SUPPORTING INFORMATION

Carbon-Sulfur Bond Strength in Methanesulfinate and Benzenesulfinate Ligands Directs Decomposition of Np(V) and Pu(V) Coordination Complexes

Valérie Vallet^{a,*}, Yu Gong^b, Mohamad Saab^a, Florent Réal^a, John K. Gibson^{b,*}

^aUniv. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, F-59000 Lille, France

^bChemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Contents

Figure S1. ESI mass spectra for actinyl methanesulfinate solutions.

Figure S2. Natural Spin Orbitals for [UO₂(CH₃SO₂)(SO₂)]⁻ and [NpO₂(C₆H₅SO₂)(SO₂)].



Figure S1. Representative ESI mass spectra for the $An^{VI}O_2(CIO_4)_2 / CH_3SO_2Na$ solutions for An = Np (top) and An = Pu (bottom). It is likely that partial or predominant reduction of Np(VI) to Np(V), and/or Pu(VI) to Pu(V) (or to even lower oxidations states) had occurred prior to or during ESI. Dominant ESI species are the indicated clusters containing sodium added to the solutions as the source of sulfonate. In addition to the expected methane sulfinate (CH₃SO₂⁻) complexes are unexpectedly abundant species containing methane sulfonate (CH₃SO₃⁻), possibly partly due to oxidation of sulfonate by the actinyl(VI) species. For the reported CID experiments the species of interest, Np^VO₂(CH₃SO₂)² or Pu^VO₂(CH₃SO₂)², was isolated from other ESI species. A contrast with previous results for uranyl is the absence here of the An(VI) complexes An^{VI}O₂(CH₃SO₂)³ for An = Np and Pu; this species was abundant for An = U. The species in the ESI mass spectra thus clearly reveal the substantially higher An(VI/V) reduction potentials for An = Np (+1.16 V) and Pu (+0.94 V) versus An = U (+0.09 V).



Figure S2. Selected Natural Spin Orbitals NSOs along the z-O_{yl} direction for SO ground state of (a) $[UO_2(CH_3SO_2)(SO_2)]^-$ and (b) $[NpO_2(C_6H_5SO_2)(SO_2)]^-$. The corresponding occupation numbers n_z are given. Isosurface values: ± 0.03 au.