

	<b>Experiment title:</b> <b>Redox behavior of neptunium species in solution</b>	<b>Experiment number:</b> 20-01-701
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> From 05-03-10 to 09-03-10 23-04-10 to 25-04-10 28-08-10 to 31-08-10 22-09-10 to 25-09-10 27-11-10 to 28-11-10	<b>Date of report:</b> 17.2.2011
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## Report:

Tetravalent actinides show strong tendencies towards hydrolysis which promotes polynucleation and colloid formation of the hydroxides or oxides. We studied the complexation of  $U^{IV}$  and  $Th^{IV}$  with formate ( $HCOO^-$ ) under moderately acidic condition.

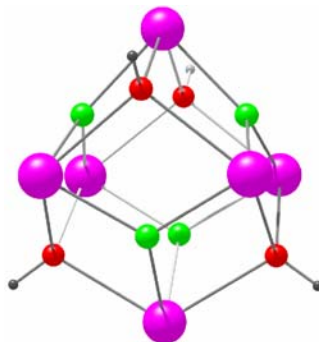
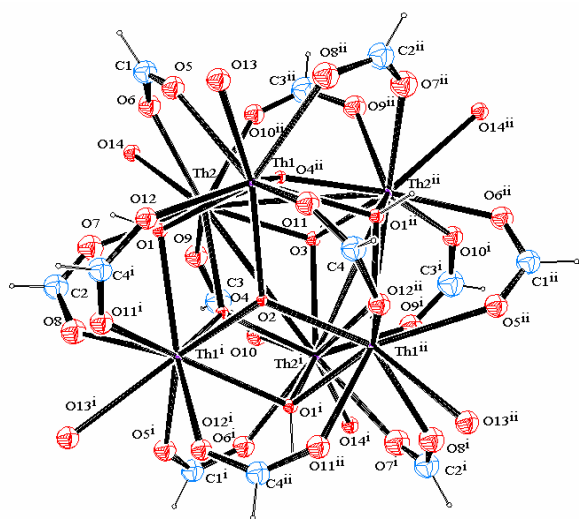


Fig 1. Structure of the complex

**Left:** ORTEP picture  
purple: Th; blue: C; red: O

**Right:** core structure (right, Purple, Th; green,  $\mu_3-O$ ; red;  $\mu_3-OH$ ; black, hydrogen) of **2**. Symmetry code i: x+1, y+1, z-1, and ii: x, y+1, z+1.

**EXPERIMENTAL.** Compound **1**:  $[U_6(\mu_3-O)_4(\mu_3-OH)_4(HCOO)_{12}(H_2O)_6](N_2H_5)_2(ClO_4)_2(H_2O)_{12}$ , deposited from an aqueous solution containing 0.5 M  $U^{IV}$  with excess  $HCOOH$  at pH 2.5 through slow evaporation of the solvent. Compound **2**:  $[Th_6(\mu_3-O)_4(\mu_3-OH)_4(HCOO)_{12}(H_2O)_6]Na_3(ClO_4)_{3.5}(H_2O)_{5.5}(H_3O)_{0.5}$  was obtained from an aqueous solution

containing 0.05 M Th<sup>IV</sup> and 1.0 M HCOOH at pH 1.0 during slow reduction of the solution volume by concentration. Crystal data were collected with a Bruker AXS SMART diffractometer at room temperature by using Mo-K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) monochromatized by a graphite crystal. X-ray absorption spectra of L<sub>III</sub> edges of U<sup>IV</sup> and Th<sup>IV</sup> were recorded at ROBL.

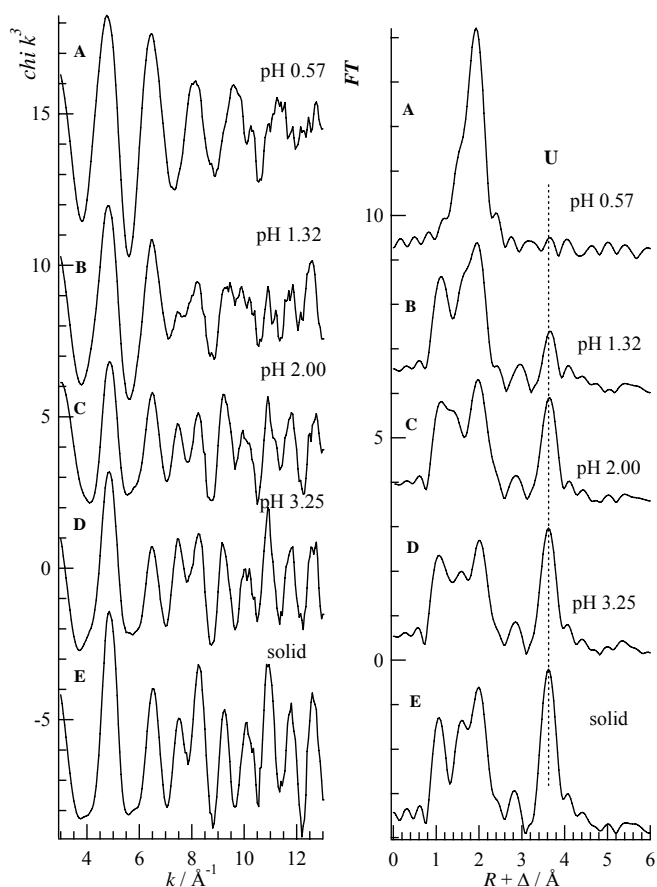


Fig. 2.  $k^3$ -weighted U L<sub>III</sub>-edge EXAFS spectra (left) and their FTs (right) of aqueous solutions of U<sup>IV</sup>-HCOOH, and of solid sample **1**. Phase shifts are not corrected on the FTs.

**RESULTS.** Fig. 1 shows the structure of **2** and its [Th<sub>6</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub>] core. The crystal structure analyses of **1** and **2** reveal [M<sub>6</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub>(HCOO)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>] cores. Each metal atom is surrounded by 4 O atoms from  $\mu$ -HCOO<sup>-</sup>, 4 O atoms from  $\mu_3$ -oxygen, and 1 O atom of the terminal water molecule. Neighboring metal atoms are bridged by  $\mu$ -HCOO<sup>-</sup> through a *syn-syn* coordination. Distortion of { $\mu_3$ -O(H)}<sub>8</sub> hexahedra arises from the presence of two kinds of  $\mu_3$ -oxygen atoms, i.e.,  $\mu_3$ -O<sup>2-</sup> and  $\mu_3$ -OH<sup>-</sup>. In order to clarify the occurrence and stability range of the [M<sub>6</sub>{ $\mu_3$ -O(H)}<sub>8</sub>] complexes in aqueous solution, EXAFS measurements were performed. Fig. 2 shows  $k^3$ -weighted EXAFS spectra and Fourier transforms of U<sup>IV</sup> with 1.0 M HCOOH at different pH. With increasing pH, U $\cdots$ U interaction at  $R + \Delta = 3.8 \text{ \AA}$  becomes more significant indicating the presence of the complex in solution. The EXAFS spectrum at pH 3.25 shows strong similarity with that of the crystalline sample **1**. It can be concluded that [U<sub>6</sub>{ $\mu_3$ -O(H)}<sub>8</sub>(HCOO)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>] is also formed as solution species. In contrast, [Th<sub>6</sub>{ $\mu_3$ -O(H)}<sub>8</sub>(HCOO)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>] in the solution is always minor component under pH 1.0-3.5. This is probably related to the lower hydrolysis capacity of Th<sup>IV</sup>.

## REFERENCE

Takao, S., Takao, K., Kraus, W., Emmerling, F., Scheinost, A.C., Bernhard, G., Hennig, C. First hexanuclear U<sup>IV</sup> and Th<sup>IV</sup> formate complexes – structure and stability range in solution Eur. J. Inorg. Chem. (2009) 4771-4775.