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Plutonium(III) complexation by humic substances studied by X-ray absorption fine structure spectroscopy

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Abstract

We determined structural parameters for the near-neighbor surrounding of plutonium(III) in complexes with humic and fulvic acids at pH 1 and for the purpose of comparison also for the plutonium(III) aquo ion by means of X-ray absorption fine structure (XAFS) spectroscopy. It could be shown that in the complexes with humic substances as well as in the plutonium(III) aquo ion sample the trivalent oxidation state of plutonium was stable within the time of the experiment. In the humate and fulvate complexes, the plutonium(III) is surrounded by about eight oxygen atoms with an average Pu–O distance of 2.48 ± 0.02 Å. The structural parameters determined for plutonium(III)–humate and –fulvate complexes were compared to structural parameters of plutonium(III) and plutonium(IV) aquo ions.
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1. Introduction

The migration behavior of actinide contaminants in environmental systems can be influenced by naturally occurring aquatic humic substances (humic acids and fulvic acids) due to their strong complexing and redox properties and their ability to form colloids [1–3]. Therefore, to understand and predict the mobility of actinides in natural aquifer systems, amongst others, information on the coordination chemistry of the actinides in humate and fulvate complexes is necessary.

In our previous investigations we studied the coordination environment of Th(IV), Np(IV), Np(V) and U(VI) in complexes with humic substances by X-ray absorption fine structure (XAFS) spectroscopy [4–7]. Since plutonium is of major environmental concern among the actinide elements, it should also be included in this series of studies. Plutonium can exist in aqueous solutions in oxidation states III, IV, V, and VI with two or three such species often present in equilibrium [8,9]. Pu(V) is the dominant species in solution in oxic systems, e.g., in marine waters [10,11]. However, under reducing conditions as prevalent in deep underground environments, Pu(III) is present and may become the dominant soluble species [8]. Pu in higher oxidation states (Pu(VI), Pu(V), Pu(IV)) can be reduced by humic substances [12–16]. Below pH 3, even under aerobic conditions, Pu(IV) was reduced by humics to Pu(III) which is strongly complexed by humic substances [17]. The interaction constant for Pu(III) with humic acid was found to be $\log\beta = 2.8$ and $\log\beta = 3.11$ at pH 2.9 and 5.0, respectively (ionic strength 0.5 M $NaClO_4$) [18]. More complexation data are available for Am(III) and Cm(III). Due to their redox stability and similar solution properties, these actinides are used as chemical analogs for Pu(III), e.g. [8,19]. The $\log\beta$ values determined for Am(III)–humates vary between 6.02 and 6.53 in the pH range 4–6 (ionic strength 0.01–5 M $NaClO_4$) [20–24] and those determined for Cm(III)–humates vary between 6.03 and 6.5 in the pH range 5–6

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(ionic strength 0.001–5 M $NaClO_4$) [23–25]. These stability constants were obtained by evaluating the respective experimental data with the metal ion charge neutralization model [26] and are therefore not directly comparable to the stability constants reported for Pu(III)–humate [18].

Structural parameters have been determined for the Pu(III) aquo ion [27–29] using XAFS spectroscopy. However, there is no information on the coordination environment of Pu(III) in complexes with humic substances formed in anoxic waters so far. This information, however, is needed to understand and predict Pu mobility.

In the present paper, we studied the coordination environment of Pu(III) in complexes with humic substances at pH 1 by XAFS spectroscopy. XAFS spectroscopy includes X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. XANES spectroscopy provides information on the electronic structure and the molecular symmetry of the absorbing atom. EXAFS spectroscopy gives information on coordination numbers and bond lengths to neighbor atoms [30]. The structural parameters obtained for Pu(III)–humate and –fulvate (referred to hereafter as Pu(III)–humate) are compared to those determined for the Pu(III) aquo ion as well as to structural parameters of Pu(III) and Pu(IV) aquo ions given in the literature.

2. Experimental

2.1. Sorbents

Two different humic substances were used in this study. The natural Kranichsee fulvic acid (KFA) was isolated from surface water of the mountain bog 'Kleiner Kranichsee' (Saxony, Germany) [31]. The synthetic humic acid type M42 (charge M81) represents a humic acid-like condensation product from xylose and glutamic acid [32] which exhibits a complexation behavior towards U(VI), Np(IV) and Np(V) comparable to natural humic acids [32,5–7]. The functional group contents of the sorbents are compiled in Table 1.

2.2. Sample preparation

A stock solution of ^{242}Pu was purified by anion exchange chromatography [35] using TEVA resin™ (Eichrom Industries, Inc.) to remove ^{241}Am. An alpha spectrum taken of the stock solution after purification showed no indication of ^{241}Am from the decay of ^{241}Pu. The purified Pu was then electrochemically reduced to Pu(III). The oxidation state purity of the Pu(III) stock solution was verified by UV–Vis–NIR absorption spectroscopy (CARY-5G, Varian) using the absorption band at 600 nm (molar extinction coefficient: 38 L mol^{-1} cm^{-1} [36]) for Pu(III). No absorption bands pointing to Pu(IV) were detected.

Pu(III)–humates were prepared in a glove box under N_2 atmosphere in order to prevent oxygen from reacting with Pu(III). Before, about 250 mg KFA and 300 mg M42 were suspended in 4 mL of 0.1 M $HClO_4$ and degassed under vacuum. Then, the volume of the humic acid suspension and the fulvic acid solution was increased to about 18 mL by adding 0.1 M $HClO_4$. Subsequently, aliquots of the Pu(III) stock solution were added. The total sample volume was 21 mL. The Pu concentration in the reaction solutions was about 8×10^{-4} M. In the case of KFA, the fulvic acid coagulated due to complexation with Pu(III) thereby forming a Pu(III)–KFA precipitate. The sample suspensions were stirred at constant pH 1.01 ± 0.05 for 24 h. Then, the reaction products were isolated by centrifugation. The Pu(III)–M42 sorbate was washed with 0.1 M $HClO_4$ to remove Pu species which remained in solution. The Pu loading of the humic substances, calculated from results of γ-spectroscopy, is given in Table 1. For XAFS spectroscopy, the Pu(III)–M42 wet paste was placed in a polyethylene (PE) vial. The Pu(III)–KFA precipitate (about 1.7 mL) was filled in a PE vial together with about 0.3 mL of the supernatant. The Pu content of Pu(III)–KFA and Pu(III)–M42, determined by γ-spectroscopy, was 1.8 and 1 mg Pu per sample, respectively. This is less than the amount of Pu applied for sample preparation, since not all the sample material was needed to fill the PE vials.

For comparison purposes, a Pu(III) solution (Pu(III) aquo ion: 50 mM Pu, pH 0) was prepared by diluting an aliquot of a Pu(III) stock solution with 1 M $HClO_4$. For XAFS measurements, 4.7 mL solution was filled in a PE vial.

All PE vials were double-sealed in PE bags for safety purposes. The Pu(III)–humate samples were transported under N_2 atmosphere.

Table 1
Functionality of humic substances and Pu loading of Pu(III)–humate complexes

Sorbent	Functionality			Sample	Pu loading	
	COOH[a] (meq/g)	Phenolic OH[b] (meq/g)	PEC[c] (meq/g)		(mg Pu/g sorbent)	(% PEC)[d]
KFA	6.1(3)	4.8(7)	5.6(1)	Pu(III)–KFA	11.6	2.6
M42	4.1(1)	2.3(4)	3.9(2)	Pu(III)–M42	3.9	1.2

[a] Determined by calcium acetate exchange [33].
[b] Phenolic OH and other acidic OH groups radiometrically determined [34].
[c] Proton exchange capacity, determined by direct titration.
[d] Calculated on the assumption that one Pu(III) ion occupies three proton exchanging sites of the sorbents.

2.3. XAFS data collection and analysis

XAFS measurements were performed at the Rossendorf Beamline (ROBL) [37,38] at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) under dedicated ring conditions (6.0 GeV, 100–200 mA). Pu L_{III}-edge X-ray absorption spectra were recorded in both transmission and fluorescence mode at room temperature using a Si(1 1 1) double-crystal monochromator in fixed-exit mode. The fluorescence spectra were collected with a four-pixel Ge fluorescence detector [39]. Argon-filled ionization chambers were used to record the transmission spectra. The transmission spectrum of a blank, i.e., a humic acid sample without Pu, was also measured to record the absorption background. The spectra were recorded up to $k = 9$ Å^{-1} in steps of 0.05 Å^{-1}. Five to six XAFS scans were collected for each sample and averaged to improve the statistics. The energy scale of the spectra was calibrated using the energy of the first inflection point of the absorption spectrum of a Zr metal foil (Zr *K*-edge at 17998 eV). The threshold energy for the Pu L_{III}-edge, E_0, was defined as 18059 eV.

EXAFS oscillations were isolated with the program AUTOBK [40] and analyzed with the EXAFSPAK software package [41]. The fluorescence data were corrected for dead time. The scattering code FEFF8.20 [42] was used to calculate phase-shift and amplitude functions in the potential of the crystal structure of $KPuO_2CO_3$ [43]. The EXAFS spectra were fitted to the EXAFS equation without further refinement (e.g., deglitching) in the *k*-range between 1.9 and 7.6 Å^{-1} using a structural model consisting of one coordination shell with oxygen atoms as backscatterer. The values of the coordination number (N), bond distance (R) and Debye–Waller factor (σ^2) were allowed to adjust freely during the fit procedure. The amplitude reduction factor (S_0^2) was held constant at 0.9. The shift in the threshold energy (ΔE_0) was allowed to vary as one global fit parameter during the fit.

3. Results and discussion

3.1. Plutonium(III) speciation

The Pu(III) species distribution in aqueous solution was calculated for a 0.01 M Pu(III) solution in the absence of humic substances (100% N_2) with the geochemical computer code EQ3/6 [44] applying the Pu(III) hydrolysis constants compiled in the NEA data base [45]. The results show that at pH 1, which was applied in our experiments, Pu(III) aquo ions (Pu^{3+}) occur with 100%.

3.2. XANES spectra

XANES spectroscopy was applied to verify the oxidation state of Pu in the samples. In Fig. 1, the normalized Pu L_{III}-edge XANES spectra of Pu(III)–KFA and Pu(III)–M42 are shown in comparison to that of the Pu(III) aquo ion. The edge energies of the three spectra, determined as the inflection point of the edge, are identical (Pu(III) aquo ion: 18059.0 eV, Pu(III)–humates: 18059.2 eV). The experimental values of the Pu L_{III}-edge energies for tri- and tetravalent Pu aquo ions in 1 M $HClO_4$ were determined by Conradson et al. [46] to be 18059.0 and 18062.2 eV (relative to the Zr *K*-edge of 17998 eV). The value reported for the Pu(III) aquo ion agrees with the edge energy determined in our study whereas that reported for the Pu(IV) aquo ion is higher. Thus, the trivalent oxidation state of Pu in the samples and its stability within the time of the experiment was verified. That means, compared to our previous XAFS study of Pu(III)–humates [47] where the Pu(III) was partly oxidized to Pu(IV), the improved preparation conditions applied to the present Pu humic substance samples (sample preparation at pH 1, sealing of the wet past samples in polyethylene vials, transport from the home institute in Dresden to the experimental station in Grenoble under N_2 atmosphere) were successful.

3.3. EXAFS spectra

Fig. 2 shows the raw Pu L_{III}-edge k^3-weighted EXAFS spectra and the corresponding Fourier transforms (FTs) of the Pu(III) complexes with the humic substances KFA and M42 and of the Pu(III) aquo ion. The FTs are not corrected for EXAFS phase shifts, thus, peaks appear at shorter distances ($R + \Delta$) relative to the distance R determined in the fits. The EXAFS spectra of the Pu(III)–humates recorded in transmission mode (not shown here) closely resemble those recorded in fluorescence mode (cf. Fig. 2). The FTs are dominated by one peak at about $R + \Delta = 1.9$ Å representing the first Pu coordination shell consisting of oxygen atoms. Thus, the raw experimental spectra were modeled using a structural model consisting of one Pu–O coordination shell.

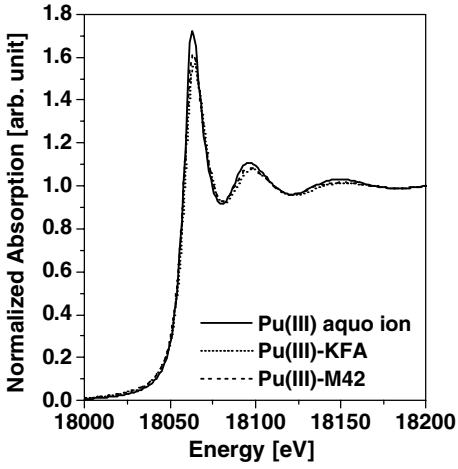


Fig. 1. Normalized Pu L_{III}-edge XANES spectra of Pu(III)–KFA and Pu(III)–M42 (both measured in fluorescence mode) in comparison to that of the Pu(III) aquo ion (measured in transmission mode). Normalization energy: 18 200 eV.

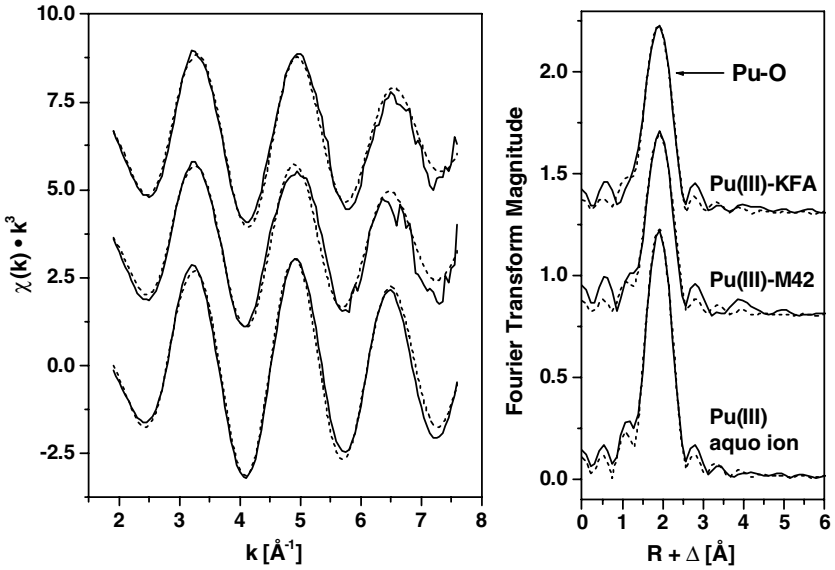


Fig. 2. Raw Pu L_{III}-edge k^3-weighted EXAFS spectra (left) and corresponding Fourier transforms (without correction for phase shift) (right) taken over $k = 1.9$–7.6 Å^{-1} for Pu(III) complexes with the humic substances KFA and M42 and for the Pu(III) aquo ion. Solid line – experimental data measured in fluorescence mode (Pu(III)–KFA, Pu(III)–M42) or transmission mode (Pu(III) aquo ion), dashed line – theoretical fit. The spectra have been shifted along the ordinate for clarity.

In Table 2, the structural parameters determined for the Pu(III)–humates and for the Pu(III) aquo ion, analyzed in the same k-range, are summarized for both the transmission and fluorescence data in comparison to literature data of Pu(III) and Pu(IV) aquo ions. The structural parameters obtained from experimental data measured in transmission and fluorescence modes are nearly the same. In the Pu(III)–humate complexes, the Pu(III) atom is surrounded by about eight oxygen atoms. Within the experimental uncertainties, this coordination number ($N_{Pu-O} = 8$) agrees with the value determined for the Pu(III) aquo ion in 1 M $HClO_4$ ($N_{Pu-O} = 9$) and also with the coordination numbers reported in the literature for aqueous Pu(III) species in various media (e.g., 0.01 M LiCl, 1 M $HClO_4$, 1 M HCl) which are in the range between 8 and 10 [27,29,48]. That means if Pu(III) ions are complexed by humic substances some of the water molecules previously attached to the Pu(III) ion in the inner coordination shell are replaced by carboxylate groups. The reason for the variation of the coordination number is not known. There could be an influence of the medium on the hydration sphere of Pu(III). Furthermore, the accuracy in the determination of coordination numbers from EXAFS is ±1 for at least two reasons: (i) uncertainties in the correct choice of the amplitude reduction factor, S_0^2 (1.0 or 0.9) [49], (ii) correlation between N and σ^2 during the fit. In fact, structural disorder in the first oxygen coordination shell (see below) can result in a fit where N is smaller than the expected value and σ^2 is increased [50].

The Pu–O bond lengths determined for Pu(III)–KFA and Pu(III)–M42 amount to 2.47 ± 0.02 and 2.49 ± 0.02 Å, respectively. The mean Pu–O bond length of the Pu(III)–humates amounts to 2.48 ± 0.02 Å. It is significantly longer than that of the Pu(IV) aquo ion (2.39 Å [48]). That means the EXAFS structural parameters confirm the conclusion drawn from the XANES spectra namely

Table 2
EXAFS structural parameters of Pu(III) complexes with humic substances in comparison to those of Pu(III) and Pu(IV) aquo ions

Sample	Medium	Mode	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)	Red. error [a]	Reference
Pu(III)–KFA	0.1 M $HClO_4$	transmission	8.2(3)	2.472(4)	0.0138(8)	1.8(3)	0.090	this work
		fluorescence	8.5(3)	2.460(3)	0.0165(6)	1.1(2)	0.051	this work
Pu(III)–M42	0.1 M $HClO_4$	transmission	7.5(4)	2.500(5)	0.014(1)	1.4(4)	0.117	this work
		fluorescence	7.8(3)	2.482(4)	0.0150(9)	1.5(3)	0.085	this work
$Pu(H_2O)_x^{3+}$	1 M $HClO_4$	transmission	9.2(2)	2.473(2)	0.0118(4)	0.5(2)	0.042	this work
$Pu(H_2O)_x^{3+}$	0.01 M LiCl	fluorescence	9.2(3)	2.51	0.010	−10.4		[27]
$Pu(H_2O)_x^{3+}$	1 M $HClO_4$	transmission	8–10	2.48				[48]
$Pu(H_2O)_x^{3+}$	1 M HCl, Zn amalgam		9.9(9)	2.51(1)	0.010(2)	2.3(6)		[29]
$Pu(H_2O)_x^{4+}$	1 M $HClO_4$	transmission	8–10	2.39				[48]

N, coordination number; R, bond distance; σ^2, Debye–Waller factor; ΔE_0, shift in threshold energy.
For N, R, σ^2, and ΔE_0 the errors are given in parenthesis as estimated by EXAFSPAK.
[a] Reduced error = sum of the squares of the differences between experimental and calculated curves/(no. of points − no. of variables).

that the humate complexes contain exclusively Pu(III). Furthermore, there is no evidence for the formation of polynuclear Pu species in the EXAFS spectra. In case of Pu(III)–M42, a small peak is visible in the FT obtained from experimental data measured in fluorescence mode at about $R + \Delta = 3.9$ Å (cf. Fig. 2) that could possibly be interpreted as Pu–Pu interaction. However, a comparable peak does not occur in the FT obtained from experimental data measured in transmission mode (not shown here). Thus, this is not a real effect but rather caused by noise. Therefore, within the detection limit of the technique the formation of polynuclear Pu species can be excluded.

The mean Pu–O bond length determined for the Pu(III)–humates (2.48 ± 0.02 Å) is comparable to the Pu–O bond distances determined for the Pu(III) aquo ion which range from 2.47 to 2.51 Å.

The number of carboxylate groups of humic substances coordinated to the Pu(III) ion cannot be determined by means of EXAFS spectroscopy. Obviously, the difference between the interatomic distances from Pu^{3+} to the oxygen atoms of the coordinated water molecules and carboxylate groups is smaller than the resolution in distance by EXAFS which is limited by $\Delta R = \pi/(2\Delta k)$ (0.28 Å for the k-range used). Furthermore, in accordance to the results of previous EXAFS studies of actinide humate complexes [4–7,51], it is only possible to detect the first shell contributions of directly coordinated oxygen atoms. Additional coordination shells consisting of carbon atoms of the binding carboxylate groups of humic substances were not observed in the FTs for several possible reasons: Firstly, the carbon atom is generally a relatively weak photoelectron scatterer, which results in weak XAFS contributions. Secondly, the angle of the Pu–O–C arrangement should be different for the various carboxylic groups in such disordered materials as humic substances. Therefore, multiple scattering effects are not expected. The structural disorder can result in destructive interferences and thus, in weaker spectral contributions of carbon atoms compared to those observed for actinide complexes of low-molecular weight compounds containing carboxylic groups in a high symmetry arrangement. Consequently, for the Pu(III)–humates, it is not possible to determine separate coordination numbers for the carboxylate groups coordinated to Pu(III) by XAFS analysis. Therefore, the number of carboxylate ligands is not exactly known.

Thus, the Pu–O bond length determined for humate complexes represents an average value over all interactions between Pu(III) ions and water molecules or carboxylate groups of humic substances. This results in a broader distribution of the Pu–O distances in the humate complexes in comparison to the Pu(III) aquo ions. This is evident in the larger values of the Debye–Waller factor as a measure of local disorder (cf. Table 2).

To identify the binding mode (monodentate, bidentate or bridging) of humic substance carboxylate groups to actinide ions, structural data of crystalline actinide complexes with model compounds containing carboxylate groups are usually used for comparison. In case of Pu(III), however, structural data have not been reported for Pu(III) carboxylates in the literature. Nevertheless, similar XAFS studies of Th(IV), Np(IV), Np(V) and U(VI) complexes with humic substances (e.g. [4–7,51]) have shown that the carboxylate groups of humic substances are predominantly monodentate coordinated to the actinide ions.

The comparison of the coordination numbers and bond lengths determined for the Pu(III) aquo ion ($N_{Pu-O} = 9$, $R = 2.47$ Å) with those determined for the Am(III) aquo ion ($N_{Am-O} = 8$–9, $R = 2.47$–2.49 Å [52]) and for the Cm(III) aquo ion ($N_{Cm-O} = 9.3$, $R = 2.46$ Å [53]) (all samples were prepared in non-complexing 1 M $HClO_4$) shows that the structural parameters of these trivalent actinides are almost identical.

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