



ROBL-CRG

	Experiment title: X-ray absorption spectroscopy investigation on uranyl complexes with α -substituted carboxylic acids	Experiment number: 20_01_31
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Report:

We are reporting the first preliminary results within this project. Alpha-substituted carboxylic acids are present in nature as degradation products and their interactions with metal-ions are therefore important. They are often assumed to form chelates using the alpha-OH group and one carboxylate oxygen. But there is no experimental proof and little information on the structure of the species formed. Szabó and Grenthe found that the alpha-OH proton can dissociate when the alpha-OH-group is coordinated [1]. The experiments in this proposal will provide experimental information about the structure of uranyl complexes with α -substituted carboxylic acids: (a) alpha-OH group: glycolic acid and alpha-hydroxyisobutyric acid, and (b) alpha-NH₂-group: alpha-aminoisobutyric acid. The soluble species will be analysed by XAS to get experimental proof if at low pH a bidentate coordination of the carboxylic group dominates and at which pH a chelating coordination to uranyl due to the deprotonation of the alpha-OH-group of the ligand will take place.

Experimental. Aliquots of the U(VI) stock solution were taken to get the final concentrations between 0.005 and 0.05 M. Appropriate amounts of glycolic acid and alpha-hydroxyisobutyric acid were dissolved to obtain the ligand concentrations. The pH values of the test solutions were adjusted using NaOH/TMA-OH and/or HClO₄. The EXAFS data were recorded in transmission or fluorescence mode at the Rossendorf Beamline (ROBL) at the ESRF in Grenoble. For energy calibration of the sample spectra, the spectrum from a Y foil was recorded simultaneously. The ionization energy of the U L_{III} electron, E₀, was arbitrarily defined as 17 185 eV. The data were

treated using the EXAFSPAK software developed by George and Pickering (1995) at SSRL [2]. Theoretical backscattering phase and amplitude functions were calculated using the FEFF6 [3] program. The MS path O-U-O (4 legged path) of the linear UO_2^{2+} unit was included in the model fitting.

First Results. In this first attempt we were investigating the structure of soluble uranyl species with the two alpha-hydroxycarboxylic acids under acidic (pH=2) and alkaline conditions (pH>10). The distance of the equatorial oxygens are an indication for the coordination mode of the ligand to the linear uranyl unit. Denecke et al. found that in the case of bidentate ligation the resulting U-O_{eq} bond distance should be 2.48 Å [4]. The average distances for monodentate and bridging ligation are 2.39 and 2.36 Å, respectively. In the test solution at pH=2, the 1:1 complexes, $\text{UO}_2(\text{HOCH}_2\text{COO})^+$ and $\text{UO}_2(\text{HOC}_3\text{H}_6\text{COO})^+$, are dominating the uranyl speciation. In both systems, the measured average distance for the equatorial oxygens were 2.39 Å. This is significantly shorter compared to 2.44 Å determined in the acetate system [5]. In contrast to the bidentate coordinated acetate, the alpha-hydroxycarboxylic acids under investigation are most likely bound in a monodentate ligation to the linear uranyl unit.

Under alkaline conditions the alpha-OH group should be deprotonated and the complexes, $\text{UO}_2(\text{OCH}_2\text{COO})_2^{2-}$ and $\text{UO}_2(\text{OC}_3\text{H}_6\text{COO})_2^{2-}$, might be the major uranyl species [1]. A decreased U-O_{eq} bond distance, 2.36 Å, with increasing pH were detected for the glycolate system. This is a strong indication for a chelating coordination to uranyl due to the deprotonation of the alpha-OH-group. The EXAFS spectrum depicted a narrow peak at 3.85 Å. This feature could be fitted as a U-U interaction. One explanation would be the formation of a polynuclear species, e.g. $[(\text{UO}_2)_2(\text{OCH}_2\text{COO})_4]^{4+}$, at pH values above 10. An average U-O_{eq} bond distance of 2.28 Å was detected in the alpha-hydroxyisobutyrate system at pH >10. This distance is, however, too short for a chelating coordination of the ligand. Whereas the value of 2.28 Å is similar to U-O_{eq} (2.26 Å) found for $\text{UO}_2(\text{OH})_4^{2-}$ [6]. We assume that under the given circumstances the mononuclear uranyl hydroxo species are dominating the U(VI) speciation instead of $\text{UO}_2(\text{OC}_3\text{H}_6\text{COO})_2^{2-}$.

In further experiments, we will measure more samples between pH 2 and 8. This approach might help to explore at which pH a chelating coordination to uranyl due to the deprotonation of the alpha-OH-group of the ligand will take place. Furthermore we will investigate the influence of the NH₂-group compared to that of the OH-group in alpha-hydroxyisobutyric acid by means of EXAFS.

References

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