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Synthesis of Uranium-in-Cryptand Complexes

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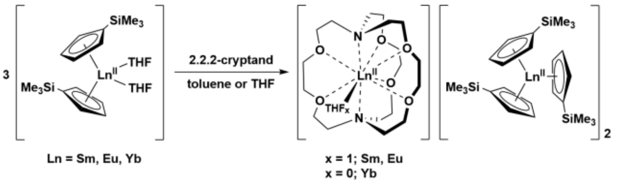
The facile encapsulation of U(III) and La(III) by 2.2.2-cryptand (crypt) using simple starting materials is described. Addition of crypt to UI_3 and $LaCl_3$ forms the crystallographically-characterizable complexes, [U(crypt)I_2]I and [La(crypt)Cl_2]Cl. In the presence of water, the U(III)-aquo adducts, [U(crypt)I(OH_2)][I]$_2$ and [Ucrypt)I(OH_2)][I][BPh_4], can be isolated.

Development of new ligand systems is critical to advancing the chemistry of any metal. We report here the first crystallographic confirmation of uranium encapsulated within the 2.2.2-cryptand (crypt) ligand. Since the crypt ligand has been known for decades,[1, 2] it was quite surprising that it had not been used extensively with actinides. Numerous studies have been published on crypt, but most focus on alkali and alkaline-earth metals.[1-4] Lanthanide crypt complexes have been reported as early as 1980 in solution[5] and several crystal structures have been subsequently reported.[6-10] Complexes of lanthanide ions encapsulated in ligands that are variations of crypt are also known.[11, 12] With uranium, there are reports on the spectroscopy and elemental analysis of U(IV) and uranyl cryptand complexes dating back to 1976,[13-16] but no X-ray crystal structures of uranium crypt complexes are in the literature to our knowledge.

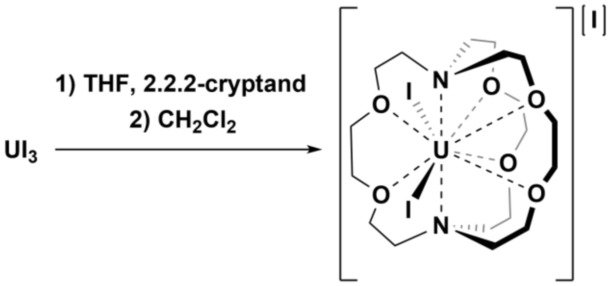
Our interest in this area was stimulated by the recent discovery that Sm(II), Eu(II), and Yb(II) can be readily encapsulated into crypt from metallocene precursors according to eq 1.[17] We sought to determine if facile encapsulation of actinides into crypt was possible in toluene or THF and could also lead to crystallographically-characterizable compounds. This would not only establish this special coordination environment for these f block metals, but it could also be valuable in manipulating the redox chemistry for these elements. Lower oxidation states of the lanthanides have been shown to stabilized by the crypt ligand.[5, 18] Hence metal-in-cryptand complexes are attractive precursors for generating low oxidation states of the rare-earth and actinide metals.[19-26]



(1)

To probe the generality of incorporating f elements into the crypt ligand shown in eq 1, simple halides of uranium and lanthanum, a rare-earth metal of similar size, were treated with crypt. We report here the first crystallographically-characterized actinide-in-cryptand and an analogous lanthanum-in-cryptand complex. In all the examples described below, there are two additional coordination sites accessible to the metal. This has allowed isolation of aquo complexes of U(III),[27-30] an ion that under other conditions can readily reduce water.[31-35]

Addition of a blue THF solution of UI_3 to a colorless THF solution of 2.2.2-cryptand (crypt) immediately forms a brown/green precipitate that is soluble in CH_2Cl_2. Recrystallization from CH_2Cl_2/Et_2O generates dichroic brown/green crystals of [U(crypt)I_2]I, **1**, eq 2. As shown in Figure 1, two iodides are coordinated to the U(III) ion in the crypt and one iodide is outer sphere.



(2)

An analogous reaction was conducted with $LaCl_3$ since the larger rare-earth metals are often used as mimics for the actinides[36] and it was of interest to see if the reaction was also applicable to 4f metals. Treatment of $LaCl_3$ with crypt in dimethylformamide (DMF) led to the insertion of La(III) into the crypt forming [La(crypt)Cl_2]Cl, **2**, as shown in eq 3.

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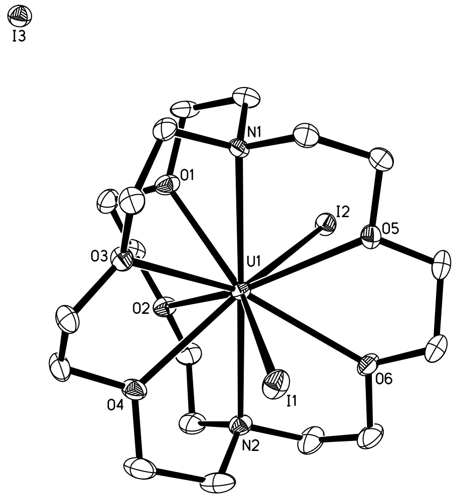
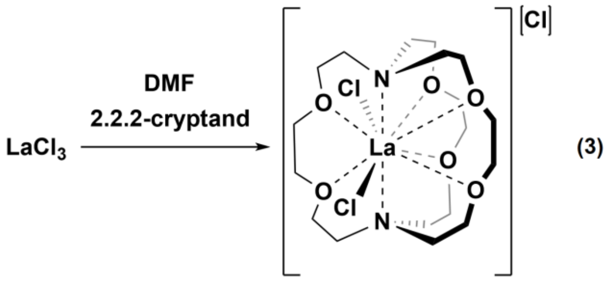


Figure 1. ORTEP representation of [U(crypt)I_2]I, **1**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.



(3)

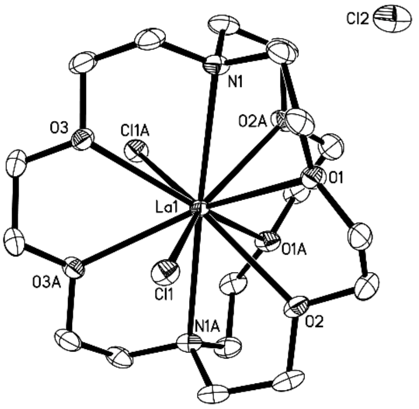


Figure 2. ORTEP representation of [La(crypt)Cl_2]Cl, **2**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

In one synthesis of **1** in THF, adventitious water was present and an aquated variant of **1** was obtained, namely [U(crypt)I(OH_2)][I]$_2$, **3**, Figure 3, which was only characterized crystallographically. The structure revealed one water molecule and one iodide ion coordinate to uranium and the complex crystallizes with two outer sphere iodide ions.

Anion exchange of an outer sphere iodide of **1** was performed by reaction with $NaBPh_4$ in acetonitrile (MeCN), eq 4. While an iodide was exchanged for $(BPh_4)^{1-}$, crystallographic characterization revealed that a water adduct again had formed, [U(crypt)I(OH_2)][I][BPh_4], **4**, Figure 4. As in **3**, compound **4** was only characterized crystallographically.

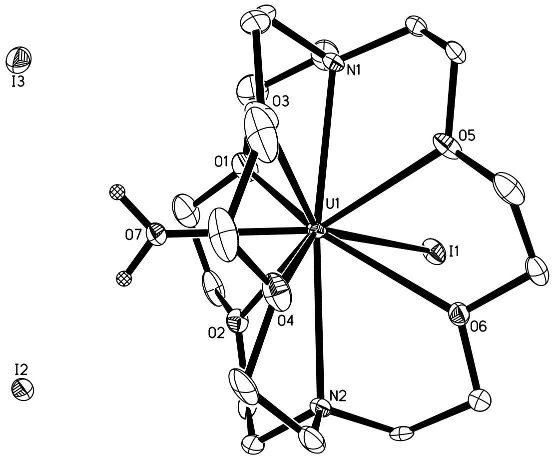
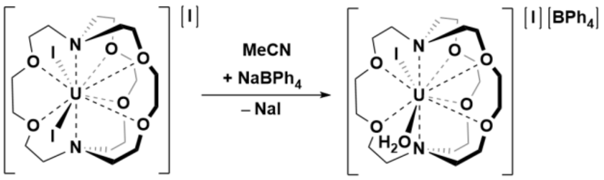


Figure 3. ORTEP representation of [U(crypt)I(OH_2)][I]$_2$, **3**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except those of H_2O were omitted for clarity.



(4)

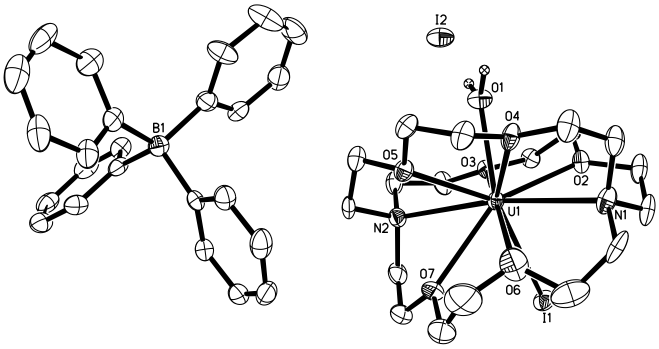


Figure 4. ORTEP representation of [U(crypt)I(OH_2)][I][BPh_4], **4**, with thermal ellipsoids drawn at the 50% probability level. Hydrogens except those of H_2O were omitted for clarity.

Metrical data on **1**-**4** are summarized in Table 1 as well as data on the aquated lanthanum complex, [La(crypt)Cl(OH_2)][Cl]$_2$,[9] for comparison. In each case, the six oxygen donor atoms of the crypt form the shortest distances to the metal. The M–N distances for the two nitrogen donors are 0.1-0.2 Å longer than the M–O distances. The six oxygen atoms of the crypt define a trigonal prismatic geometry, but the range of M–O distances show this has some distortion from a pure D_{3h} symmetry. The N atoms of the crypt cap the trigonal faces and the additional two ligands in each complex cap two of the three square faces of the O_6 trigonal prism. The U(III)−O(OH_2) bond distances, 2.549(7) and 2.503(3) Å, in **3** and **4**, respectively, are distinct from terminally bound U(IV)−O(OH) distances, which range from 2.040(2)-2.137(7) Å.[31, 33, 34, 37, 38] The U(III)-O(OH_2) distances are in the 2.47(3)-2.595(3) Å range reported for $UCl_3(OH_2)_7$,[27] $UCl_3(OH_2)_6$,[27] $[U(OH_2)_9][OTf]_3$,[28] $(NH_4)[U(OH_2)_5(MeCN)_2Br_2][Br]_2$,[29] and $(NH_4)U(SO_4)_2(OH_2)_3$•H_2O.[30]

Table 1. Summary of bond distance ranges (Å) of compounds $[U(crypt)I_2]I$ **1**, $[La(crypt)Cl_2]Cl$ **2**, $[U(crypt)I(OH_2)][I]_2$ **3**, $[U(crypt)I(OH_2)][I][BPh_4]$ **4**, and $[La(crypt)Cl(OH_2)][Cl]_2$.[9]

	$[U(crypt)I_2]I$, **1**	$[U(crypt)I(OH_2)][I]_2$, **3**	$[U(crypt)I(OH_2)][I][BPh_4]$, **4**
U−I	3.3106(5)-3.3292(6)	3.2563(7)	3.2845(6)
U−N_{crypt}	2.803(3)-2.853(3)	2.80(1)-2.814(8)	2.781(3)-2.822(3)
U−O_{crypt}	2.568(2)-2.697(2)	2.602(9)-2.683(7)	2.606(3)-2.659(4)
U−OH_2		2.549(7)	2.503(3)

	$[La(crypt)Cl_2]Cl$, **2**	$[La(crypt)Cl(OH_2)][Cl]_2$[9]
La−Cl	2.8161(5)	2.827(2)
La−N_{crypt}	2.893(2)	2.800(7)-2.814(6)
La−O_{crypt}	2.673(1)-2.716(1)	2.651(6)-2.725(6)
La−OH_2		2.539(6)

In complex **1**, the outer sphere iodide anion is 3.2 Å from the nearest atom in the $[U(crypt)I_2]^{1+}$ cation. In **3** and **4**, however, the outer sphere iodide ions are closer to the cation and the hydrogen atoms of the coordinated water are oriented toward the outer sphere iodides. In **3**, the H**…**I distances are approximately 2.6 and 2.7 Å and the H**…**I distance in **4** is 2.6 Å. The H**…**Cl distance in $[La(crypt)Cl(OH_2)][Cl]_2$[9] is 2.7 Å. The ranges of U−O(crypt) and U−N(crypt) bond distances in **1**, **3**, and **4** all overlap and show a similarity despite the difference in the other ligands on uranium and the extent of hydrogen bonding.

In summary, simple salts of uranium and lanthanum can readily form crystallographically-characterizable complexes with 2.2.2-cryptand. The crypt coordination environment allows additional ligands to bind to the metals such that productive chemistry is possible with this ligation. The formation of the aquo adducts **3** and **4** is unusual since U(III) in other coordination environments is known to reduce water to form U(IV)-hydroxo complexes.[31-35] It should also be noted that the solubility of $[U(crypt)I_2]I$, **1**, differs from the starting reagent UI_3. Although UI_3 is soluble in THF, **1** is not. In contrast, the starting UI_3 is not soluble in CH_2Cl_2, but **1** is soluble in this solvent. These differences in solubility suggest interesting possibilities for recycling/extraction of radioactive nuclear waste if an appropriately cost-effective chelate were available.

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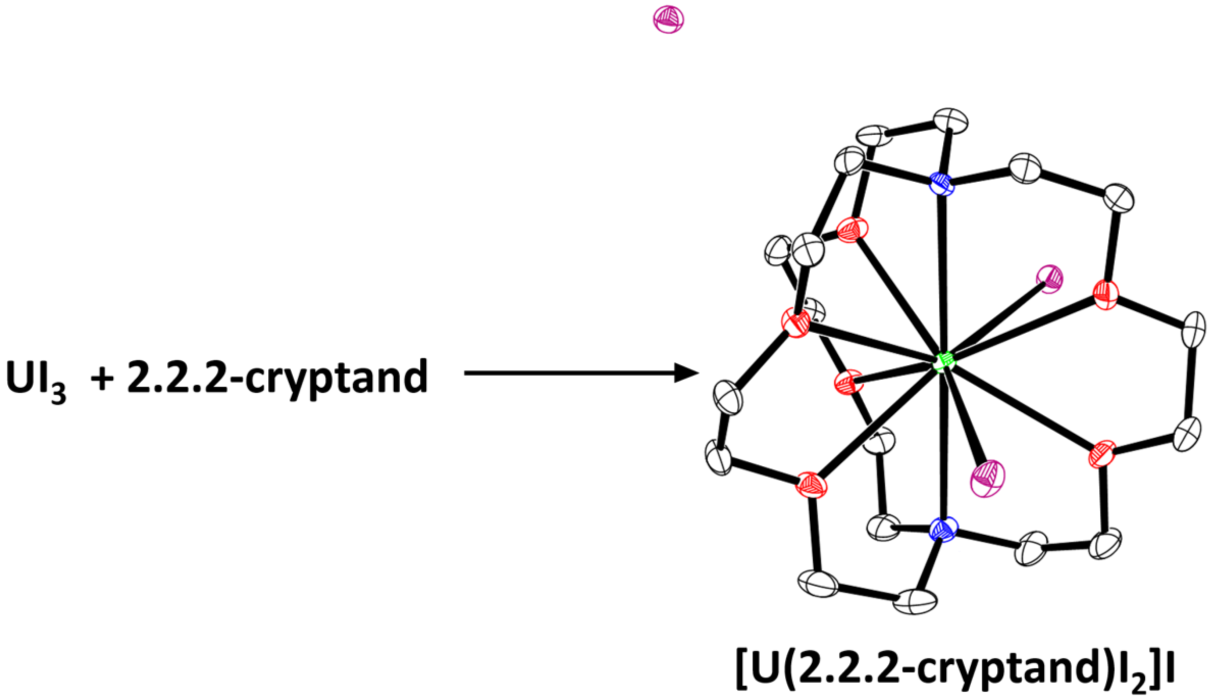

Uranium-in-cryptand complexes can be readily synthesized by reacting UI_3 with 2.2.2-cryptand.