Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Towards the developpement of chitosan nanoparticules for plutonium pulmonary decorporation

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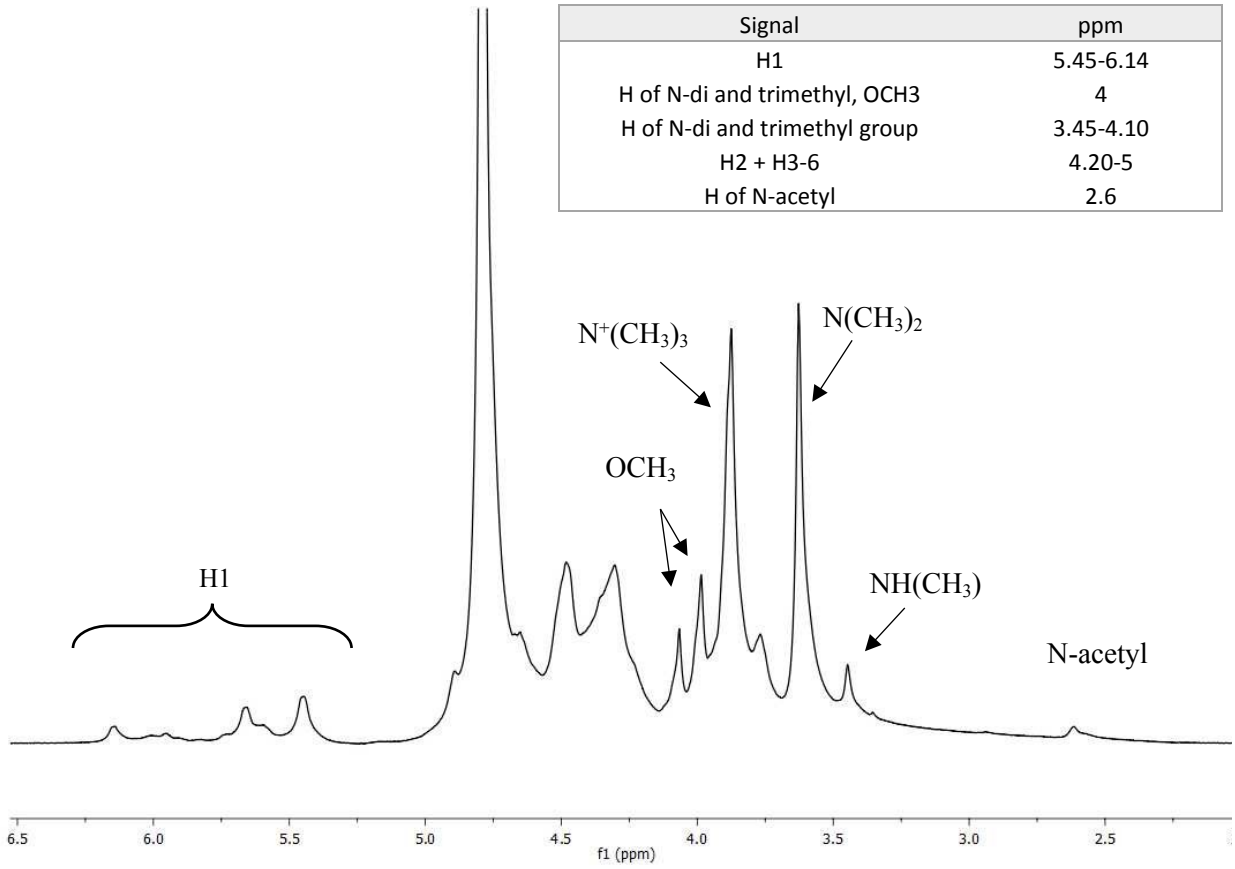
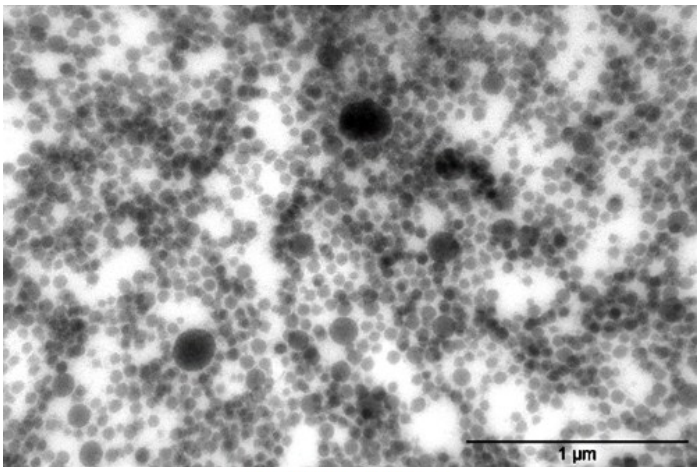


Figure 1S: RMN spectrum of TMC with the by-products. The polymer presented several pics for the H anomeric due to the composition of the sample: N-trimethyl chitosan, N-dimethyl chitosan, N-methyl chitosan and O-methyl chitosan.

a)



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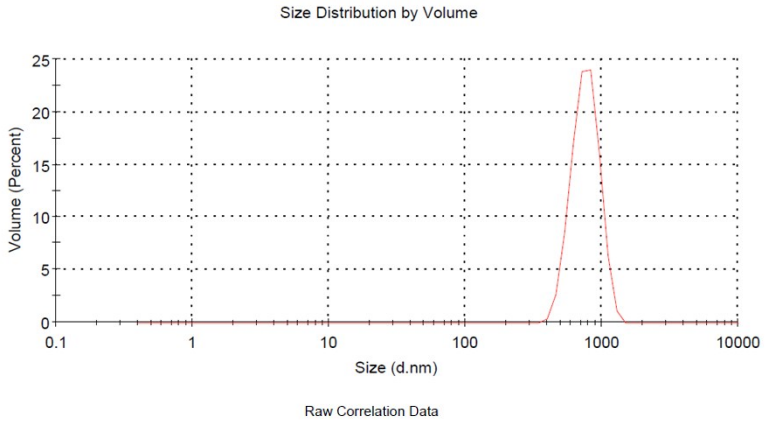

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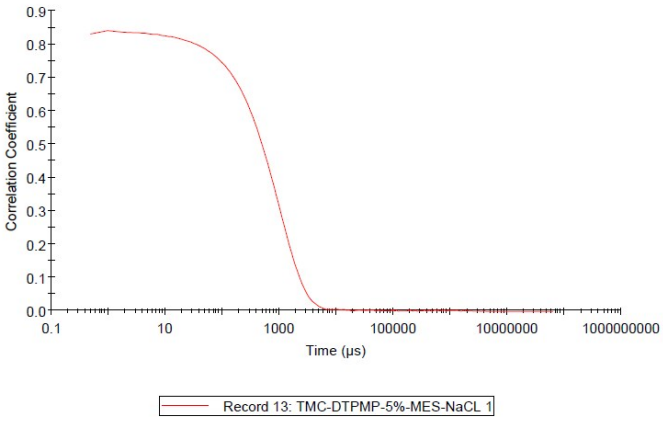
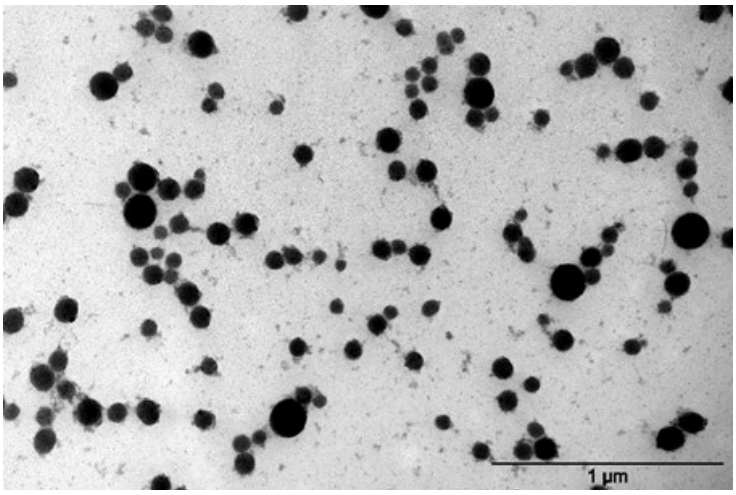


Figure 2S: Characterization of TMC-DTPMP(5 %): a) TEM image; b) DLS profile and c) Correlation curve.

a)



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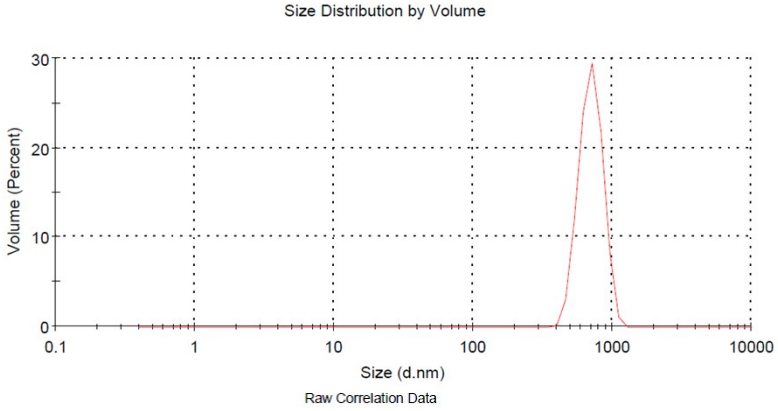


c)

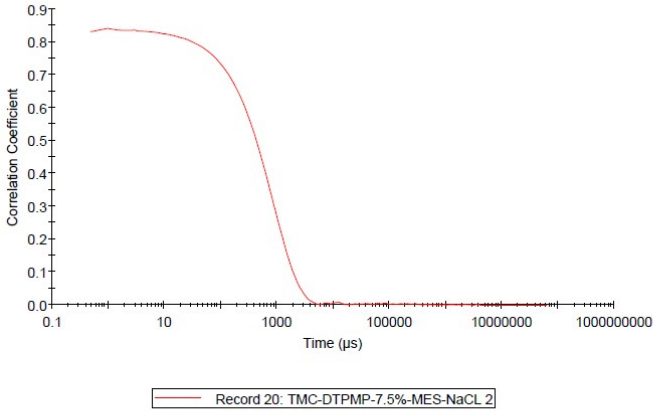
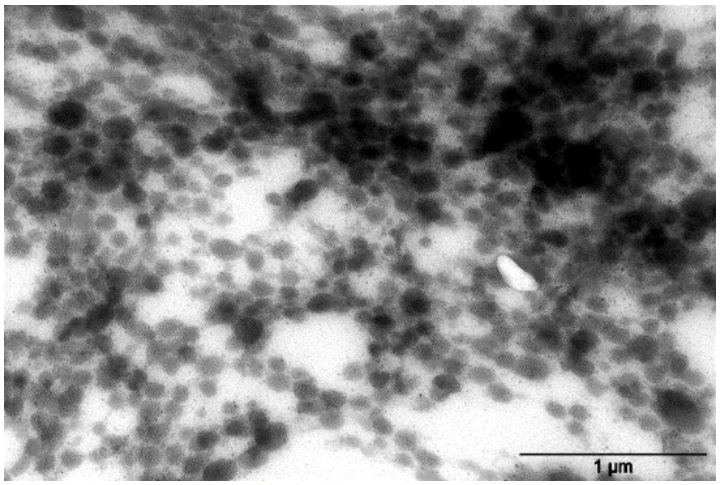
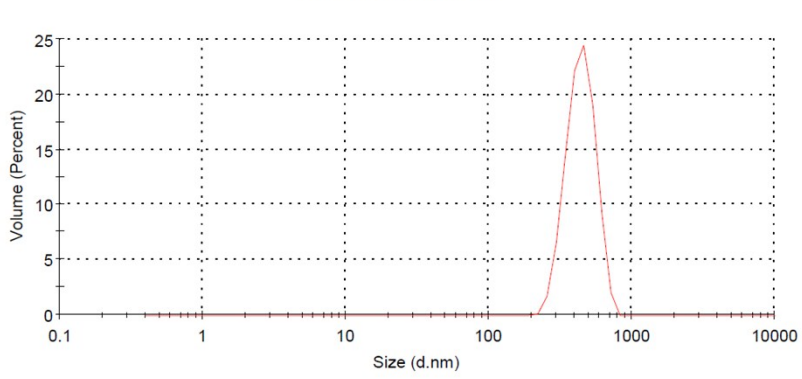


Figure 3S: Characterization of TMC-DTPMP(7.5 %): a) TEM image; b) DLS profile and c) Correlation curve.

a)



b)



c)

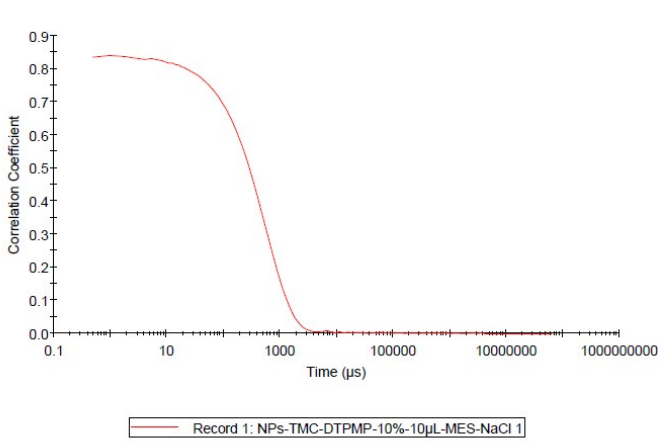


Figure 4S: Characterization of TMC-DTPMP(10 %): a) TEM image; b) DLS profile and c) Correlation curve.

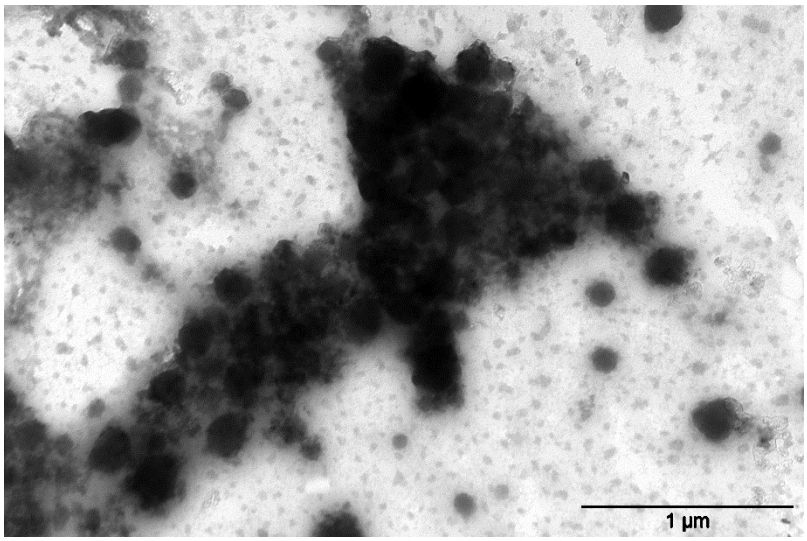
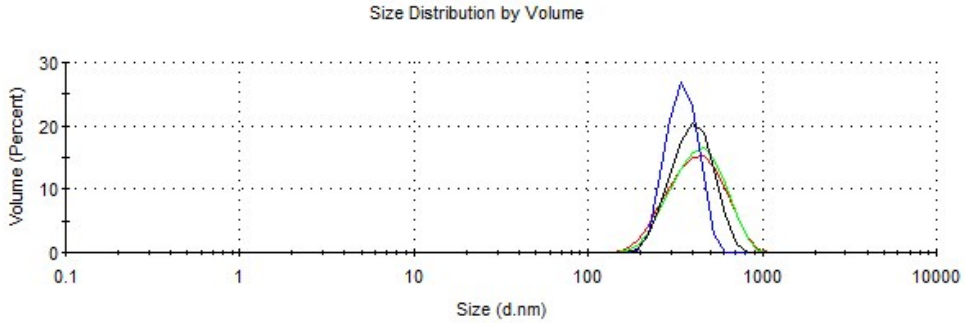
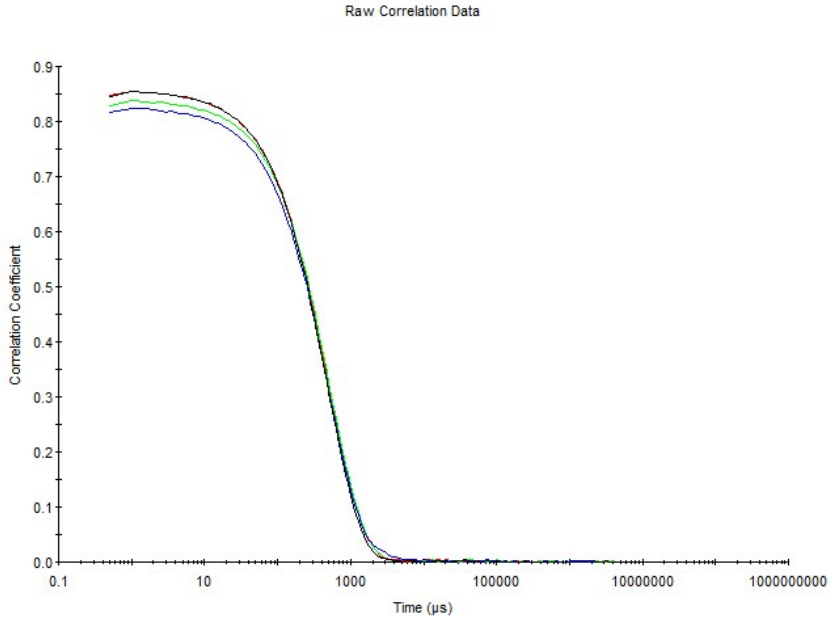


Figure 5S: TEM images of an aggregate of TMC-DTPMP(10%).

a)



b)



c)

Ratio Th : DTPMP (NPs)	Size (nm)	PDI
1	455 ± 105	0.16
2.5	382 ± 45	0.21
5	403 ± 38	0.15
Without Th	393 ± 38	0.17

Figure 6S: DLS characterization of TMC-DTPMP(10 %) NPs with different ratio of Th(IV) (1, 2.5, 5) a) DLS profiles ; b) Correlation curves and c) Summary table of size and polydispersity index.

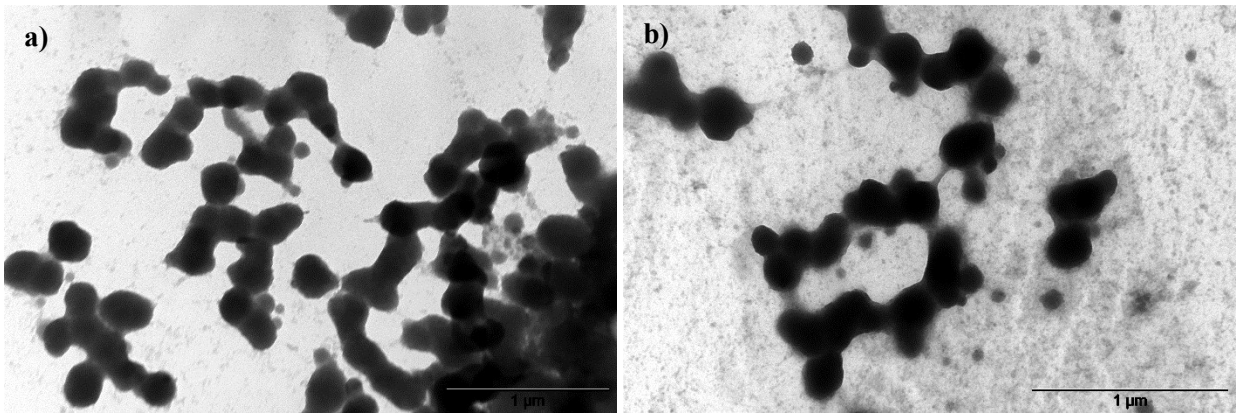


Figure 7S: TEM images of TMC-DTPMP(10%) NPs in the presence of Fe(III) (DTPMP : Fe = 1 : 2) at a) t: 0 h and b) t: 24 h. Fe(III) does not seem to affect the nanostructuration of TMC-DTPMP during 24 hours.

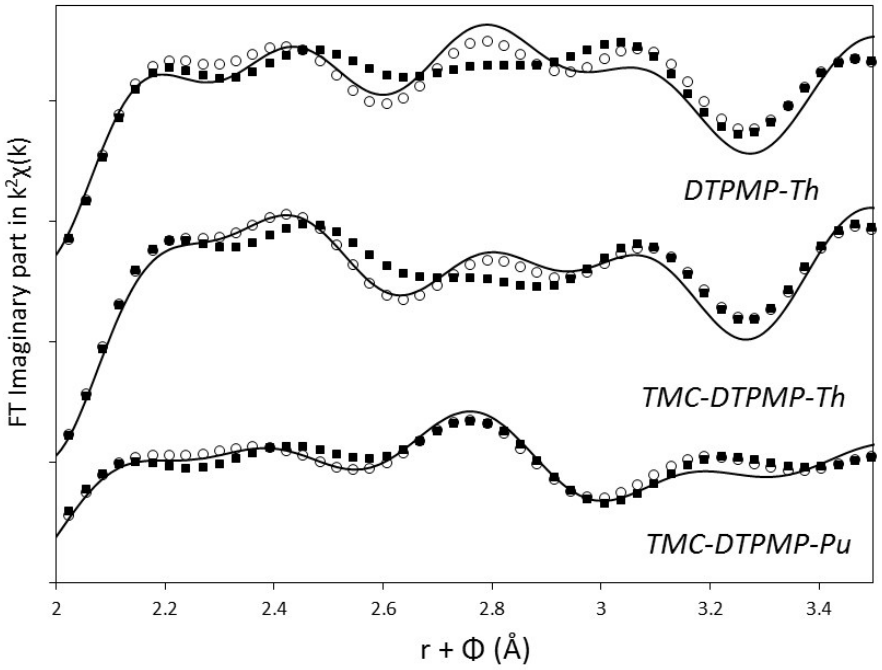


Figure 8S: Imaginary part of the FT of the EXAFS spectrum of the free DTPMP-Th complex and TMC-DTPMP NPs-An(IV) (An = Th and Pu) complexes in MES/NaCl pH 6.5 solution; Solid line = experimental spectrum, dots = adjustment with one bidendate phosphonate and two monodentate phosphonate, squares = adjustement with only monodendate coordination.

Table 1S: Full list of calculated distances of *DTPMP-An* complexes with DFT (An = Th, Pu).

	Distance (Å)	Mean (Å)
Th-Omono	2.21	2.33
	2.23	
Th-Obi	2.39	
	2.49	
Th-P	3.8	3.77
	3.74	
	3.13	3.13
Th-OH2	2.83	2.7225
	2.68	
	2.72	
	2.66	
Angle Th-O-P	172	162.5
	153	

	Distance (Å)	Mean (Å)
Pu-Omono	2.09	2.25
	2.11	
Pu-Obi	2.27	
	2.53	
Pu-P	3.7	3.665
	3.63	
	3.09	3.09
Pu-OH2	2.97	2.6925
	2.71	
	2.5	
	2.59	
Angle Pu-O-P	169	160.5
	152	

Data calculations form DFT: Pu(IV) in interaction with two monodentate phosphonates, one bidentate phosphonate and four water molecules

	x	y	z
P	-2.993519	-0.298169	-1.458123
O	-3.268636	-0.518244	-2.945267
O	-4.020236	-0.840365	-0.451515
O	-1.581311	-1.009133	-1.075864
C	-2.691011	1.55604	-1.32124
H	-3.38014	1.952893	-2.072047
H	-1.677226	1.719362	-1.720201
N	-2.878967	2.319885	-0.067121
P	-5.547842	3.24263	-0.202662
O	-6.300946	4.536306	-0.149415
O	-5.892186	2.248237	1.041609
O	-5.843	2.299047	-1.483281
H	-6.271673	2.729966	1.79859
H	-6.785223	2.083123	-1.605724
C	-3.733556	3.488351	-0.248541
H	-3.578722	4.18183	0.586111
H	-3.513742	4.060358	-1.167842
C	-1.631977	2.707329	0.621201
C	-0.897254	1.467604	1.126826
H	-1.913523	3.311746	1.490849
H	-0.98797	3.335157	-0.023795
H	-1.660343	0.850099	1.605027
H	-0.526576	0.893642	0.280154
N	0.17839	1.714486	2.10951
P	5.773749	3.128841	-0.299711
O	6.80312	3.836177	0.525948
O	5.095899	4.089252	-1.430058

O	6.293102	1.881858	-1.19305
H	5.183758	5.032511	-1.202416
H	7.014078	2.104674	-1.809609
C	4.429314	2.368208	0.687906
H	4.035623	3.202249	1.280066
H	4.920065	1.68657	1.401463
N	3.354847	1.727443	-0.069688
P	2.539677	-0.638855	-1.426288
O	3.059449	-0.406094	-2.833517
O	1.025555	-0.205594	-1.181317
O	2.477287	-2.138668	-0.947219
C	3.592477	0.276694	-0.196728
H	4.619819	0.152568	-0.550748
H	3.522964	-0.254104	0.766976
C	2.008049	2.164247	0.35686
C	1.563255	1.485953	1.65718
H	1.314835	1.938086	-0.4536
H	2.030976	3.254136	0.472634
H	1.737015	0.407926	1.549941
H	2.217057	1.824109	2.473337
P	-0.024168	-0.958337	3.222877
O	-1.116931	-1.476546	4.152682
O	1.400445	-1.530441	3.430221
O	-0.402778	-1.268436	1.666343
C	-0.049728	0.932819	3.332051
H	0.699047	1.220323	4.081662
H	-1.032313	1.193033	3.739665
Pu	0.044453	-2.030821	-0.248275
O	-0.215653	-4.726265	-0.182649
H	0.629526	-5.206826	-0.199451

H	-0.780477	-5.167083	-0.839743
O	1.649187	-3.111097	1.335356
H	1.66982	-2.543111	2.17505
H	2.455093	-2.906204	0.814899
O	-2.656137	-3.030377	0.476794
H	-3.100974	-3.886493	0.378315
H	-3.246964	-2.343753	0.073571
O	0.342039	-2.817105	-2.697264
H	1.282007	-3.063488	-2.779722
H	-0.176336	-3.524041	-3.117208

Data calculations form DFT: Th(IV) in interaction with two monodentate phosphonates, one bidentate phosphonate and four water molecules.

	x	y	z
P	-2.916636	-0.201386	-1.549953
O	-3.111619	-0.255084	-3.069785
O	-4.035164	-0.791429	-0.667053
O	-1.592173	-1.012576	-1.1458
C	-2.6206	1.636542	-1.242176
H	-3.304554	2.08764	-1.965439
H	-1.604545	1.860341	-1.606415
N	-2.856585	2.275326	0.072191
P	-5.503034	3.261872	-0.12592
O	-6.25075	4.554211	0.004212
O	-5.942049	2.158714	0.98838
O	-5.716679	2.453088	-1.512477
H	-6.371617	2.570508	1.759245
H	-6.650256	2.26761	-1.725409
C	-3.685198	3.47407	-0.036987
H	-3.563615	4.074675	0.871022
H	-3.406138	4.130243	-0.882121
C	-1.627374	2.581107	0.834736
C	-0.872315	1.30061	1.193082
H	-1.923235	3.082682	1.762279
H	-0.973276	3.278148	0.275459
H	-1.617802	0.585141	1.545151
H	-0.44284	0.865541	0.28994
N	0.165734	1.489	2.234291
P	5.43832	3.486507	-0.255687
O	6.511823	4.225505	0.482121
O	4.416948	4.475263	-1.054531

O	5.927878	2.48886	-1.437261
H	4.418039	5.374694	-0.685377
H	6.474845	2.920503	-2.119818
C	4.42198	2.370359	0.786526
H	4.037658	3.009347	1.590979
H	5.115424	1.665598	1.266563
N	3.33954	1.709757	0.0616
P	2.602618	-0.587808	-1.452764
O	3.183381	-0.331391	-2.831968
O	1.087281	-0.163245	-1.267411
O	2.529803	-2.1008	-0.988953
C	3.628964	0.284768	-0.166494
H	4.658523	0.210871	-0.531013
H	3.578362	-0.308971	0.761751
C	1.984357	2.056849	0.550269
C	1.564395	1.290901	1.813362
H	1.285142	1.852487	-0.258464
H	1.966516	3.136997	0.729616
H	1.769136	0.223773	1.663244
H	2.196897	1.60525	2.654656
P	-0.092017	-1.203362	3.277836
O	-1.193656	-1.745015	4.19181
O	1.338047	-1.761522	3.539728
O	-0.417628	-1.484273	1.731774
C	-0.115599	0.68072	3.431086
H	0.601176	0.951974	4.216825
H	-1.112027	0.943783	3.802164
Th	0.125949	-2.137852	-0.334
O	-0.048654	-4.856999	-0.318596
H	0.765778	-5.306174	-0.037577

H	-0.365082	-5.336085	-1.101746
O	1.664694	-3.378665	1.459802
H	1.629385	-2.794439	2.293099
H	2.570645	-3.306744	1.107976
O	-2.463239	-3.154114	0.216303
H	-2.843371	-4.034501	0.051884
H	-3.089945	-2.473656	-0.142509
O	0.388395	-2.834467	-2.915874
H	1.30318	-3.01175	-3.201336
H	-0.202211	-3.318816	-3.519632