SUPPORTING INFORMATION

Uranyl-(12-Crown-4) Ether Complexes and Derivatives: Structural Characterization and Isomeric Differentiation

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Figure S1. ESI mass spectrum of the uranyl/12C4 solution. The species produced by ESI that were studied by IRMPD are $[UO_2(12C4)_2]^{2^+}$ (311 m/z) and $[UO_2(12C4)_2(OH)]^+$ (639 m/z). Also apparent are very high abundances of (12C4)Na⁺ (199 m/z) and (12C4)₂Na⁺ (375 m/z) due to ubiquitous Na⁺ contamination and the high affinity of Na⁺ for the 12C4 ligand.



Figure S2. CID mass spectrum of $(12C4)H^+$ (177 m/z) isolated from the ESI mass spectrum shown in Fig. 1. The sequential loss of 44 Da corresponds to fragmentation elimination of C₂H₄O units from the *cyclo*-(C₂H₄O)₄ ring. This fragmentation pattern is not observed for 12C4 coordinated to uranyl, indicating the crucial role of the binding of the ligand to the uranyl moiety in establishing the observed chemistry of the coordination complexes.



Figure S3. Mass spectrum after isolation of $[UO_2(12C4)_2(OH)]^+$ (639 m/z) from the ESI mass spectrum followed by an applied reaction time of 4 s. The absence of a product peak at 657 m/z indicates that addition of H₂O does not occur to within the detection limit, this in contrast to facile H₂O addition to $[UO_2(12C4)(OH)]^+$ and $[UO_2(12C4-H)]^+$. The absence of hydration is attributed to the high-coordination that prevents addition of an inner-sphere water molecule to the uranium metal center.



Figure S4. Mass spectrum after isolation of $[UO_2(12C4)_2]^{2+}$ (311 m/z) from the ESI mass spectrum followed by an applied reaction time of 4 s. The absence of a product peak at 320 m/z indicates that addition of H₂O to yield $[UO_2(12C4)_2(H_2O)]^{2+}$ does not occur to within the detection limit, this in contrast to facile H₂O addition to $[UO_2(12C4)(OH)]^+$ and $[UO_2(12C4-H)]^+$. As for $[UO_2(12C4)_2(OH)]^+$, the absence of hydration is attributed to the high-coordination that prevents addition of an inner-sphere water molecule to the uranium metal center.



Figure S5. Computed structures of $[UO_2(12C4)_2]^{2+}$ and $[UO_2(12C4)_2(OH)]^+$. ΔE is the relative energy with respect to the ground-state (GS) structure.



Figure S6. Computed structures of GS and high-energy $[UO_2(12C4-H)]^+$.



Figure S7. Computed structures of GS and high-energy hydrate and hydroxide isomers $[UO_2(12C4-H)(H_2O)]^+$ and $[UO_2(12C4)(OH)]^+$.



Figure S8. IRMPD spectra of $[UO_2(12C4)_2]^{2+}$ is in black. In red is the computed IR spectrum for the high-energy $[UO_2(12C4)_2]^{2+}$ isomer shown in Fig. S5. Harmonic frequencies were computed at the B3LYP/ECP60MWB_ANO (U):cc-pVTZ(C, H, O) level of theory, scaled by a factor of 0.98 and convoluted with a 10 cm⁻¹ fwhm Gaussian lineshape function.



Figure S9. IRMPD spectra of $[UO_2(12C4-H)]^+$ is in black. In red is the computed IR spectrum for the high-energy $[UO_2(12C4-H)]^+$ isomer shown in Fig. S6. Harmonic frequencies were computed at the B3LYP/ECP60MWB_ANO (U):cc-pVTZ(C, H, O) level of theory, scaled by a factor of 0.98, and convoluted with a 10 cm⁻¹ fwhm Gaussian lineshape function.



Figure S10. IRMPD spectra of (a) $[UO_2(12C4)(OH)]^+$ and (b) $[UO_2(12C4-H)(H_2O)]^+$ are in black. In red are shown the corresponding computed spectra for the high-energy isomers shown in Fig. S7. Harmonic frequencies were computed at the B3LYP/ECP60MWB_ANO (U):cc-pVTZ(C, H, O) level of theory, scaled by a factor of 0.98, and convoluted with a 10 cm⁻¹ fwhm Gaussian lineshape function (red).



Figure S11. IRMPD spectra obtained after gas-phase water addition to $[UO_2(12C4-H)]^+$; the black spectra is the same as shown in Fig. S10b. In red is the computed spectrum for GS structure of $[UO_2(OH)(12C4)]^+$ shown in Fig. S7. The absence of any computed absorptions in the region around 1650 cm⁻¹ supports the assignment of the species as GS $[UO_2(12C4-H)(H_2O)]^+$.