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Solution and solid-state characterization of rare silyluranium(III) complexes†

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A uranium(III) silylate complex $[K(DME)_4][UI_2\{(Si(SiMe_3)_2SiMe_2)_2O\}]$ (1) was stabilized by the addition of 18-crown-6, forming $[K(18\text{-crown-6})][UI_2\{(Si(SiMe_3)_2SiMe_2)_2O\}]$ (1-crown). Crystallization under multiple conditions resulted in three distinct molecular structures. Compound 1-crown was further characterized in the solution state *via* ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, and electronic absorption spectroscopy.

Interactions of uranium and silicon have been elucidated in different chemical environments, both from anthropogenic and natural sources.[1] For instance, spent nuclear fuels are sometimes stored in silica based glasses, as these materials are more effective at withstanding high temperatures than plastic or concrete containers and are more durable than metals.[2] Naturally, uranium and silicon also intermix at high temperatures, and can be found together in the glasses of volcanic rocks proximal to uranium ore deposits.[3] Shales in Europe and Asia have also been discovered to be rich in uranium and silicon as well.[4] As such, understanding the basic bonding of these two elements is critical for future energy needs where extraction and separation are utilized.

These two elements, U and Si, also happen to be important in the field of organometallic chemistry, where uranium mediated hydrosilylation catalysis of unsaturated alkyls has been demonstrated.[5] Silyl based ligands have also provided a robust framework to support catalytically active uranium ions for hydroamination chemistry.[6] Mazzanti has recently used siloxide ligands for uranium, showing that these ligands can support highly reduced uranium centres capable of small molecule activation.[7,8] Molecular systems that contain both uranium and silicon such as these offer a unique opportunity to study U–Si interactions at the fundamental level, rather than the macroscale that is found in naturally occurring systems.

The field of coordination chemistry involving uranium and p-block main group elements has grown significantly since the 1970s and continues (Fig. 1).[9] Yet, uranium complexes featuring the heavy Group 14 (tetrel) elements, including Si, Ge, Sn, and Pb, are significantly less common as compared to their lighter congener, carbon,[10] and their pnictogen and chalcogen counterparts. With the abundance of organouranium coordination complexes,[11,12] silicon serves as the knowledge bridge between carbon and the heavier tetrel congeners for understanding their fundamental bonding principles with uranium.[13]

The debut of U–Si interactions in a molecular system was first reported in 1989 by Porchia and co-workers, who synthesized $Cp_3U^{IV}(SiPh_3)$ ($Cp = \eta^5\text{-}C_5H_5$) during their exploration of uranium-tetrel complexes (Chart 1).[14–16] King and Marks reported the first use of $Si(SiMe_3)_3$ for U(IV) systems as a ligand to study U–Si reactivity.[17] In 2001, Cummins and co-workers

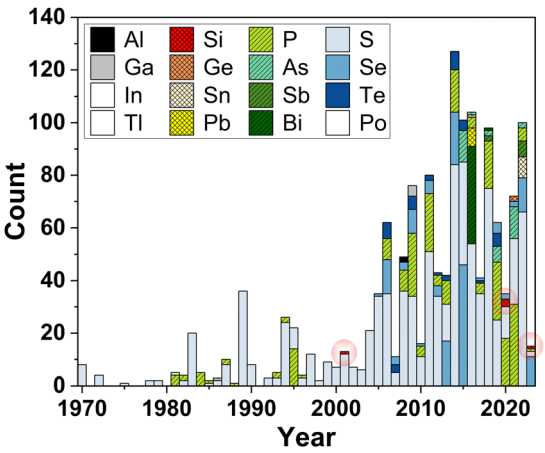

Fig. 1 Graph of number of characterized U–E bonds in the CCDC (Sept. 2023). Total count: Al = 2, Si = 5, P = 232, S = 881, Ga = 4, Ge = 2, As = 35, Se = 150, In = 0, Sn = 10, Sb = 8, Te = 36, Tl = 0, Pb = 7, Bi = 38, Po = 0. Red highlighted areas show U–Si bonds.

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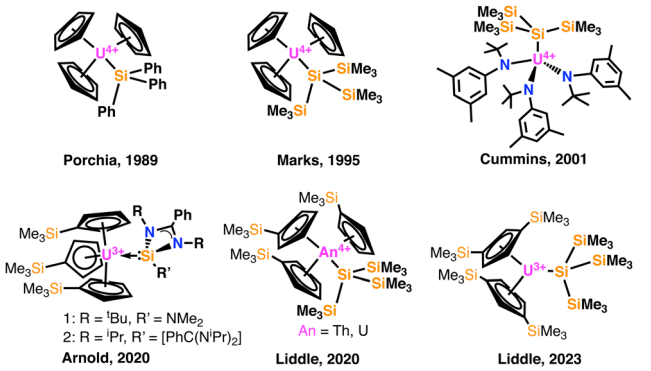
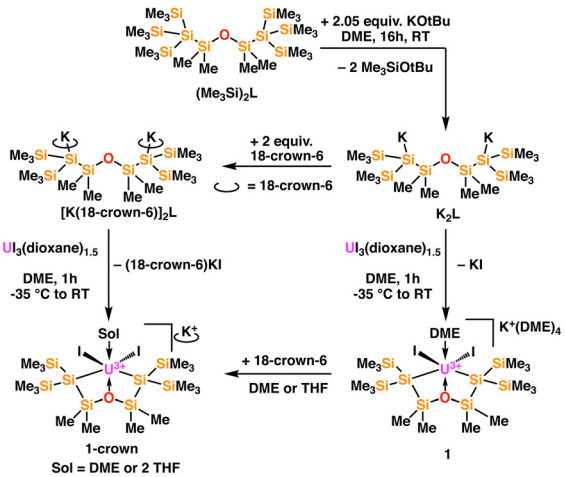


Chart 1 Previously reported examples of uranium–silicon coordination compounds.

reported the first structurally characterized molecular U–Si complex though X-ray diffraction.[17] Kaltsoyannis, Liddle, Mills, and co-workers compared U and Th analogs $Cp'_3An^{IV}(Si(SiMe_3)_3)$ ($Cp' = \eta^5$-$C_5H_4SiMe_3$, An = Th, U).[18] Arnold and co-workers reported the first uranium(III) silylene complexes.[19] More recently Chilton, Liddle, Mills, and co-workers reported Cp''_2U^{III}-$Si(SiMe_3)_3$ ($Cp'' = \eta^5$-$C_5H_3(SiMe_3)_2$) as the first U(III) silanide complex to be studied through EPR spectroscopy and SQUID magnetometry.[20]

Baumgartner, Marschner and co-workers have observed solvent activation as a major byproduct of forming rare-earth-silicon bonds, which encouraged their design of a chelating silyl ligand, $[Si(SiMe_3)_2Si(Me)_2]_2O$ (L), to stabilize low-valent rare-earth silyl complexes.[21–23] Based on the success of this ligand to support trivalent rare earth complexes, we hypothesized this ligand may also be a robust framework to isolate low-valent uranium–silicon bonds. Because of the importance of trivalent uranium in small molecule activation[24] and its presence in spent nuclear fuels,[25] this represents an area where additional understanding would have broad scientific impacts. Herein, we report a family of uranium(III)–silyl derivatives stabilized by $[Si(SiMe_3)_2Si(Me)_2]_2O$ (L). These species were isolated and fully characterized *via* ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, electronic absorption spectroscopy, and single-crystal X-ray crystallography.

Our studies commenced with generating the potassium silanide form of the ligand, $[KSi(SiMe_3)_2Si(Me)_2]_2O$ (K_2L). This was done by treating $(Me_3Si)_2L$ with two equivalents of KO^{t}Bu, followed by 2 equivalents of 18-crown-6. Following workup, a solution of $[K(18\text{-crown-6})]_2L$ was isolated and added dropwise to a 1,2-dimethoxyethane (DME) solution of $UI_3(dioxane)_{1.5}$ at −35 °C. A blue-green powder was isolated from workup and identified as $[K(18\text{-crown-6})][UI_2\{(Si(SiMe_3)_2SiMe_2)_2O\}]$ (**1-crown**). Compound **1-crown** can be synthesized in 88% yield and was pure based on combustion analysis. If 18-crown-6 is not introduced during the synthesis, $[K(DME)_4][UI_2\{(Si(SiMe_3)_2SiMe_2)_2O\}]$ (**1**) can still be made; however, the longevity of **1** is shortened to a few hours in solution and upon drying it readily decomposes into an intractable brown substance. Alternatively an equivalent of 18-crown-6 can be added to a crude sample of **1** to generate **1-crown** (Scheme 1).



Scheme 1

The ^{1}H NMR spectrum of **1-crown** in THF-d_8 shows a large resonance at 2.7 ppm that corresponds to the protons of the $[K(18\text{-crown-6})]^+$ cation. There are also two paramagnetically shifted singlets at −0.79 ($SiMe_3$) and 8.76 ppm ($SiMe_2$) that correspond to the silane arms of the ligand (Fig. S5, ESI†). ^{13}C NMR spectra were also collected, revealing a upfield shifted resonance at −13.0 ppm, likely corresponding to the $SiMe_2$ arm (Fig. S6, ESI†). The ^{29}Si NMR spectrum (collected as its polarization transfer INEPT spectrum) shows a singlet at −50.0 ppm likely corresponding to the $SiMe_3$ arm (Fig. 2). The ^{29}Si resonances of **1-crown** are shifted in comparison to the isostructural rare-earth analogs which have a ^{29}Si shift range of −4.9 to −9.0 ppm for $SiMe_3$ and 13.3 to 42.9 ppm for $SiMe_2$.[21]

The ^{29}Si signal of **1-crown** is shifted downfield as compared to previously reported silicon-containing U(III) complexes (−120 to −250 ppm) as tabulated by Windorff and Evans.[26] Furthermore, this is a common instance where ^{29}Si NMR signals could not be detected for a U–Si interaction, as many paramagnetic M–Si compounds have Si atoms that are not observable by both ^{29}Si INEPT and ^{29}Si{^{1}H} NMR spectroscopy.[18,20,21,26]

To confirm the molecular structures of the new U(III) silyl species, single crystals of **1** and **1-crown** suitable for X-ray diffraction were grown at −35 °C in three separate solvent systems (Table 1 and Fig. 3). Collection and refinement of the diffraction data reveal that the uranium ions in all three systems are 7-coordinate distorted pentagonal bipyramids and

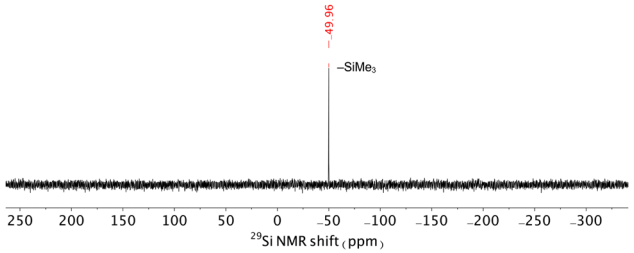


Fig. 2 ^{29}Si INEPT spectrum (THF-d_8, 79.49 MHz) of **1-crown**. δ (ppm): −50.0 ($SiMe_3$).

Table 1 Selected crystallography data for **1** and **1-crown**

	Growth conditions	Coord. solv.	Space group	U–Si (Å)	Si–U–Si (°)	U–O_{Si} (Å)	U–O_{solv} (Å)	U–I (Å)	I–U–I (°)
1	DME/pentane	DME	$P\bar{1}$	3.1281(12) 3.1457(13)	128.94(5) 129.96(5)	2.528(4) 2.587(4)	2.553(18) 2.71(2)	3.1065(4) 3.1319(3)	159.157(19) 162.177(16)
1-crown	Et_2O/pentane	DME	$P2/c$	3.1149(6) 3.1276(6)	130.014(16)	2.5613(13)	2.6149(17)	3.1125(6) 3.1256(2)	164.321(6)
1-crown	THF/pentane	THF	$C2/c$	3.1713(14) 3.1377(15)	129.59(4)	2.554(3)	2.579(3) 2.578(3)	3.0845(10) 3.1086(11)	166.017(13)

the molecular fragments are isostructural to the rare-earth silylate compounds crystallographically characterized by Baumgartner, Marschner and co-workers (Y, Ce, Pr, Sm, Tb, and Dy).[21] **1** was grown from diffusion of pentane into a DME solution of **1**, **1-crown** (DME) adduct was grown from pentane diffusion into an Et_2O solution of **1-crown**, and **1-crown** (THF adduct) was grown from pentane diffusion into a THF solution of **1-crown**.

The U–I distances range from 3.0845(10) to 3.1256(2) Å, and are in agreement with the U–I bonds in $UI_3(THF)_4$ (3.05–3.17 Å), thus corroborating a U(III) oxidation state.[27] The siloxane oxygen atom is datively interacting with the uranium ion with U–O_{Si} distances ranging from 2.528(4) to 2.587(4) Å for **1** and 2.554(3) to 2.5613(13) Å for **1-crown**. The outer-sphere potassium countercation of **1-crown** crystallized from DME and THF is sequestered by 18-crown-6 and is weakly coordinated to an iodide ligand of the uranium anion with K···I distances of 3.4608(5) and 3.3535(13) Å, respectively, which is similar to (18-crown-6)K–I (3.4131(7) Å).[28] Without 18-crown-6, as in the structure of **1**, the K^+ ion is coordinated to four DME molecules.

The potassium cation is not permanently tethered to a uranium-bound iodide ligand, as suggested by the symmetric structure observed in the ^1H and ^{13}C NMR spectra. The U(III)–Si distances range from 3.1149(6) to 3.1713(14) Å, comparable to $Cp''_2U^{III}Si(SiMe_3)_3$ (3.116(2) Å), with only a difference of approx. 0.001 to 0.06 Å (Table 2).[20] These U(III)–Si bonds are approx. 0.02 to 0.1 Å longer than the U(IV)–Si bonds found in $Cp'_3U^{IV}Si(SiMe_3)_3$ (3.0688(8) Å)[18] and $[Me_2C_6H_3(^tBu)N]_3U^{IV}Si(SiMe_3)_3$ (3.091(3) Å), due to the difference in ionic radius of U^{IV} and U^{III}, and they are significantly longer than the sum of the Pyykkö covalent radii of U–Si single bonds (2.86 Å).[29] The U–Si distances in **1** and **1-crown** in comparison to U(III) interactions with *N*-heterocyclic silylenes (formally Si(II)) (3.1637(7) to 3.1750(6) Å) differ by approx. 0.008 to 0.06 Å,[19] indicating that U–Si distances are more affected by the ionic radius of uranium rather than that of silicon.

Table 2 Crystallographically reported U–Si interactions; Ar = 3,5-$Me_2C_6H_3$, R = ^{t}Bu or ^{i}Pr, R′ = NMe_2 or $[PhC(N^iPr)_2]$. OS = oxidation state

Compound	U–Si (Å)	OS of U	OS of Si
1-crown	3.1149(6)–3.1713(14)	3+	4+
$Cp''_2U[Si(SiMe_3)_3]$[20]	3.116(2)	3+	4+
$Cp'_3U[Si(SiMe_3)_3]$[18]	3.0688(8)	4+	4+
$[Ar(^tBu)N]_3U[Si(SiMe_3)_3]$[17]	3.091(3)	4+	4+
$Cp'_3U\{Si[PhC(NR)_2]R'\}$[19]	3.1637(7)–3.1750(6)	3+	2+

The electronic absorption spectrum of **1-crown** collected from 300 to 1600 nm in THF shows a broad ligand-based absorbance at 390 (ε = 2930 M^{-1} cm^{-1}). The color-producing band, which is responsible for the blue-green hue of **1-crown**, is likely at 582 nm, which absorbs in the red-orange region. The absorbances at 580 (ε = 1250 M^{-1} cm^{-1}) and 750 (ε = 820 M^{-1} cm^{-1}) are assigned as the 5f to 6d transitions commonly reported for U(III).[30] The NIR portion of the spectrum is consistent with the oxidation state assignment as U(III); the broad near-infrared bands at 910 (ε = 120 M^{-1} cm^{-1}), 1040 (ε = 60 M^{-1} cm^{-1}), 1090 (ε = 60 M^{-1} cm^{-1}), and 1200 nm (ε = 100 M^{-1} cm^{-1}) correspond to f–f transitions of

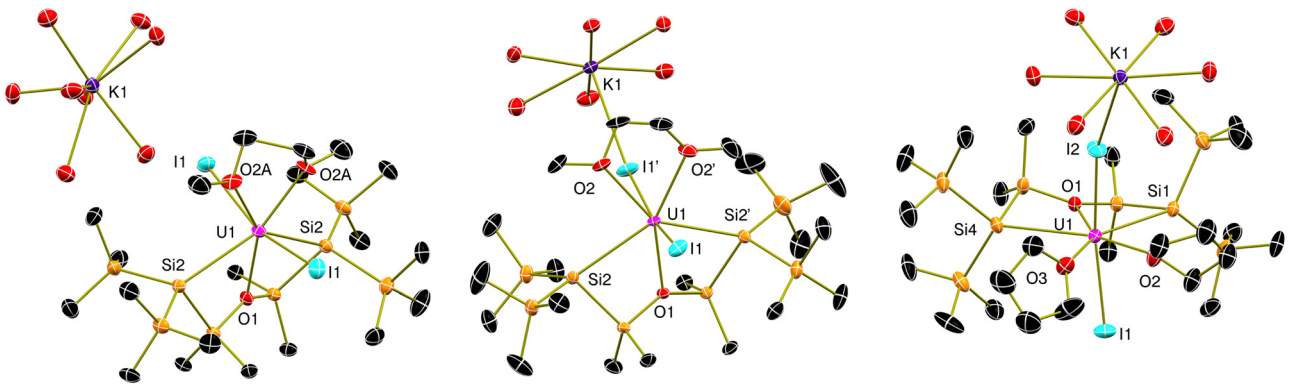


Fig. 3 Molecular structures of compound **1** grown from DME (left), compound **1-crown** grown from diethyl ether (center), and **1-crown** grown from THF (right) displayed with 30% probability ellipsoids. Hydrogen atoms, carbons from the potassium-bound DME and 18-crown-6, disordered moieties and outer-sphere solvent molecules are omitted for clarity. Colors for atoms are magenta (U), light blue (I), purple (K), orange (Si), red (O), and black (C).

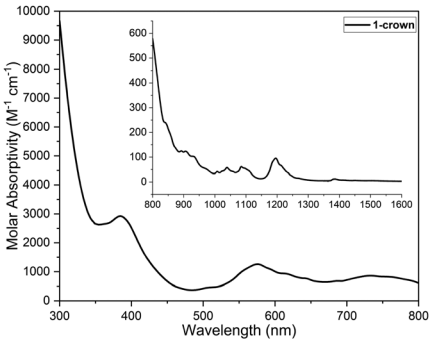


Fig. 4 Solution state electronic absorption spectra (THF, ambient temperature) of **1-crown**.

the three uranium based electrons and are in agreement with known U(III) compounds (Fig. 4).[31]

The synthesis of the uranium(III) silyl species reported here is significant as previous derivatives have only featured a very bulky monodentate silyl ligand. Compounds **1** and **1-crown** are rare in that two concurrent silyl bonds are formed *trans* to each other, and there is a relatively unhindered uranium ion that is capable of further chemistry. In these cases, the chelate effect from the bidentate ligand serves to stabilize these unusual silyl species.

In summary, new uranium(III) coordination compounds featuring uranium–silicon bonds have been isolated and fully characterized. The salt metathesis reaction between UI_3(dioxane)$_{1.5}$ and [K(18-crown-6)]$_2$L resulted in the formation of the silyluranium species, **1-crown**. Electronic absorption spectroscopy confirms the presence of a U(III), f^3 ion due to the strong f–f transitions noted in the near-infrared region of the spectrum. ^{1}H and ^{13}C NMR spectroscopy reveals that **1-crown** is C_{2v} symmetric in THF-d_8. Although rare in the presence of a paramagnetic ion, a ^{29}Si NMR spectroscopic signal was detectable for **1-crown**. The uncrowned species, **1**, where K^+ is sequestered by DME solvent molecules, is less stable than **1-crown**, but both were able to be characterized by X-ray crystallography. The geometries around the uranium ions are analogous to those of the previously reported rare-earth silyl species, but the actinide examples crystallize in different unit cells depending on both the coordinated solvent and crystallization conditions. When compared to known U–Si bond lengths, the U–Si distance of **1-crown** indicates that the ionic radius of uranium (*vs.* silicon) has a greater effect on the U–Si distance, as a comparison of ionic U–Si *vs.* silylene dative interactions. Compounds **1** and **1-crown** represent the only examples where more than one bond to silicon is present on the same uranium center, and where a bidentate ligand encapsulates a uranium(III) ion. Future work will focus on the reactivity of the low-valent uranium ion towards small molecules, and to determine what role the silyl groups, if any, play in this activation.

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Conflicts of interest

There are no conflicts to declare.

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