AB INITIO SPECIATION Of Tc-GLUCONATE COMPLEXES IN AQUEOUS SYSTEMS

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^{99}Tc is a long-lived radio isotope ($t_{1/2} = 2.121 \cdot 10^5$ a) produced with high yield during nuclear fission in power-reactors from the fission of ^{235}U and ^{239}Pu. A large inventory of this radionuclide is accordingly found in spent nuclear fuel, in specific waste streams of low and intermediate level waste, as well as associated with sites for plutonium production or nuclear fuel processing and plays a special role in clean up efforts, e.g. at the Hanford legacy site[1]. Tc has a very rich redox chemistry with possible oxidation states ranging from *−I* to *+VII*, where Tc(VII) is the most stable oxidation state under most environmental conditions. In aqueous media, it is predominantly found in the form of the highly mobile TcO_4^- pertechnetate ion. Under more reducing conditions, as expected in underground repositories, sparingly soluble Tc hydrous oxides in the oxidation state *+IV* can be expected. The presence of certain organic ligands may result in the formation of stable aqueous complexes with Tc(IV), eventually increasing the solubility and potentially enhancing the mobility of Tc.

Tc-gluconate complexes in aqueous systems were recently reported and characterized by Tc L_3-edge X-ray absorption near-edge structure (XANES) measurements and Dardenne *et al.*[1]. Although Tc L_3-edge XANES was shown to be superior to differentiate between Tc oxidation states compared to Tc K-edge XANES, the puzzling result was reported that the Tc L_3-edge XANES of the sample containing Tc(IV)-gluconate species differs substantially from that of the Tc(IV)O_2(am,hyd) hydrous oxide reference sample, whereas the Tc K-edge XANES spectra of both Tc species did not differ significantly. Polly *et al.*[2] studied this observation with theoretical methods and tracked the unknown Tc(IV)-gluconate species in a three-step procedure:

(1) developing chemical models for the unknown Tc(IV)-gluconate species in the sample based undersaturation solubility experiments with TcO_2(am, hyd),

(2) optimizing the equilibrium structures of the selected chemical models and

(3) simulating the corresponding Tc L_3-edge XANES spectra based on relativistic multireference *ab initio* calculations.

We speciated the *a priori* unknown Tc(IV)-gluconate species present in the sample by comparing the experimental data with the theoretical results. For the structures we compare with the EXAFS measurements of the Tc-O distance of the Tc(IV)-gluconate species by Dardenne *et al.*[1] and Lukens *et al.*[3] and for the Tc L_3-edge XANES spectra we compare the simulated spectra with those reported by Dardenne *et al.*[1].

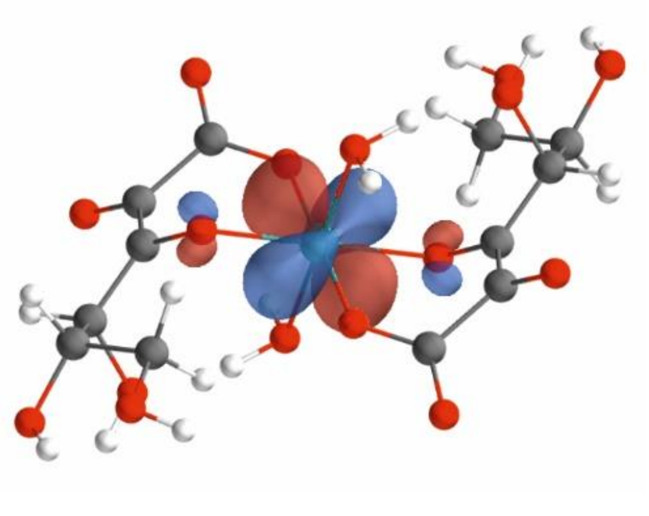

Fig. 1: Occupied 4d orbital of the $[Tc(IV)(Glu_{-2H})_2(H_2O)_2]^{-2}$ complex

With this three-step approach, we identified the $[Tc(IV)(Glu_{-2H})_2(H_2O)_2]^{-2}$ conformation as the most likely Tc(IV)-gluconate species prevailing in our samples under hyperalkaline pH conditions, with Glu_{-2H} representing a gluconate ligand with two deprotonated alcohol groups. This assignment agrees with earlier results by Lukens *et al.*[3]. Due to the changing coordination environment, the ground state of the Tc(IV)-gluconate species is a doublet state whereas the ground state of the $Tc(IV)O_2$(am, hyd) model is a quartet state. This in turn explains why the Tc L_3-edge XANES spectrum of Tc(IV)-gluconate features a double peak structure, contrasting the broad single peak XANES feature observed for the hydrous Tc(IV) oxide.

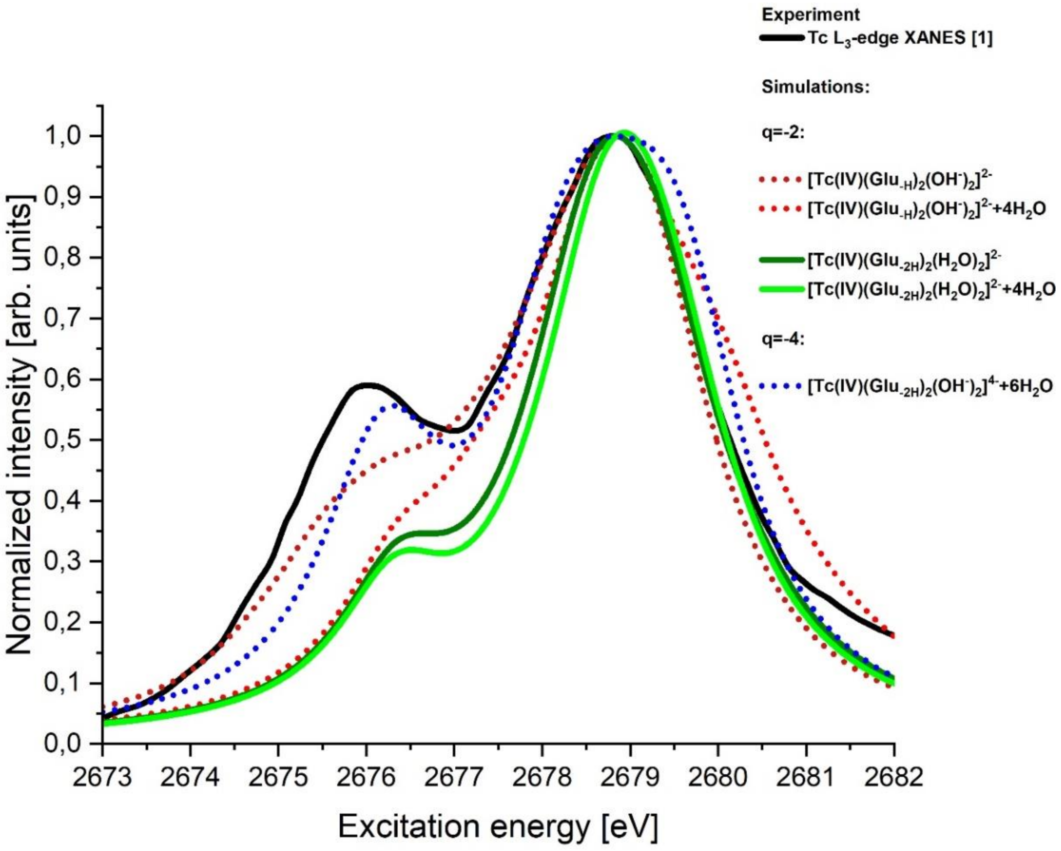

Fig. 2: Simulated Tc L_3-edge XANES spectra of selected Tc(IV)-gluconate models. All simulated spectra have been individually shifted by ~20 eV to align with the experimental data

Based on these encouraging results, we revisited the Tc(V)-gluconate species as well and applied the same procedure as for the Tc(IV)-gluconate species and identified the $[Tc(V)O(Glu_{-H})_2]^{-1}$ conformation as the most likely Tc(V)-gluconate species.

The optimization of the equilibrium structures of the chemical models chosen on the bases of solubility experiments for the unknown Tc(IV)-gluconate species together with the *ab initio* simulation of Tc L_3-edge XANES spectra proved to be a very sensitive theoretical tool for the speciation of unknown chemical species[2].

[1] Dardenne, K. and Duckworth, S. and Polly, R. and Schimmelpfennig, B. and Gaona, X. and Prüssmann, T. and Rothe, J. and Altmaier, M. and Geckeis, H. (2021). Inorg. Chem. 2021, 60, 12285-12298.

[2] Polly, R. and Dardenne, K. and Duckworth, S. and Gaona, X. and Prüssmann, T. and Rothe, J. and Altmaier, M. and Geckeis, H., https://doi.org/10.1021/acs.inorgchem.4c05115.

[3] Lukens, W. W. and Shuh, D. K. and Schroeder, N. C. and Ashley, K. R. (2004). Identification of the Non-Pertechnetate Species in Hanford Waste Tanks, Tc(I)-Carbonyl Complexes. *Environ. Sci. Technol.* 2004, *38*, 229.