Spectroscopic Characterization of Aqua [*fac*-$Tc(CO)_3]^+$ Complexes at High Ionic Strength

TG LEVITSKAIA,[1] S CHATTERJEE,[1] GB HALL,[1] MH ENGELHARD,[1] Y DU,[1] CI PEARCE,[1] NM WASHTON,[1] WW LUKENS,[2] S LEE[3]

[1]Pacific Northwest National Lab, Richland, WA 99354, USA (*correspondence:Tatiana.Levitskaia@pnnl.gov)
[2] Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
[3] Argonne National Laboratory, Argonne, Illinois 60439, USA

Understanding the fundamental chemistry of technetium (Tc) is important to the environmental remediation of nuclear waste and the reprocessing of nuclear fuel; however current knowledge of the electronic structure, and spectral signatures of low-valent Tc compounds significantly lags behind the remainder of the *d*-block elements. Technetium is a major risk-driver during processing and storage of used nuclear fuel and legacy nuclear waste generated during the Cold War era, which is currently stored at the United States Department of Energy (DOE) Hanford and Savannah River sites. Among radioactive constituents in the Hanford tank waste, ^{99}Tc presents a unique challenge due to the long half-life, complex chemical behavior, and high mobility in subsurface environment. In particular, identification of Tc speciation in legacy nuclear waste is challenging due to the lack of reference data particularly for Tc compounds in the less common oxidation states (I – VI). In an effort to establish a spectroscopic library of the Tc(I) tricarbonyl complexes found in the Hanford nuclear waste, compounds with the general formula of [*fac*-$Tc(CO)_3(OH_2)_{3-n}(OH)_n]^{1-n}$ were prepared and systematically examined by a range of spectroscopic techniques including ^{99}Tc/^{13}CO NMR, IR, XPS, and XAS spectroscopies. This has led to the first characterization of the [*fac*-$Tc(CO)_3]^+$ complexes by XPS and [*fac*-$Tc(CO)_3Cl_3]^{2-}$ by XAS. To assist in the interpretation of the experimental ^{99}Tc NMR spectra, computational approaches utilizing Density Functional Theory (DFT) have been tested and validated.[1]

In the series of monomeric aqua species, step-wise hydrolysis results in the increase of the Tc metal center electron density and corresponding progressive decrease of the Tc–C bond distances, Tc electron binding energies, and carbonyl stretching frequencies in the order [*fac*-$Tc(CO)_3(OH_2)_3]^+$ > [*fac*-$Tc(CO)_3(OH_2)_2(OH)$] > [*fac*-$Tc(CO)_3(OH_2)(OH)_2]^-$. These results correlate with established trends of their up-field chemical shift of ^{99}Tc

This abstract is too long to be accepted for publication. Please revise it so that it fits into the column on one page.

and down-field shift of ^{13}C carbonyl resonances. The lone exception is [*fac*-Tc(CO)$_3$(OH)]$_4$ which exhibits a comparatively low electron density at the metal center attributed to the μ_3-bridging nature of the $^-$OH ligands causing less σ-donation and no π-donation.

The work provides for an in-depth understanding of the effect of ancillary ligand on the properties of the aqua [*fac*-Tc(CO)$_3$]$^+$ complexes.

[1] Hall GB, A Andersen, S Chatterjee, NM Washton, Levitskaia TG. 2016. "Theoretical modeling of 99Tc NMR chemical shifts." Inorganic Chemistry 55: 8341–8347. **DOI:** 10.1021/acs.inorgchem.6b00458.