 ROBL-CRG	<b>Experiment title:</b>  Investigation of the aqueous phase in the ternary sorption system uranium(VI), Goethite, organic model compounds.	<b>Experiment number:</b>  20-01-675
<b>Beamline:</b>  BM 20	<b>Date of experiment:</b>  from:                                  to:  01.03.                                  04.03.08  23.07.                                  27.07.08  10.11.                                  14.11.08	<b>Date of report:</b>  20.03.08
<b>Shifts:</b>  30	<b>Local contact(s):</b>  A. Rossberg	<i>Received at ROBL:</i>
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**EXPERIMENTAL.** Sample solutions were prepared by dissolving  $\text{UO}_3$  in perchloric acid and adding the needed amount of solid DL-tartaric acid. After the pH was adjusted to pH 7 the UV-visible pH titration experiment was performed by adding negligible small volumes of highly concentrated acids. The UV-vis data was collected on a Cary 50 spectrophotometer in the spectral range from 700 to 350 nm. At seven selected pH points solutions were prepared for measuring both EXAFS and UV-vis. The uranium  $L_{\text{III}}$ -edge EXAFS measurements were performed in transmission.

**RESULTS.** The UV-visible pH titration data was treated using the program pHab [1]. For the computation complex stability constants from literature [2,3,4] were used as initial values. It has been approved that between pH 3 and 5 the dimeric uranyl tartrate  $(\text{UO}_2)_2(\text{H}_1\text{Tar})_2^{2-}$  is the dominant species and that at higher pH values a further oligomerization to the trimer  $(\text{UO}_2)_3(\text{H}_1\text{Tar})_3(\text{OH})_2^{5-}$  occurs. Furthermore there was found no evidence for the occurrence of a tridentate monomer which was also postulated in literature [2-4]. EXAFS analyses were done using iterative target transform factor analyses. Three factors were found to be sufficient for fitting the data. According to the speciation these factors must be the hydrated uranyl ion, the dimer and the trimer. This suggestion is supported by the fact that the relative concentrations of those factors fit very well to the speciation that was computed using the UV-vis data. Factor 2 and 3 show a strong U-U interaction at 3.93 Å and 3.81 Å respectively (Tab. 1). These distances are in fair agreement with U-U distances of dimers or trimers of the

Table 1: EXAFS structural parameters for the three factors.

	Atom	N	R	$\sigma^2$
Factor 1	Oax	2*	1.766(1)	0.00112(6)
	Oeq	5*	2.404(3)	0.0075(3)
Factor 2	Oax	2*	1.787(9)	0.00129(6)
	Oeq	5*	2.356(2)	0.0061(2)
	C	2.1(8)	3.28(1)	0.006(3)
	U	1*	3.927(6)	0.0054(4)
	U-U distance of $(\text{UO}_2)_2(\text{OH})_2^{++}$ : 3.87 [5]			
Factor 3	Oax	2*	1.803(1)	0.00142(7)
	Oeq	5*	2.360(4)	0.0113(4)
	C	1.5(5)	3.29(2)	0.006*
	U	2*	3.806(2)	0.0048(2)
	U-U distance of $(\text{UO}_2)_3(\text{O})(\text{OH})_3^+$ : 3.83 [5]			

\* fixed (-) - standard deviation

hydrolysis species in aqueous phase from DFT calculations [5]. The determined U-C distances give evidence for the formation of five or six membered rings. According to the sum formulas of both complexes the tartrate ion connects tridentately to uranium using one hydroxyl and two carboxyl groups. These pieces of information lead to the postulation of the following structures (Fig. 1).

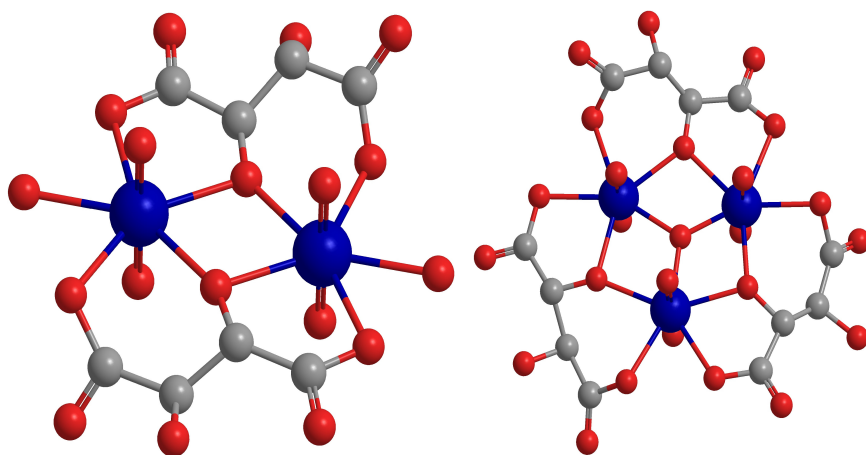


Figure 1: Proposed structures for the uranium tartrate dimer (left) and uranium tartrate trimer (right).

## REFERENCES

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