

	Experiment title: Development of a 2nd generation spectro-electrochemical cell for in-situ electrolysis	Experiment number: 20-01-681
Beamline: BM 20	Date of experiment: From 31/01/2010 to 01/02/2010 03/02/2010 to 06/02/2010 30/06/2010 to 02/07/2010 11/03/2009 to 12/03/2009 09/06/2009 to 12/06/2009 30/09/2009 to 02/10/2009	Date of report: 17.2.2011
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Report:

To clarify the coordination of the limiting U(IV) carbonate complex, we investigated a crystal structure by X-ray diffraction, followed by a comparative investigation of the $[\text{U}(\text{CO}_3)_n]^{4-2n}$ complex in solid and solution state by U L₃-edge EXAFS spectroscopy [1]. EXAFS is an appropriate method to test if the solution species is preserved in a crystal structure [2] or undergoes a ligand rearrangement [3] during crystallization. Because most of the authors mentioned difficulties to prevent the reoxidation of U(IV), we applied a new electrolysis route to obtain a pure U(IV) carbonate solution.

EXPERIMENTAL. Single crystals were obtained from 0.05 M U(IV) solution in 1 M NaHCO₃ after several weeks without evaporation of the solution (sample **A**). The U(IV) solution sample was prepared by bulk electrolysis of 0.05 M U(VI) carbonate in the 1.0 M NaHCO₃ solution at a constant potential of -1.45 V, using a 4.9 cm² Hg pool electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode (sample **B**).

RESULTS. The solid compound Na₆[U(CO₃)₅]·12H₂O crystallizes in the triclinic space group $P\bar{1}$ with two $[\text{U}(\text{CO}_3)_5]^{6-}$ anions in the unit cell. The U(IV) atom is coordinated by five carbonate ligands resulting in a coordination number of 10. The carbonate ligands coordinate exclusively in bidentate mode as shown in Fig. 1.

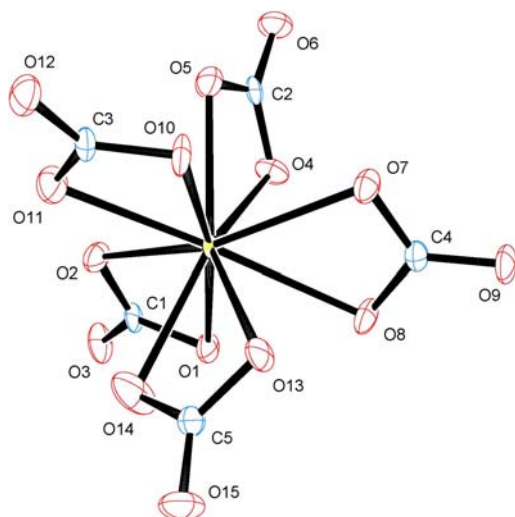


Fig. 1: $[\text{U}(\text{CO}_3)_5]^{6-}$ anionic complex obtained from single crystal diffraction.

Figure 2 compares the crystalline $\text{Na}_6[\text{U}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}$ with the solution of 0.05 M U(IV) in 1 M NaHCO_3 . The carbonate coordination shows a linear arrangement of uranium, the carbon atoms C and the distal oxygen O_{dist} . The bidentate-chelating coordination mode of the carbonate group is related with specific multiple scattering effects. The collinear arrangement of two ligand atoms C and O_{dist} with the absorbing atom results in strong multiple-scattering processes which usually increase the scattering power of a more distant atom like O_{dist} about several magnitudes.

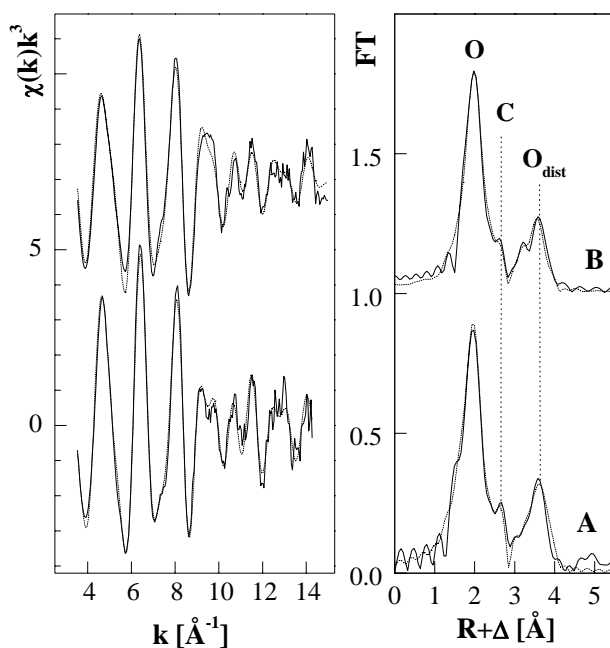


Fig. 2: U L_3 -edge k^3 -weighted EXAFS data and the Fourier transforms (FT) of $\text{Na}_6[\text{U}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}$ (A) and the solution of 0.05 M U(IV) in 1 M NaHCO_3 (B). Experimental data – solid line, fit results – dotted line.

The data fit of the solution sample reveal within the typical error limits 5 bidentate coordinated carbonate ligands with distances similar to the ones observed in the solid state. This result corroborate the existence of the $[\text{U}(\text{CO}_3)_5]^{6-}$ anionic species in solution with the same coordination mode as the solid U(IV) carbonate complex.

REFERENCES

- [1] C. Hennig et al. *Dalton Transactions* (2010) **39** 3774.
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- [3] C. Hennig et al. *Inorg. Chem.* (2008) **47**, 2987.