0.0964367
H	3.2966658	-1.7345029	-1.8681208
H	2.8997732	-0.9621641	-3.1798052
H	-1.9146404	-0.6541917	0.1797515
H	-2.2323457	0.3440215	-0.9935018

H	0.0358089	-2.8776172	-1.7128505
H	-0.5135901	-2.0687108	-2.9453213
H	3.4605911	1.1120599	0.2204711
H	3.3313928	1.9063501	-1.1314250

$UO_2(H_2O)_5^{2+}$

U	0.0000000	0.0000000	0.0000000
O	1.9937617	1.4485526	0.0000000
O	0.0000000	0.0000000	1.7696909
O	1.9937617	-1.4485526	0.0000000
O	-2.4644249	0.0000000	0.0000000
O	0.0000000	0.0000000	-1.7696909
O	-0.7615492	2.3438074	0.0000000
O	-0.7615492	-2.3438074	0.0000000
H	-3.0476935	0.0000000	0.7962654
H	-3.0476935	0.0000000	-0.7962654
H	-0.9417891	-2.8985288	0.7962654
H	-0.9417891	-2.8985288	-0.7962654
H	2.4656359	-1.7913893	0.7962654
H	2.4656359	-1.7913893	-0.7962654
H	2.4656359	1.7913893	0.7962654
H	2.4656359	1.7913893	-0.7962654
H	-0.9417891	2.8985288	0.7962654
H	-0.9417891	2.8985288	-0.7962654

$(Np\text{-}U\text{-}CCI)_{aq}$

O	0.3485238	-1.9935258	2.1119575
O	-0.1485717	-1.8489015	-1.4655805
O	-2.3636352	-2.4587264	0.6448440
O	-1.3025486	0.1835946	0.6466389

O	1.5433305	0.2187717	-0.0089375
H	-2.6491494	-1.9625085	1.4465946
H	-2.8627163	-2.0563855	-0.1019656
S	-1.2907902	1.6873712	0.4667350
S	1.5966825	1.6367425	0.5478225
C	-1.7273983	1.8984419	-1.3733596
O	-2.3081726	2.4465689	1.1990438
N	0.1623981	2.3686245	0.6519833
C	2.4497479	2.5874491	-0.8605784
O	2.4416051	1.8538422	1.7301208
F	-2.9378134	1.3547593	-1.5786782
F	-0.8272789	1.2769206	-2.1416356
F	-1.7634307	3.1960751	-1.6839206
F	1.6945887	2.5705182	-1.9627843
F	3.6202267	1.9816007	-1.1128046
F	2.6703650	3.8474853	-0.4859703
O	0.3567535	-4.3440370	0.0032884
O	2.6869524	-2.1849967	0.1646794
H	2.7966218	-1.2422972	-0.1358346
H	2.9326537	-2.1542456	1.1183977
H	0.6892661	-4.5529689	-0.8975624
H	0.8904499	-4.8639340	0.6425931
Np	0.0984901	-1.8475431	0.3240705

$NpO_2(NTf_2)$ $(H_2O)_3$

O	0.3485238	-1.9935258	2.1119575
O	-0.1485717	-1.8489015	-1.4655805
O	-2.3636352	-2.4587264	0.6448440
O	-1.3025486	0.1835946	0.6466389
O	1.5433305	0.2187717	-0.0089375
H	-2.6491494	-1.9625085	1.4465946

H	-2.8627163	-2.0563855	-0.1019656
S	-1.2907902	1.6873712	0.4667350
S	1.5966825	1.6367425	0.5478225
C	-1.7273983	1.8984419	-1.3733596
O	-2.3081726	2.4465689	1.1990438
N	0.1623981	2.3686245	0.6519833
C	2.4497479	2.5874491	-0.8605784
O	2.4416051	1.8538422	1.7301208
F	-2.9378134	1.3547593	-1.5786782
F	-0.8272789	1.2769206	-2.1416356
F	-1.7634307	3.1960751	-1.6839206
F	1.6945887	2.5705182	-1.9627843
F	3.6202267	1.9816007	-1.1128046
F	2.6703650	3.8474853	-0.4859703
O	0.3567535	-4.3440370	0.0032884
O	2.6869524	-2.1849967	0.1646794
H	2.7966218	-1.2422972	-0.1358346
H	2.9326537	-2.1542456	1.1183977
H	0.6892661	-4.5529689	-0.8975624
H	0.8904499	-4.8639340	0.6425931
Np	0.0984901	-1.8475431	0.3240705

$UO_2(NTf_2)_2(H_2O)$

O	0.7481994	-1.6641379	1.8157418
O	0.3621435	-1.9218243	-1.7185675
O	-1.7692634	-2.6799067	0.3074745
O	-1.1643241	-0.1104088	0.1694764
O	1.5858615	0.3231945	-0.2062723
H	-2.3317704	-1.8688037	0.2521819
H	-2.0713362	-3.3064607	-0.3879138
S	-1.3426114	1.3908290	0.4290030

S	1.5288234	1.5952094	0.6531957
C	-1.7864335	2.0186779	-1.3142346
O	-2.4579161	1.7670071	1.2979184
N	0.0171259	2.1399815	0.8482996
C	2.3011748	2.8918785	-0.5074940
O	2.3167343	1.6113253	1.8864004
F	-2.9926956	1.5410065	-1.6372237
F	-0.8791757	1.5780660	-2.1912731
F	-1.8106689	3.3502937	-1.3130985
F	1.5839464	2.9699399	-1.6310915
F	3.5472838	2.5114796	-0.7868512
F	2.3090997	4.0696370	0.1129814
F	0.1475619	-6.2124948	2.3249353
C	1.4128408	-5.8960444	2.0419704
S	1.5076121	-5.4215271	0.1991101
F	1.7975402	-4.8568515	2.7875767
F	2.2071917	-6.9405351	2.2706706
O	1.0290649	-6.5802871	-0.5555235
O	0.6227893	-4.1733577	0.1458159
N	3.0633440	-5.1119103	-0.0652671
S	3.7683980	-3.6844429	-0.3276598
O	2.8195715	-2.4983593	-0.1289552
C	4.9480020	-3.5009885	1.1548945
O	4.5956724	-3.6633602	-1.5335262
F	4.2389201	-3.4845497	2.2857404
F	5.6148905	-2.3554175	1.0167470
F	5.7950874	-4.5290737	1.1629973
U	0.5881206	-1.8060432	0.0473386

(Np-U-CCI)$_{RTIL}$

O	-2.1181726	-4.6027324	3.2336253

O	1.1216014	-3.0887389	2.8363289
O	-0.7073911	-2.6387371	5.1236362
O	-1.5367828	-1.7225155	2.6623891
S	-1.0943706	-1.3112091	5.7763717
S	-1.2181814	-0.2836913	3.1039919
C	-2.8745211	-1.6617877	6.3535532
O	-0.3305746	-0.9145419	6.9576165
N	-1.2303932	-0.1079462	4.7090904
C	-2.7991537	0.6420051	2.5837070
O	-0.0852308	0.3636977	2.4326500
F	-2.8450912	-2.6525243	7.2449390
F	-3.6129041	-2.0196589	5.2976595
F	-3.3797473	-0.5601638	6.9071152
F	-3.8514371	0.0885315	3.1879046
F	-2.9193381	0.5359499	1.2620555
F	-2.6869541	1.9202201	2.9362505
F	1.4660670	-6.9284878	7.1160562
C	1.2184149	-7.5344164	5.9576933
S	-0.3398421	-6.7520975	5.1942790
F	2.2504129	-7.3654716	5.1223975
F	1.0050942	-8.8349572	6.1542167
O	-1.4142911	-6.9057558	6.1718532
O	0.1538705	-5.3606530	4.8426404
N	-0.6477011	-7.6742401	3.8702375
S	-0.2169280	-7.3242056	2.3800493
O	0.5286848	-5.9898192	2.2299898
C	1.0999185	-8.6231514	1.8993644
O	-1.3034770	-7.5465310	1.3936794
F	2.2448571	-8.3819463	2.5379653
F	1.2945322	-8.5295063	0.5767134
F	0.6456810	-9.8325979	2.2077073

F	-3.7629315	-4.0800348	-4.5179183
C	-2.8103301	-3.1423145	-4.5314845
S	-2.7770604	-2.3197330	-2.8109065
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F	-3.0840520	-2.2295752	-5.4625968
O	-4.1733648	-2.0384924	-2.4703812
O	-2.0672391	-3.3586888	-1.9526352
N	-1.9216244	-0.9727150	-3.0689156
S	-0.5341096	-0.5239243	-2.3977495
O	-0.7386893	-3.8219816	0.8045180
O	0.7940959	-4.1037105	-2.5611426
O	-0.8606836	-6.1809181	-0.9787036
O	-0.0132470	-1.4977364	-1.3382386
O	1.8790275	-5.3047185	-0.0051760
O	1.8969191	-2.5807076	0.2114094
C	0.7489805	-0.6812933	-3.8109746
O	-0.5247022	0.8886995	-2.0125596
H	-1.1596884	-6.6761683	-0.1588243
H	-0.5931375	-6.8357056	-1.6578750
F	0.4825856	-1.7574788	-4.5535891
F	1.9666951	-0.7990756	-3.2639242
F	0.7013549	0.4138052	-4.5667968
H	1.5750434	-5.6193681	0.8946218
H	2.6414471	-4.6947047	0.1329483
H	1.7471084	-1.6606913	-0.1160686
H	1.7226669	-2.5675817	1.1989000
Np	0.0324994	-3.8995728	-0.9503352
U	-0.5284630	-3.8088830	3.0701593