Supplementary Information

Complexation-Assisted Reduction: Complexes of Glutaroimide-dioxime with Tetravalent Actinides (Np(IV) and Th(IV))

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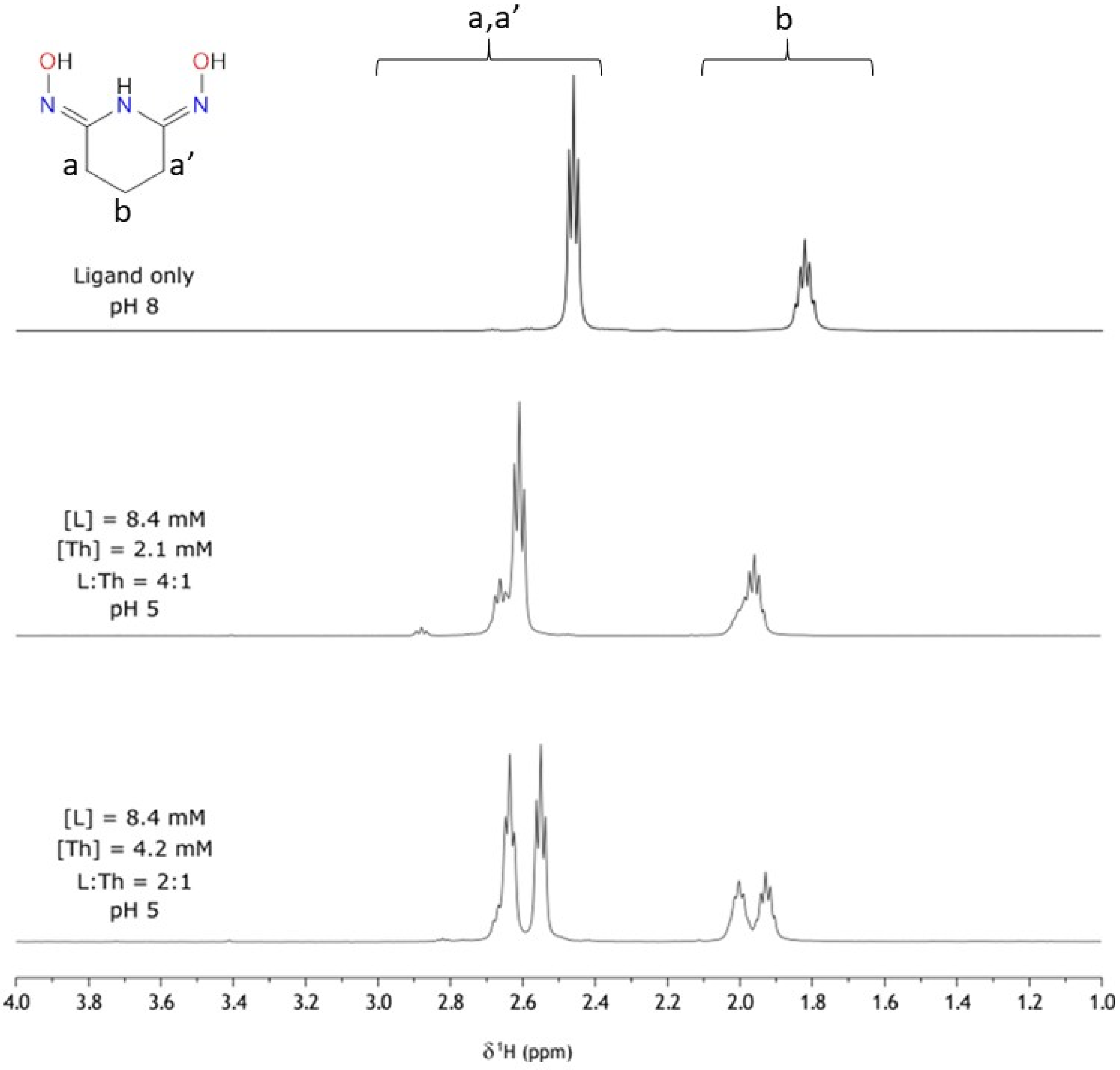

Figure S1. ^{1}H NMR spectra of Th(IV)/glutaroimide-dioxime mixtures in aqueous solution. The ligand-only solution was at pH 8 due to the very low solubility of the free ligand at pH 5.

The chemical shifts in Figure S2 are assigned to the two sets of protons (a/a’ and b) based on the ^{1}H COSY NMR data in a previous work.[1] No quantitative information is obtained from the ^{1}H NMR spectra of this work. However, these data indicate that the equivalencies of the H atoms in the free ligand remain unchanged in the Th(IV)/glutaroimide-dioxime complexes. In other words, the same number of ^{1}H resonances (two) with the same spin–spin coupling fine structures is observed for the complex and the free ligand, which agrees with the coordination modes of the ligand in the complexes suggested by thermodynamic data and confirmed by the crystal structure.

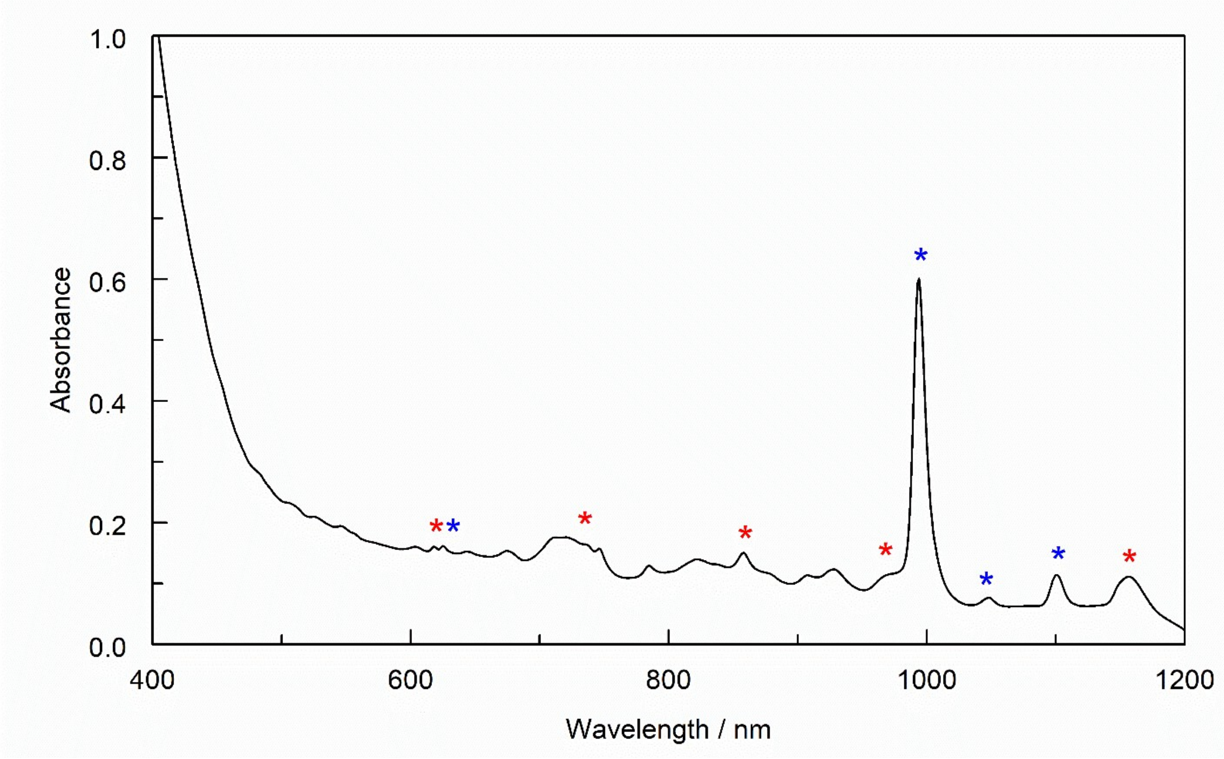

Figure S2. Absorption spectra of the mother liquor (seven weeks after mixing Np(V) and glutaroimide-dioxime) from which Np(H_2L)$_3$·ClO_4(cr) crystalized. Symbols: (*) peaks for Np(V)/glutaroimide-dioxime complexes at around 1102, 1050, 993, and 630 nm, (*) peaks for Np(IV)/glutaroimide-dioxime complexes at around 1159, 969, 860, 730, and 619 nm.

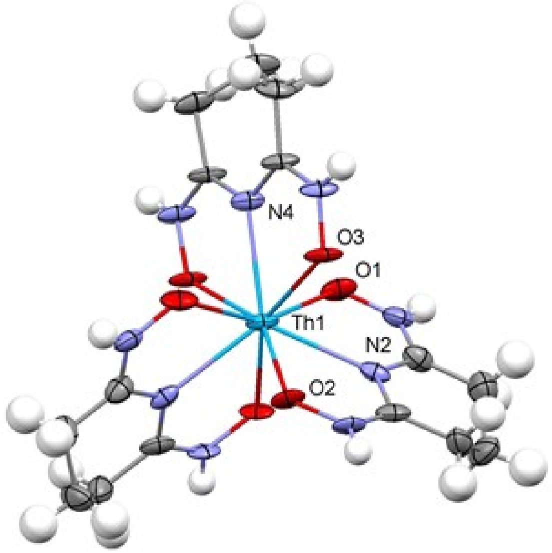

Figure S3. X-ray crystal structure of glutaroimide-dioxime complexed with Th(IV), Complex **III**, $[Th(H_2L)_3][NO_3]$. Thermal ellipsoids are set to 50% probability. Outer sphere ions and solvent molecules have been excluded for clarity.

Table S1. Crystallographic data and refinement information for complex **III**.

	Complex III
Empirical formula	C15 H30 N10 O12 Th
Formula weight (g/mol)	774.53
Temperature (K)	100 (2)
Wavelength (Å)	0.7749
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions (Å)	a = 24.609(4) b = 10.4339(14) c = 11.1854(16) α = 90° β = 111.038(4)° γ = 90°
Volume ($Å^3$)	2680.6(7)
Z	4
Density (calculated) (Mg/m^3)	1.889
Absorption coefficient (mm^{-1})	2.950
F(000)	1456
Crystal size (mm^3)	0.130 x 0.050 x 0.010
Theta range for data collection	2.337 to 27.811°
Index ranges	$-29 <= h <= 27$ $0 <= k <= 12$ $0 <= l <= 13$
Reflections collected	35637
Independent reflections	2853 [R(int) = 0.0849]
Completeness to theta = 27.706°	99.8%
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.7456 and 0.5339
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2853 / 19 / 191
Goodness-of-fit on F^2	1.249
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.0743$ $wR2 = 0.1918$
R indices (all data)	$R1 = 0.0922$ $wR2 = 0.2007$
Largest diff. peak and hole (e.Å^{-3})	2.064 and -1.802

Structure of Complex III: $[Th(H_2L)_3][NO_3]$

Complex **III**, the thorium analog of **II**, crystallizes from its aqueous reaction solution in the space group *C2/c*, with the cation $Th(H_2L)_3^+$ lying along a 2-fold axis. The cation $Th(H_2L)_3^+$ proved to be easily modelled in the structure of **III**, however, the nitrate anion was found to be severely disordered across multiple sites, with several similarly disordered water molecules. While we were unable to obtain a crystal of **3** of the same quality as those analyzed of complexes **I** and **II**, we are able to note some similarities and key differences in the bonding parameters of the glutaroimide-dioxime ligand to Th(IV) as compared to Np(IV). Like complex **II**, complex **III** displays an approximate tri-capped trigonal prismatic geometry. Also, similar to complex **II** (as well as complex **I**), a -1 charged H_2A^- ligand, resulting from the relocation of the protons of the oxime groups (-CH=N-O**H**) from oxygen to nitrogen atom and the deprotonation of the middle imide group (-CH-**N**H-CH-), coordinates to Th in a tridentate mode *via* the two oxime oxygen atoms and the imide nitrogen atom in complex **III**.

The Th-O distances 2.442(14) Å, 2.444(11) Å, and 2.438(13) Å, are all statistically longer than the analogous distances observed in the structure of complex **II**. Likewise, the distances between the metal center and the anionic central nitrogen of the glutaroimide-dioxime ligand in **III**, 2.557(17) Å and 2.54(2) Å, are also significantly longer than the same parameters measured in **II**. These larger bond lengths in **III** as compared to **II** are consistent with the general trend that Np^{4+} is smaller than Th^{4+} due to the larger nuclear charge of Np that causes “contraction” of atomic/ionic radii along the actinide series. A slight contraction in size along actinide series was observed in quantum mechanical calculations on a series of actinide(IV) complexes bound by nitrilotriacetic acid (NTA).[2] The same study also suggested that coordination numbers of actinide(IV) NTA complexes varied, such that the NTA complexes of Np(IV) and Pu(IV) had lower coordination numbers than the NTA complexes of Th(IV) or U(IV).[2] Also, a similar contraction in size has been determined for the actinide(III) ions (from U to Cf) using X-ray absorption techniques.[3]

References

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