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|   ROBL-CRG | Experiment title: EXAFS investigations on uranium(VI) complexes formed by selected Schiff bases and 1,3 β -Diketones | Experiment number: 20-01-727 |
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Report:

Complexing agents with N, O, S donor functions are in development for cleaning contaminated areas and for the enrichment and the separation of metals of the d- and f-block. Important components of such multifunctional organic ligands are 1,3- β -diketones and Schiff bases. Pentan-2,4-dion (Acac), 1-Phenyl-butan-1,3-dion (Phe), and 1,3-Diphenylpropan-1,3-dion (DiPhe), N-Benzylideneaniline (NBA), Alpha-(4-hydroxy-phenylimino)-p-cresol (HPIC) and 2-(2-Hydroxybenzylidenamino)-phenol (HBAP) were selected for the determination of the structural parameters of the formed U(VI) complexes in methanolic solution. The U(VI) complex solutions and corresponding references were prepared from $\text{UO}_2(\text{ClO}_4)_2$ and stock solutions of the organic ligands with an uranium to ligand concentration ratio of 1:50 and a redox voltage in the range of 0 to 330 mV. The U L_{III} -edge spectra were measured in fluorescence mode at room temperature. The EXAFS spectra were analyzed using the program suite EXAFSPAK. The theoretical scattering phases and amplitudes were calculated by using X-ray structural data of Bis(2-benzoyl-1-phenylethenolato- k^2 -O,O')(ethanol- k O)dioxido-uranium(VI) /1/ and $\text{UO}_2(2-(2\text{-hydroxyphenylbenzoxazol}))_2(\text{CH}_3\text{OH})$ /2/ with the FEFF codes 8.2.

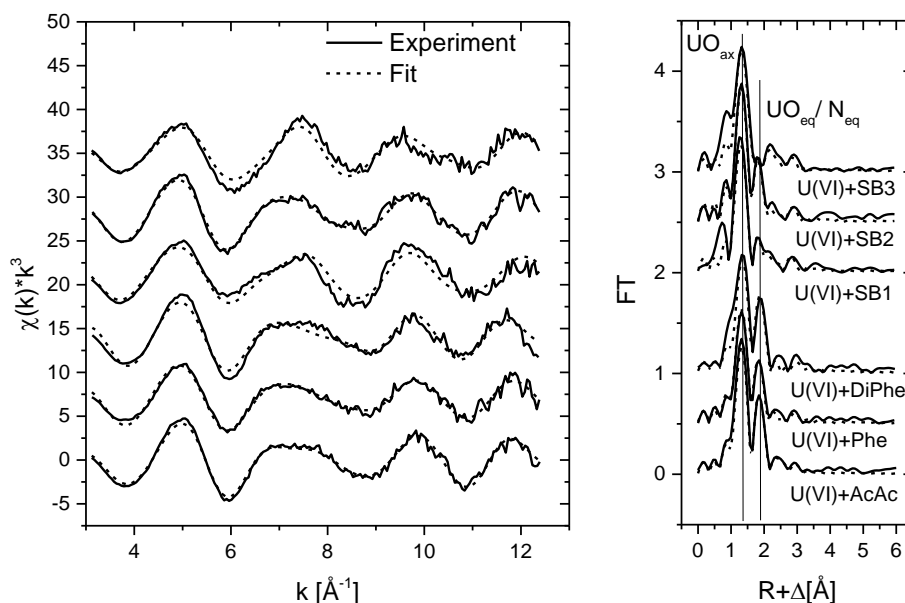


Fig. 1. Raw U L_{III}-edge k^3 -weighted EXAFS spectra (left) and corresponding Fourier transforms (right) of different uranium β -diketone (0 mV) and uranium-Schiff base (120 mV) systems in methanolic solution.

In all measured U L_{III}-edge k^3 -weighted EXAFS spectra (examples in Fig. 1) the contribution of two axial oxygen atoms U-O_{ax} at a distance of 1.77-1.79 Å were obtained. In the uranium β -diketone systems 1:2 complexes are formed at 0 mV. The spectra are very similar. A bidentate binding of the UO₂ unit (coordination number (CN) = 4) by the two keto functions with U-O_{eq1} distances in the range of 2.35 to 2.37 Å was determined. Additionally a methanol or water molecule (CN = 1) seems to be integrated in the complex with a U-O_{eq2} distance in the range of 2.52 and 2.53 Å.

In the equatorial shell of the 1:2 U(VI) complexes with the selected Schiff bases a fivefold coordination to other atoms in the nearest neighborhood was found, whereby two nitrogen atoms and three oxygen atoms were detected. Thus a U-N interaction by the imin group is very likely. The averaged U-N distance of 2.49 Å is longer than the averaged U-O distance of 2.28 Å. In the case of the hydroxyl group containing Schiff base (example SB3) it is at the moment not clear, whether the coordinated hydroxyl oxygen stems from the metal complex, due to formation of a chelate, or from an uranium oxygen interaction caused by solvent molecules. The differences between U-O and U-N atom distances determined using EXAFS measurements and DFT calculations could not be clarified within the timeframe of the project /3/ but are still under investigation.

References

- /1/ Takao, K., Ikeda, Y.: Acta Crystallographica Section E-Structure Reports online (2008), 64, M219-M220.
- /2/ Back, D.F. et al.: Inorganic Chimica Acta (2010), Vol. 363, 4, 807-812.
- /3/ BMBF-Abschlussbericht (project number: 02NUK014B).