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Identification of hexanuclear Actinide(IV) carboxylates with Thorium, Uranium and Neptunium by EXAFS spectroscopy

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Abstract. Hydrated actinide(IV) ions undergo hydrolysis and further polymerization and precipitation with increasing pH. The resulting amorphous and partly crystalline oxyhydroxides $\text{AnO}_n(\text{OH})_{4-2n} \cdot x\text{H}_2\text{O}$ can usually be observed as colloids above the An(IV) solubility limit. The aging process of such colloids results in crystalline AnO_2 . The presence of carboxylates in the solution prevents the occurrence of such colloids by formation of polynuclear complexes through a competing reaction between hydrolysis and ligation. The majority of recently described carboxylates reveals a hexanuclear core of $[\text{An}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$ terminated by 12 carboxylate ligands. We found that the An(IV) carboxylate solution species remain often preserved in crystalline state. The An(IV) carboxylates show An–An distances which are ~ 0.03 Å shorter than the An–An distances in AnO_2 like colloids. The difference in the distances could be used to identify such species in solution.

1. Introduction

Carboxylates comprise a large group of organic ligands, including peptides and proteins as well as natural organic material like humic and fulvic acids. The carboxylates form stable complexes with various metal ions. These carboxylato complexes are often highly soluble in aqueous solution and have to be considered with respect to metal migration in the natural environment.

Previous investigations by potentiometric titration on tetravalent actinides with several carboxylates assumed exclusively mononuclear solution species [1]. The recent discovery of polynuclear An(IV) carboxylate complexes in aqueous solution [2–5] makes it likely that the thermodynamic data have to be reassessed at least to some extent. The discovery of such polynuclear complexes in solution

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indicated that the species appear already in the aqueous phase and remain preserved in the crystalline state, which is in contrast to other solid structures with infinite $-(\text{RCOO}-\text{M}^{4+})_n-$ chains that appear only during the crystallization process.

Tetravalent actinides as U(IV), Th(IV), Np(IV) and Pu(IV) are strikingly alike with respect to their strong tendency to hydrolyze in aqueous solution. The hydrolysis products undergo polymerization, resulting in the formation of amorphous, nanometer sized $\text{AnO}_n(\text{OH})_{4-2n} \cdot x\text{H}_2\text{O}$ particles which usually afford stable aqueous colloidal suspensions [6]. The complexation of An(IV) with carboxylates results in a competing reaction between hydrolysis and ligation [4]. The recently reported structures of polynuclear An(IV) carboxylates in aqueous solution were determined with EXAFS spectroscopy. The question arises if this technique is able to differentiate polymeric hydrolysis products, whose structure can be considered as precursors of AnO_2 , from polynuclear An(IV) carboxylates. At the first glance it occurs not to be difficult to differentiate these structures, as each absorbing center is surrounded by 12 next An(IV) neighbors in the AnO_2 structures, while there are only 4 neighbors in the hexanuclear An(IV) carboxylate clusters. However, these coordination numbers can strongly deviate from the limiting values either through structural disorder [7, 8] or through pH dependent species fraction [4–6]. Therefore, an alternative way to distinguish these species might be to compare the interatomic metal-metal distances. The subsequent discussion is focused on that issue.

2. Results and Discussion

The hydrolyzed An(IV) ions undergo polymerization and condensation through different mechanisms. As such, ololation and oxolation processes were suggested by Henry et al. [9].

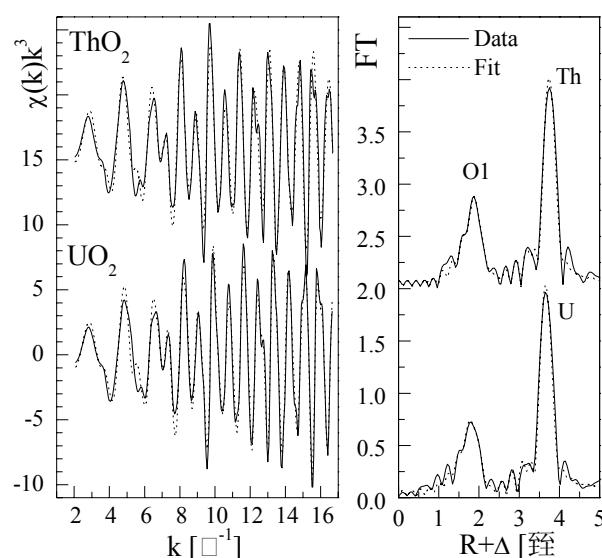


Figure 1. L_3 -edge k^3 -weighted EXAFS data (left) and corresponding Fourier Transforms (right) of ThO_2 and UO_2 .

Olation results in a hydroxo bond between the metal ions. It originates from a nucleophilic attack of a hydroxylated metal ion onto a hydrated metal cation by replacement of the water molecule by a hydroxo bond between both metal centers ($\text{M}-\text{OH} + \text{M}-\text{OH}_2 \rightarrow \text{M}-\text{OH}-\text{M} + \text{H}_2\text{O}$). Oxolation appears if hydroxo groups of two hydroxylated metal ions react together by releasing a water molecule and formation of an oxo bond between the metal ions ($\text{M}-\text{OH} + \text{OH}-\text{M} \rightarrow \text{M}-\text{O}-\text{M} + \text{H}_2\text{O}$). Further polymerization results in formation of amorphous An(IV) oxyhydroxides $\text{AnO}_n(\text{OH})_{4-2n} \cdot x\text{H}_2\text{O}(\text{am})$. With increasing pH there is a preferred tendency toward oxolation [9]. It has been observed that the amorphous structure undergoes an aging process that transforms the amorphous and disordered

$\text{AnO}_n(\text{OH})_{4-2n} \cdot x\text{H}_2\text{O}(\text{am})$ structure into ordered and crystalline $\text{AnO}_2(\text{cr})$ [10]. In the AnO_2 structures each An^{IV} is coordinated by 8 oxygen atoms in the first coordination shell and surrounded by 12 An^{IV} atoms in the second coordination shell. The crystal structure can be described by a juxtaposition of octahedral polyhedra (Figure 3a) which are structurally similar to the octahedral core found in the hexanuclear $\text{An}(\text{IV})$ carboxylate clusters (Figure 3b, top). The structural features of selected AnO_2 samples were characterized by An L_3 -edge EXAFS spectroscopy. Figure 1 displays the corresponding ThO_2 and UO_2 spectra. The metal-metal interaction under discussion is the peak at $R + \Delta = 3.6 \text{ \AA}$. The EXAFS data fit reveals a Th–Th distance of $3.957(2) \text{ \AA}$ for ThO_2 , which is in close agreement with the reported crystallographic values, e.g. 3.957 \AA [11], 3.958 \AA [12] and 3.960 \AA [13]. Similarly, the U–U distance deduced from the EXAFS data fit of a UO_2 sample, $3.867(2) \text{ \AA}$, correspond well with that found by X-ray diffraction measurements, e.g. 3.868 \AA [14] and 3.869 \AA [13].

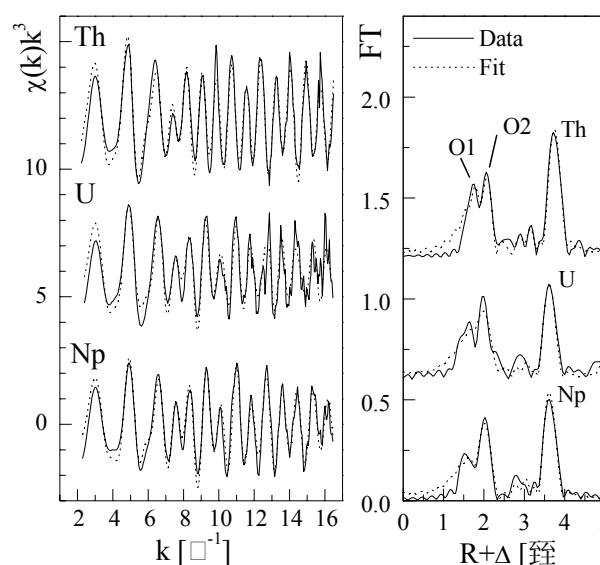


Figure 2. L_3 -edge k^3 -weighted EXAFS data (left) and corresponding Fourier Transforms (right) of $\text{An}(\text{IV})$ glycinate complexes.

The presence of carboxylates prevents the formation of $\text{An}(\text{IV})$ oxyhydroxides. Indeed, solution studies of $\text{An}(\text{IV})$ carboxylates revealed several polynuclear species [2–5], most of them possessing a hexanuclear $[\text{An}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$ core terminated by 12 carboxylate ligands. Besides the above mentioned solution studies of $\text{An}(\text{IV})$ carboxylates, several solid-state structures of $\text{An}(\text{IV})$ carboxylates have been described in the literature [4, 15–17]. We report herein as examples for the hexanuclear $\text{An}(\text{IV})$ carboxylates three aqueous samples of $\text{An}(\text{IV})$ glycinate complexes with $\text{An} = \text{Th}(\text{IV})$, $\text{U}(\text{IV})$ and $\text{Np}(\text{IV})$, investigated by EXAFS spectroscopy. The An L_3 -edge EXAFS spectra of these glycinate complexes are shown in Figure 2. Because the EXAFS data alone are not sufficient to determine the complete complex structure, a solid sample is used here as reference. The species $[\text{Th}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6(\text{Gly})_6(\text{HGly})_6]^{6+}$ was preserved in a crystal [5]. The crystal structure of this compound (Figure 3b, bottom) consists of a hexanuclear $[\text{Th}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{12+}$ core with six Th(IV) atoms arranged at the corners of a nearly regular octahedron. The Th–Th edge distances are deviating from each other by less than 0.01 \AA . Each face of the octahedron is bridged alternatively by either a $\mu_3\text{-O}$ or a $\mu_3\text{-OH}$ group. The twelve edges of the octahedron are bridged by chelating carboxylic groups of glycine ligands. Each Th atom shows a coordination number of 9 and is bound to two $\mu_3\text{-O}$, two $\mu_3\text{-OH}$, four oxygen atoms from the carboxyl groups of glycine, and a terminal water molecule. The different metal-oxygen distances involving either oxo, hydroxo, or carboxylate oxygen atoms give rise in the EXAFS spectra to a splitting of the oxygen shell at $R + \Delta = 1.9 \text{ \AA}$. Each corner atom of the

hexanuclear cluster has 4 next An neighbors, as evidenced by the peak at $R + \Delta = 3.6$ Å. The extracted An–An distances for the various glycinate complexes are: 3.921(2), 3.829(2), and 3.816(2) Å for Th(IV), U(IV), and Np(IV) respectively. Most remarkably, these An–An distances are significantly different from the corresponding values found for AnO₂ samples.

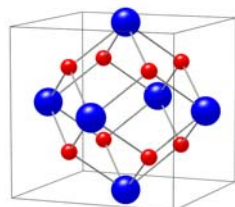


Figure 3a. Unit cell of AnO₂ with the section of the face-centered octahedral polyhedron.

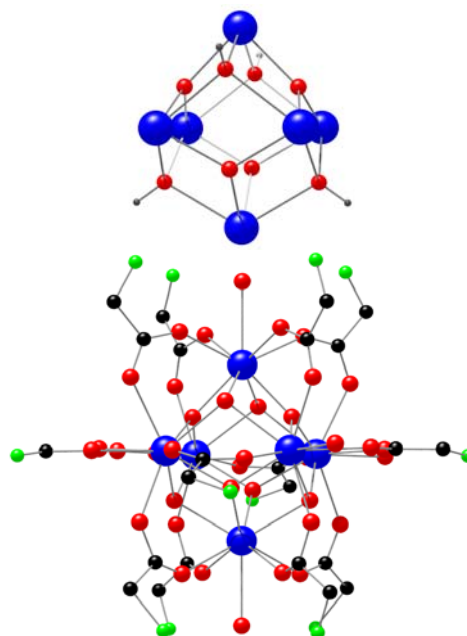


Figure 3b. Hexanuclear complex unit $[\text{Th}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6(\text{Gly})_6(\text{HGly})_6]^{6+}$ (bottom) and the simplified $[\text{An}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6]^{12+}$ core (top) from Ref. [6]

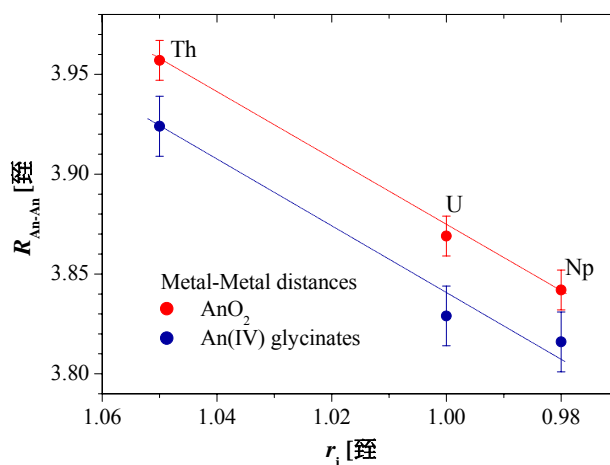


Figure 4. Correlation of the An–An distances in AnO₂ and hexanuclear An(IV) glycinate complexes with the Shannon ionic radius r_i [18].

Figure 4 compares the An–An distances of AnO₂ (An = Th, U, and Np) with those found for the An(IV) glycinate complexes. The latter are ~ 0.03 Å shorter than the former, suggesting a tighter

packing of the metal centers in the carboxylic-bridged structures. The same tendency can be observed for other An(IV) carboxylates [4, 5].

3. Conclusion

The presence of carboxylates results in a competing reaction between hydrolysis and ligation affording hexanuclear complexes. These An(IV) carboxylate clusters prevail in solution at pH values where the ololation and oxolation reaction products as $\text{AnO}_n(\text{OH})_{4-2n} \cdot x\text{H}_2\text{O}(\text{am})$ and $\text{AnO}_2(\text{cr})$ would appear in the absence of carboxylic or amino acids. Characteristic features for $[\text{An}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_6(\text{L})_{12}]$ structural units are: a specific splitting of the An–O shell, an An^{4+} coordination number of 9, and An–An distances which are $\sim 0.03 \text{ \AA}$ shorter than in AnO_2 .

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