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Polyethyleneimine Methylenecarboxylate: a macromolecular DTPA analogue for the plutonium (IV) chelation

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Complexation curves

The Th(IV) solution (from Th nitrate) used for each point of the complexation curves was protected with nitriloacetic acid (at ratio Th : NTA = 1 : 2) in order to avoid hydrolysis that occurs typically above pH 1–2 for actinides at oxidation state +IV. A quick check of Th speciation under these conditions using JChess simulation with BASSIST data base[1] indicates that less than 10% of the initial Th is hydrolyzed.

PEI-MC-Th experimental points

25 µL of thorium nitriloacetate $(Th(NTA)_2)^{2-}$ [Th] = $3x10^{-3}$ M, pH 1) were added to 70µL, 35µL, 25µL, 22µL, 17µL, 15µL of PEI-MC solution in distilled water (10 $mg.mL^{-1}$) and 50 µL of thorium nitriloacetate $(Th(NTA)_2)^{2-}$ [Th] = $5x10^{-3}$ M, pH 1) were added to 25µL, 17µL 10 µL, 8.0 µL, 6.0 µL, 4.0 µL, 3.0 µL and 2.5 µL of the same PEI-MC. The final volume was fixed at 400 µL by addition TBS buffer (to obtain 50 mM Tris and 150 mM NaCl in each aliquot) and the pH was finally adjusted to 6.5 by addition of sodium hydroxide (1 M). The corresponding PEI-MC:Th monomer molar ratio was equal to 22.40, 11.20, 8.00, 7.04, 5.44, 4.80, 2.40, 1.63, 0.96, 0.77, 0.58, 0.38, 0.29 and 0.24 respectively. The fourteen solutions of PEI-MC-Th complexes were purified by micro-centrifugation on Amicon® filters (Millipore, MWCO 10 kDa) at 10 000 g and washed twice with 200 µL TBS buffer at pH = 7. To measure the quantity of the PEI- MP-Th complex, the Amicon® filters were then digested with nitric acid (65%) into a microwave furnace for 2 h (200 °C). Each digested solution was dried and dissolved in a nitric acid solution at pH 1.5. In order to measure the quantity of Th in this fraction, 1800 µL of Xylenol orange at pH 4 (10^{-4} M buffered with acetate at pH = 4) were added to 200 µL of this solution. UV measurements (Agilent technologies Cary 60 UV- vis spectrometer, Tungsten lamp, ε = 85 000 in these conditions at 564 nm) were repeated 3 times for each fraction in order to obtain 27 independent values. Blanks were analyzed under the same conditions ($[Th(NTA)_2] = 5 \times 10^{-4}$ M, pH = 6.5) in the absence of the polymer. Under these conditions, 92 ± 2% of the input Th was recovered from the filtrate.

DTPA-Th experimental points

100 µL of thorium nitriloacetate $(Th(NTA)_2)^{2-}$ [Th] = $8.9x10^{-4}$ M, pH 1) were added to 5 µL, 7 µL, 10 µL, 15 µL, 18 µL, 20 µL, 25 µL, 30 µL, 35 µL, 40 µL, 45 µL, 50 µL, 60 µL, 68 µL, 78 µL, 98 µL and 130 µL of DTPA solution (DTPA= 1 $mg.mL^{-1}$, pH 7). Then 200 µL of MES buffer solution (2-(N-morpholino)ethanosulfonic acid, 50 mM, pH 7) containing 150 mM of NaCl, to fix the ionic strength, have been added to each solution to stabilized the pH at 7. The corresponding DTPA:Th molar ratio was equal to 0.14, 0.20, 0.28, 0.42, 0.51, 0.70, 0.84, 0.98, 1.12, 1.26, 1.40, 1.69, 1.91, 2.19, 2.75 and 3.65 respectively. The obtained solutions are micro-centrifugated using a Amicon® filter. (7000 rpm during 45 min). The amount of complexed Th(IV), presents in the filtrate, was calculated through back titration from a colorimetric measurement with Xylenol Orange (XO) following the same process than the PEI-MC-Th.

Fitting

The experimental points obtained are graphically presented as the percentage of complexed thorium in function of the chelating agent quantity: initial Th(IV) quantity ratio. Both PEI-MC-Th and DTPA-Th experimental points have been fitted by a Hill function representing a truncated sigmoid and was analyzed with OriginPro 8.5 software. (R^2 and Chi_r^2 are given as statistical factors relating to quality result of the fit):

$$y = a + \frac{(b - a) \times x^n}{(k^n + x^n)}$$

y is the expected response at dosage step x, a is the response at step = 0, b = the maximum response at infinite step, k is the inflection point, and n is the slope of the linear part of the curve. The parameter a has been fixed to 5% according to the hydrolyzed fraction of Th(IV) define by the JChess software.

	a	b	k	n	Quality factors
PEI-MC-Th	5	123.93 ± 37.24	5.93 ± 4.27	0.97 ± 0.17	R^2=0.85 Chi_r^2=0.22
DTPA-Th	5	102.1 ± 1.55	0.47 ± 0.02	2.38 ± 0.25	R^2=0.97 Chi_r^2=0.02

Table S1: Fitting parameters of the uptake curves with Th(IV).

Extended X-ray absorption fine structure (EXAFS) of PEI-MP-Th and PEI-MP-Pu

Sample preparations

PEI-MC-Pu sample. 100 µL of a solution of plutonium chloride ([Pu] = 5x10^{-4} M, pH 0) was added to 100 µL of a PEI-MC solution (10 mg.mL^{-1}) containing TBS buffer (pH = 1.0, [tris] = 5x10^{-5} M, [NaCl] = 15x10^{-5}M). Then 200 µL of a solution of sodium hydroxide 1 M was added to adjust the pH to 7.0. This corresponds to a stoichiometry of the Pu : PEI-MC monomer molar ratio of 0.02 (this large under-stoichiometry of Pu ensures that the limit complex was obtained).

PEI-MC-Th sample. 26 µL of a solution of thorium nitrate ([Th] = 8,9x10^{-3} M, pH 1) was added to 50 µL of a TBS buffer solution (pH = 1.0, [tris] = 5x10^{-5} M, [NaCl] = 15x10^{-5}M) containing 5,90 mg PEI-MC. Then 150 µL of distillated water are added and the pH is adjusted to 7.0 by addition of a solution of sodium hydroxide 1 M. This corresponds to a stoichiometry of the Th : PEI-MC monomer molar ratio of 0.02 (this large under-stoichiometry of Th ensures that the limit complex was obtained).

Data recording and processing

EXAFS experiments at the Pu and Th L_{III} edge were carried out on the ROBL beamline of ESRF synchrotron facility. The ROBL beamline is devoted to the investigation of radioactive materials in the hard X-ray range. Because of the low concentration of the samples, EXAFS measurements were performed in fluorescence mode using a 13-element high purity germanium detector with specifically designed 200 µL cells (Ets CANAPLE). The ROBL beam line is equipped with a Si (111) water cooled monochromator in the channel cut mode. Two Pt coated mirrors were used for harmonic rejection. Monochromator energy calibration was performed with Y foil at 17 052 eV at the edge maximum. The same conditions were used for both Pu and Th L_{III} edges (18057 eV and 16300 eV respectively). Data processing was carried out using the ATHENA code[2]. The e_o energy was identified at the maximum of the absorption edge data fitting. Fourier Transformation (FT) in k^2 was performed between 2.7 and 10.5 Å^{-1} with Hanning windows using the ARTEMIS code[2]. The difference of range is due to the low concentration of Pu in the recorded sample triggering larger noise on the EXAFS data. Only one global amplitude factor S_0^2 and one energy threshold correction factor e_0 were used for all paths. Phases and amplitudes were calculated using the FEFF9 simulation code[3]. The model for phases and amplitude calculations was taken from a quantum chemical model described and published elsewhere for Pu and Th[4]. For both Pu and Th, the first coordination sphere was set with a 5O + 3N coordination mode in the first coordination sphere[5]. Two independent single scattering paths, An-O (5 degenerate) and An-N (3 degenerate) were included for the first coordination sphere. For the second coordination sphere, the following paths were included: one single scattering path, An…Cα(O), accounting for the Cα(O) atoms of the carboxylate (5 degenerate); one single scattering path, An…Cα(N), accounting for the Cα(N) atoms of the amine functions (9 degenerate); and one triple scattering path An…Cα(O)-O of the carboxylate (10 degenerate). Both An…C single scattering paths were linked with the corresponding An-O and An-N distances (with geometrical relations). The triple scattering path was also linked to the corresponding An-O path in the same manner. Finally, for the third coordination shell, an independent triple scattering path (An…C-O), accounting for the distal O atom of the carboxylate, was included (10 degenerate).

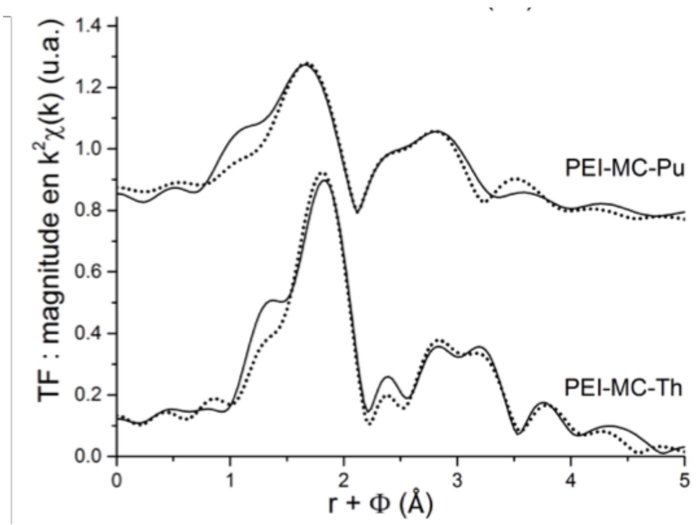

Fig. S1: Corresponding Fourier transform of the EXAFS spectra in $k^2\chi(k)$ of the PEI-MC-Pu and PEI-MC-Th complexes in pseudo physiological conditions. Solid line = experimental spectrum, dotted line = adjustment. Spectra have been shifted in ordinates for clarity.

Ab initio Molecular Dynamics calculations

In the framework of DFT-PAW formalism we used the ABINIT code[6] for performing AIMD simulations on both Th and Pu-PEIMC models. For each case, we have treated an isolated charged complex in a large simulation box in order to simulate the gaseous phase system. We also performed simulation in the presence of 22 water molecules in order to mimic the solvent effects. The simulations are run in the isokinetic ensemble at 298 K until equilibration is achieved, i.e. until the variations in pressure stabilize to an oscillatory pattern, without any long-term trend. The size of the simulation cell (20 Bohr) is chosen in order to obtain a pressure close to zero. Following equilibration, the pressure and energy are calculated by averaging over the next 2000 times steps of 0.48 fs each. All calculations have been done at the Γ point, the center of the Brillouin zone. For carbon, oxygen and hydrogen the pseudo potentials are taken from the ABINIT data base, for thorium and plutonium a PAW data set has been fixed and a pseudo-potential built[7] and checked. The data were generated for the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with relativistic corrections to the wave function[8] including spin-orbit coupling. We have chosen a standard actinide basis set with 7s, 6p, 6d, 5f in the valence band and 6s and 6p as the semicore orbitals. In ABINIT the energy cut off is an important parameter and we investigated the convergence needed for obtaining reliable results. This cut off was fixed at 760 eV.

In plutonium systems, the presence of correlated *5f* electrons leads to an improper description of the electronic and the structural properties by density functional theory. To overcome these shortcomings of DFT the DFT+U (Generalized Gradients Approximation GGA+U) approach has been shown to effectively correct the deficiencies. Subsequently, except for thorium (no *5f* electron in Th9), we introduce Hubbard U and Hund's J parameters for the onsite interaction strength. Although the choice of U and J are debatable we used the classical values obtained for tetravalent plutonium oxide (U=4 eV, J=0.2 eV)[9].

	Pu-O	Pu-N	Pu-C
PEI-MC-Pu	2.142 Å	2.592 Å	3.227 Å / 3.412 Å
	Th-O	Th-N	Th-C
PEI-MC-Th	2.195 Å	2.724 Å	3.359 Å / 3.465 Å

Table S2: An(IV)-PEI-MC interatomic distances obtained from the initial calculation performed at 298K.

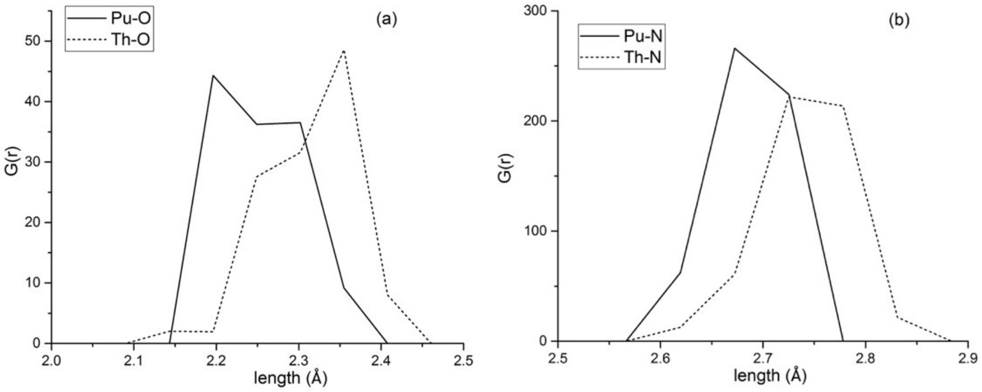

Fig. S2ab: Pair distribution functions (G(r)). a) oxygen atoms; b) nitrogen atoms, line. plutonium complex = straight line; thorium complex = dotted line.

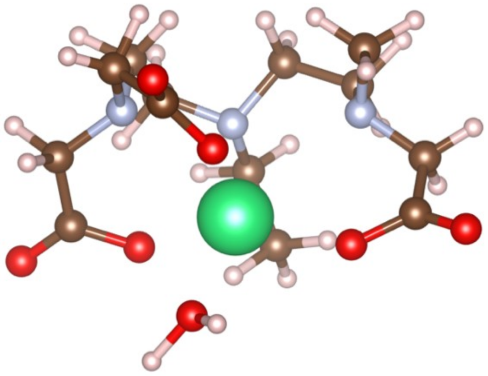

Fig. S3: Snapshot of the PEI-MC-Th complexation site (3O + $1O_{wat}$ + 3N) in the final stage calculated by *ab Initio* MD. Th = green, O = red, N = blue, C = brown.

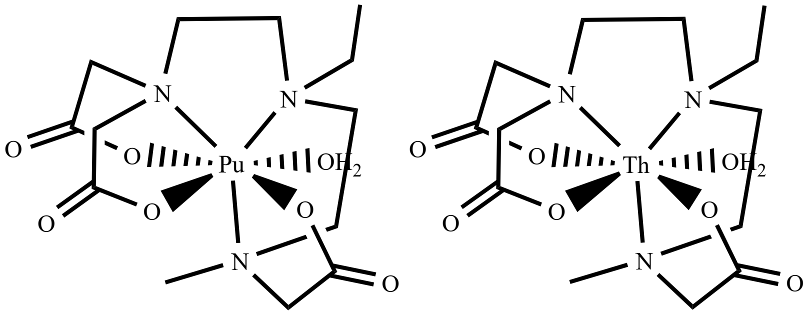

Fig. S4ab: Schemes of PEI-MC-Pu and PEI-MC-Th complexation sites calculated by *ab Initio* MD.

	CN in literature[10]	CN from EXAFS	CN from MD
PEI-MC-Pu(IV)/Th(IV)	8-12	8	7

Table S3: PEI-MC-Pu(IV)/Th(IV) coordination number (CN) obtained from the EXAFS and molecular dynamics calculation compared to the literature data.

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