

Supporting Information for

**Solution and Solid-State Characterization of a Rare
Silyluranium(III) Complex**

Nathan J. Lin, Matthias Zeller, Suzanne C. Bart*^[a]

[a] N.J. Lin, Dr. M. Zeller, Prof. Dr. S.C. Bart
H. C. Brown Laboratory, Department of Chemistry
Purdue University
West Lafayette, Indiana 47907
E-mail: sbart@purdue.edu

Table of Contents

General Considerations	4
Synthesis of [(DME) ₄ •K][(DME)•U(I) ₂ {Si(SiMe ₃) ₂ SiMe ₂ } ₂ O] (Compound 1).....	5
Synthesis of [(18-crown-6)K][(Solv)•U(I) ₂ {Si(SiMe ₃) ₂ SiMe ₂ } ₂ O] (1-crown) (Solv = THF or DME).....	5
Evans' Method Calculation for 1-crown	13
Infrared Spectra	14
Crystallographic Details	15
Crystallographic References	16
Special Refinement Details	17
Tables of Geometric Parameters	19
SolidG of Complex 1	21
References	25

Table of Figures

Figure S1. ¹ H NMR Spectrum (400 MHz, 26 °C, C ₆ D ₆) of (KSi[SiMe ₃] ₂ SiMe ₂) ₂ O (K ₂ L).....	7
Figure S2. ¹³ C NMR Spectrum (100 MHz, 26 °C, C ₆ D ₆) of (KSi[SiMe ₃] ₂ SiMe ₂) ₂ O (K ₂ L).	7
Figure S3. ²⁹ Si INEPT NMR Spectrum (79.49 MHz, 26 °C, C ₆ D ₆) of (KSi[SiMe ₃] ₂ SiMe ₂) ₂ O (K ₂ L).	8
Figure S4. ¹ H NMR Spectrum (400 MHz, 25 °C, THF-d ₈) of 1-crown	8
Figure S5. ¹ H NMR Spectrum (zoomed-in) (400 MHz, 25 °C, THF-d ₈) of 1-crown	9
Figure S6. ¹³ C NMR spectrum (and zoom) (100.62 MHz, 25 °C, THF-d ₈) of 1-crown	9
Figure S7. ²⁹ Si INEPT NMR Spectrum (79.49 MHz, 25 °C, THF-d ₈) of 1-crown . (External Standard = Si(SiMe ₃) ₄ = -9.8 ppm)	10
Figure S8. ²⁹ Si{ ¹ H}NMR Spectrum (79.49 MHz, 25 °C, THF-d ₈) of 1-crown . (External Standard = Si(SiMe ₃) ₄ = -9.8 ppm)	10
Figure S9. Comparison of ²⁹ Si{ ¹ H}NMR Spectra (79.49 MHz, 25 °C, THF-d ₈) of a purified sample of 1-crown (top) and a sample of 0.164 g of 1-crown doped with 0.014 g of Si(SiMe ₃) ₄ (a common byproduct) (bottom). (Internal Standard = Si(SiMe ₃) ₄ = -9.8 ppm).....	11
Figure S10. ¹ H NMR Spectrum (400 MHz, 26 °C, C ₆ D ₆) of 1-crown	11
Figure S11. ¹ H NMR Spectrum (zoomed-in) (400 MHz, 26 °C, C ₆ D ₆) of 1-crown	12
Figure S12. ¹ H NMR spectrum (Pyridine-d ₅ , 499.83 MHz, 25 °C) of 1-crown and a capillary of pyridine-d ₅	12
Figure S13. FTIR spectrum (KBr Salt Plate, THF solution) of 1-crown	14
Figure S14. 1-crown (DME adduct) 18-crown-6(K ⁺) and solvent molecules removed from the .xyz file. ^[5]	21

Table of Tables

Table S1. Crystallographic data for compound 1 and 1-crown	15
Table S2. Selected geometric parameters of compound 1 (Å, °).....	19
Table S3. Selected geometric parameters of compound 1-crown (DME adduct) (Å, °).	19
Table S4. Selected geometric parameters of compound 1-crown (THF adduct) (Å, °).....	20

General Considerations

All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or using an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well used for freezing samples with liquid nitrogen, dry ice and acetone baths, as well as two $-35\text{ }^{\circ}\text{C}$ freezers for cooling samples and crystallizing compounds. Solvents for sensitive manipulations including THF, toluene, and pentane were dried and deoxygenated using literature procedures with a Seca solvent purification system.^[1] 1,2-dimethoxyethane (DME) was purified by stirring over CaH_2 for at least two days before distillation and stored over molecular sieves and sodium. THF- d_8 was purchased from Cambridge Isotope Laboratories (CIL) and stored over sodium in the glovebox freezer. Pyridine- d_5 was purchased from CIL, stirred over CaH_2 , distilled, and stored over sieves. Benzene- d_6 (C_6D_6) was purchased from CIL, dried with molecular sieves and sodium, and degassed with three freeze-pump-thaw cycles. $(\text{Me}_3\text{Si})_4\text{Si}$ was purchased from TCI, and KOtBu , and 18-crown-6 was purchased from Sigma-Aldrich and used without further purification. $\text{UI}_3(\text{dioxane})_{1.5}$ ^[2] and $[\text{Si}(\text{SiMe}_3)_3\text{Si}(\text{Me})_2]_2\text{O}(\text{L})$ ^[3] were synthesized according to literature procedures.

Caution! U-238 is a weak α -emitter with a half-life of $t_{1/2} = 4 \times 10^9$ years. All manipulations were performed in an inert-atmosphere glovebox in a laboratory equipped with proper detection equipment.

^1H NMR spectra were recorded on a Bruker AV400 spectrometer operating at a frequency of 400 MHz. ^1H NMR chemical shifts are reported relative to ^1H residual chemical shifts of benzene- d_6 (C_6D_6 , 7.16 ppm), THF- d_8 (1.72 ppm), or pyridine- d_5 (8.74 ppm). ^1H spectra were collected with 0.5 s acquisition time, 0 s delay time, a sweep width of 50 to 400 ppm, and for 128 scans. For paramagnetic molecules, the ^1H NMR data are reported with the chemical shift, followed by the peak-width-at-half-height in Hertz, the integration value, multiplicity, and, where possible, the peak assignment. Multiplicities are assigned as singlet (s), doublet (d), triplet (t), or multiplet (m), and some moieties are abbreviated as trimethylsilyl (Me_3Si or SiMe_3). ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer operating at a frequency of 100.62 MHz and referenced to the internal solvent signal. ^{13}C NMR spectra were collected with 0.08 s acquisition time, 0.1 s delay time, 400 ppm sweep width, and at least 1024 scans. ^{29}Si NMR spectra were recorded on a Bruker AV400 spectrometer operating at a frequency of 79.49 MHz and sometimes with the ^{29}Si INEPT pulse sequence.^[4] ^{29}Si NMR spectra are referenced to an external or internal standard ($(\text{Me}_3\text{Si})_4\text{Si}$, -9.8 ppm and/or -135.5 ppm). ^{29}Si NMR spectra were collected using 0.5 s acquisition time and 1 s delay time. Data were collected for at least 30 minutes or until sufficient s/n (8:1) was achieved using a highly concentrated sample ($> 300\text{ mg}$ **1-crown** in $\sim 0.5\text{ mL}$, $\sim 0.43\text{ M}$). The 600 ppm scan window was moved between -1000 to +1000 ppm to search for other ^{29}Si signals. Solid state infrared spectra were recorded using a Thermo Nicolet 6700 spectrophotometer; samples were made by dropping and drying a concentrated THF solution of **1-crown** on a KBr salt plate and data notated as weak (w), medium (m), and strong (s). Electronic absorption spectroscopic measurements were recorded at 294 K in sealed 1 cm quartz cuvettes with a JASCO V-770 UV/vis-NIR spectrophotometer. CHN Elemental analysis was performed at Midwest Microlabs (Indianapolis, IN).

Single crystals suitable for X-ray diffraction of **1**, **1-crown (THF adduct)**, and **1-crown (DME adduct)**, were coated with poly(isobutylene) oil in the glovebox and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon II area

detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 K.

Synthetic Procedures

Synthesis of [(DME)₄•K][(DME)•U(I)₂{Si(SiMe₃)₂SiMe₂}₂O] (Compound **1**)

A 20-mL scintillation vial was charged with a stirbar, [Si(SiMe₃)₃Si(Me)₂]₂O (“TMS₂L”, 0.042 g, 0.067 mmol), KOtBu (2.05 equiv., 0.016 g, 0.134 mmol), and DME (4 mL). The mixture was allowed to stir at ambient temperature, turning from a colorless suspension to a yellow mixture overnight, forming “K₂L”. The vial was placed under vacuum to remove volatiles including Me₃SiO^tBu and DME. The yellow oil was redissolved in DME (2 mL) and placed in the freezer at –35 °C. A separate, clean 20-mL scintillation vial was charged with a stirbar, UI₃•(dioxane)_{1.5} (1 equiv., 0.050 g, 0.067 mmol), and DME (10 mL) which was cooled in the freezer at –35 °C. After sufficient cooling, the yellow “K₂L” solution was added dropwise to the dark purple suspension of UI₃ over the course of 2 min. The mixture was allowed to stir at ambient temperature for 30 min turning an intense, dark blue color. The solution was filtered through a bed of Celite and the filter cake was washed with THF (3 x 5 mL) into a filter flask, leaving a white precipitate in the frit. The volume was carefully reduced *in vacuo* to approximately 1 mL. Crystals suitable for X-ray diffraction were grown from slow vapor diffusion of pentane into the concentrated DME solution of **1**. Crystals of compound **1** will decompose upon drying therefore the yield of the reaction could not be obtained.

Synthesis of [(18-crown-6)K][(Solv)•U(I)₂{Si(SiMe₃)₂SiMe₂}₂O] (**1-crown**) (Solv = THF or DME)

A 20-mL scintillation vial was charged with a stirbar, [Si(SiMe₃)₃Si(Me)₂]₂O (“TMS₂L”, 0.453 g, 0.723 mmol), KOtBu (2.05 equiv., 0.181 g, 1.482 mmol), and DME (10 mL). The mixture was allowed to stir at ambient temperature, turning from a colorless suspension to a yellow mixture overnight, forming “K₂L”. The vial was placed under vacuum to remove volatiles including Me₃SiO^tBu and DME. The yellow oil was redissolved in DME (4 mL) and placed in the freezer at –35 °C. A separate, clean 20-mL scintillation vial was charged with a stirbar, UI₃•(dioxane)_{1.5} (1 equiv., 0.542 g, 0.723 mmol), and DME (15 mL) which was cooled in the freezer at –35 °C. After sufficient cooling, the yellow “K₂L” solution was added dropwise to the dark purple suspension of UI₃ over the course of 2 min. The mixture was allowed to stir at ambient temperature for 45 min turning an intense, dark blue color. The solution was filtered through a bed of Celite and the filter cake was washed with THF (3 x 10 mL) into a filter flask, leaving a white precipitate in the frit. To the blue solution in the flask was added a stirbar and 18-crown-6 (1 equiv., 0.191 g, 0.723 mmol) which was then allowed to stir at ambient temperature for 1 hr. Volatiles were removed *in vacuo*, triturated with pentane (3 x 5 mL) and dried again, and the solids were transferred to a clean frit. The solids were washed with pentane (5 x 5 mL), Et₂O (1 x 5 mL), toluene (1 x 2 mL), and pentane again (1 x 5 mL), leaving a blue filter cake which was characterized as **1-crown** (0.869 g, 88 % yield) which when stored in the freezer as a solid turns dark aquamarine. Crystals suitable for X-ray diffraction were grown from slow vapor diffusion of pentane into a concentrated Et₂O solution of **1-crown** affording **1-crown (DME adduct)** or grown from slow vapor diffusion of pentane into a concentrated THF solution of **1-crown** affording **1-crown (THF adduct)**.

Alternatively, 2 equiv. of 18-crown-6 can be added to K₂L (thereby forming [K(18-crown-6)]₂L) stirring for 2 hours before metalation with UI₃(dioxane)_{1.5}, though purity of the final sample

does result in more 18-crown-6 than necessary for sequestration. It is recommended to add 1 equiv. 18-crown-6 after metalation to avoid excess contamination of unused 18-crown-6.

1-crown is insoluble in pentane and hexane, is slightly soluble in diethyl ether, toluene, and benzene, soluble in THF, DME, and pyridine, and is unstable in MeCN and DCM.

^1H NMR (THF- d_8 , 25 °C, 400 MHz) δ (ppm): -0.79 (5.09, 36H, s, SiMe₃), 2.67 (2.54, s, 24H, 18-crown-6), 3.24 (2.90, 4H, s, DME), 8.76 (9.42, 8H, s, SiMe₂). ^{13}C NMR (THF- d_8 , 25°C, 100.06 MHz) δ (ppm): -13.01 (s, SiMe₂), 28.16 (s, SiMe₃), 70.13 (s, 18-crown-6). ^{29}Si INEPT NMR (THF- d_8 , 25 °C, 79.49 MHz) δ (ppm): -49.96 (SiMe₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8 , 25 °C, 79.49 MHz) δ (ppm): -49.96 (SiMe₃). ^1H NMR (C₆D₆, 26 °C, 400 MHz) δ (ppm): -6.41 (11.30, 36H, s, SiMe₃), 3.19 (4.36, s, 361H, 18-crown-6/DME), 3.35 (3.63, 4H, s, DME), 19.98 (16.27, 8H, s, SiMe₂). ^1H NMR (Pyridine- d_5 , 26 °C, 400 MHz) δ (ppm): -0.10 (6.04, s, SiMe₃), 3.38 (2.44, s, 18-crown-6), 9.08 (41.37, s, SiMe₂). FTIR (THF, KBr Salt plate) 527 (w), 621 (m), 673 (m), 774 (m), 832 (s), 911 (w), 960 (m), 1029 (m), 1106 (s), 1244 (m), 1283(w), 1350 (m), 1452 (w), 2885 (m), 2944 (m). Elemental analysis: Anal. Calcd. for C₂₈H₇₂USi₈O₇KI₂: C: 26.35 %, H: 5.69 %, N: 0.00 %; Found: C: 25.85 %, H: 4.87 %, N: 0.00 %.

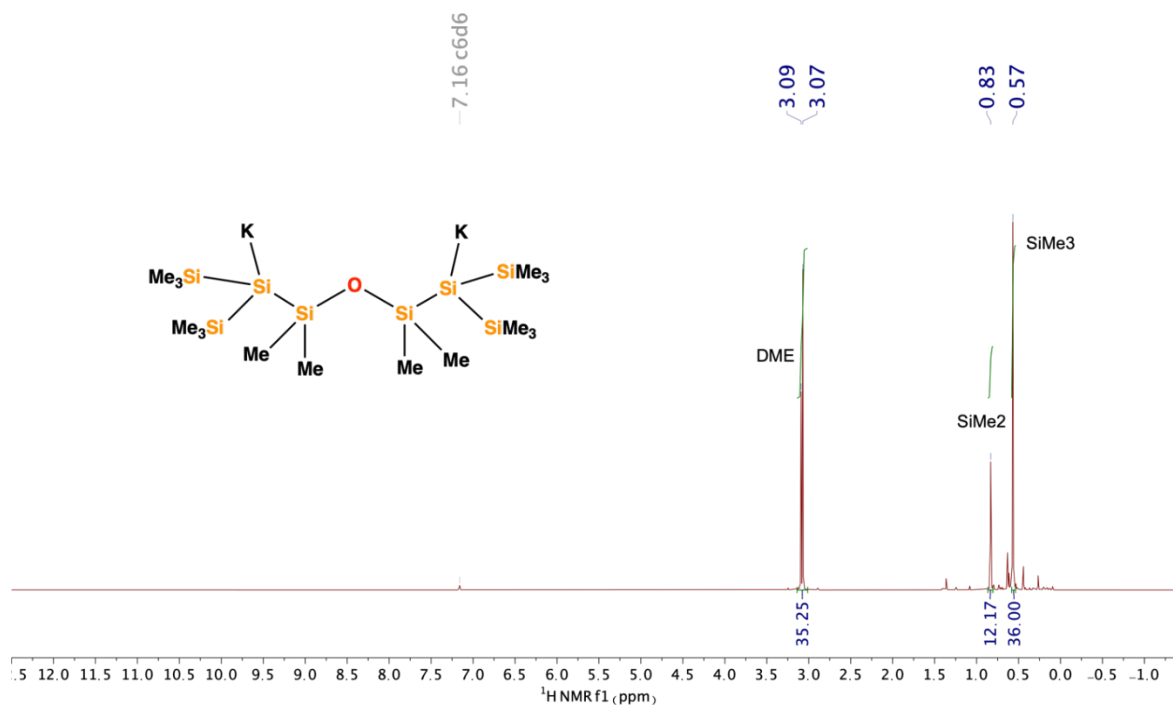


Figure S1. ¹H NMR Spectrum (400 MHz, 26 °C, C₆D₆) of (KSi[SiMe₃]₂SiMe₂)₂O (K₂L).

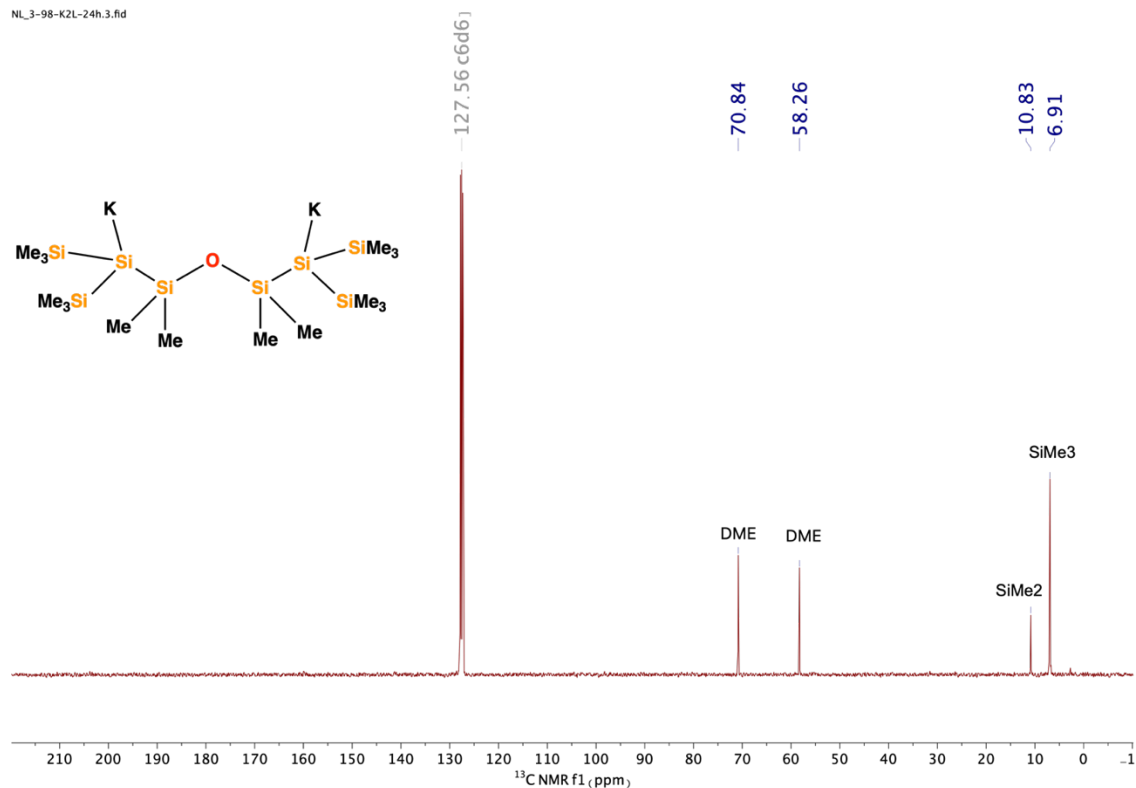


Figure S2. ¹³C NMR Spectrum (100 MHz, 26 °C, C₆D₆) of (KSi[SiMe₃]₂SiMe₂)₂O (K₂L).

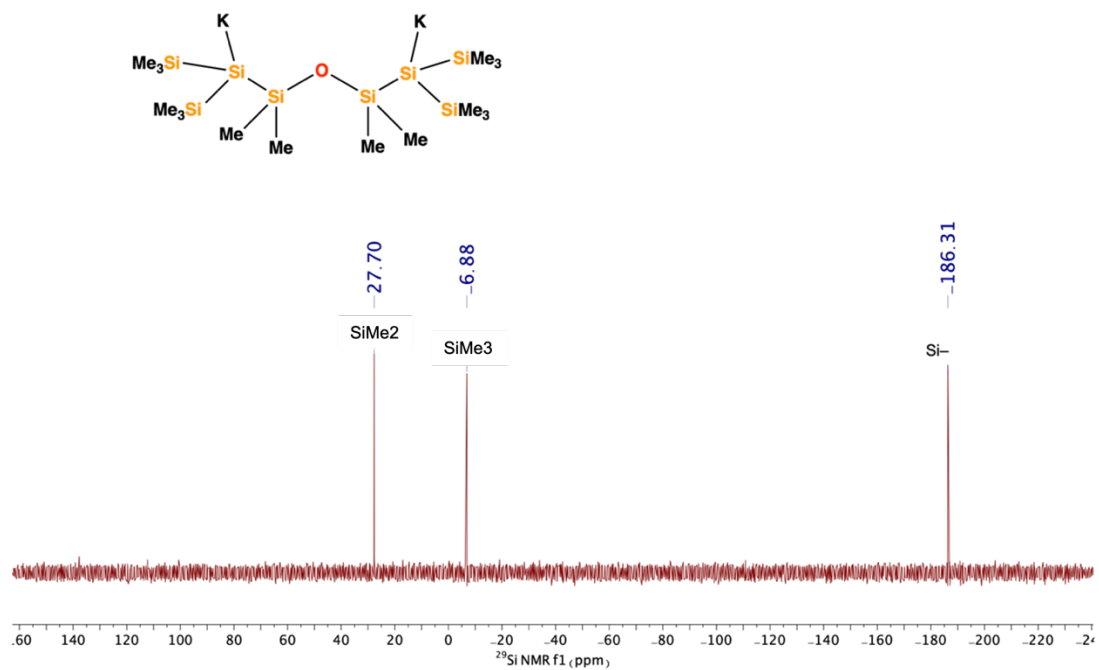


Figure S3. ^{29}Si INEPT NMR Spectrum (79.49 MHz, 26 °C, C_6D_6) of $(\text{KSi}[\text{SiMe}_3]_2\text{SiMe}_2)_2\text{O}$ (K_2L).

1-crown-300mgconc.1.fid
H1 standard parameters, BBO SmartProbe.

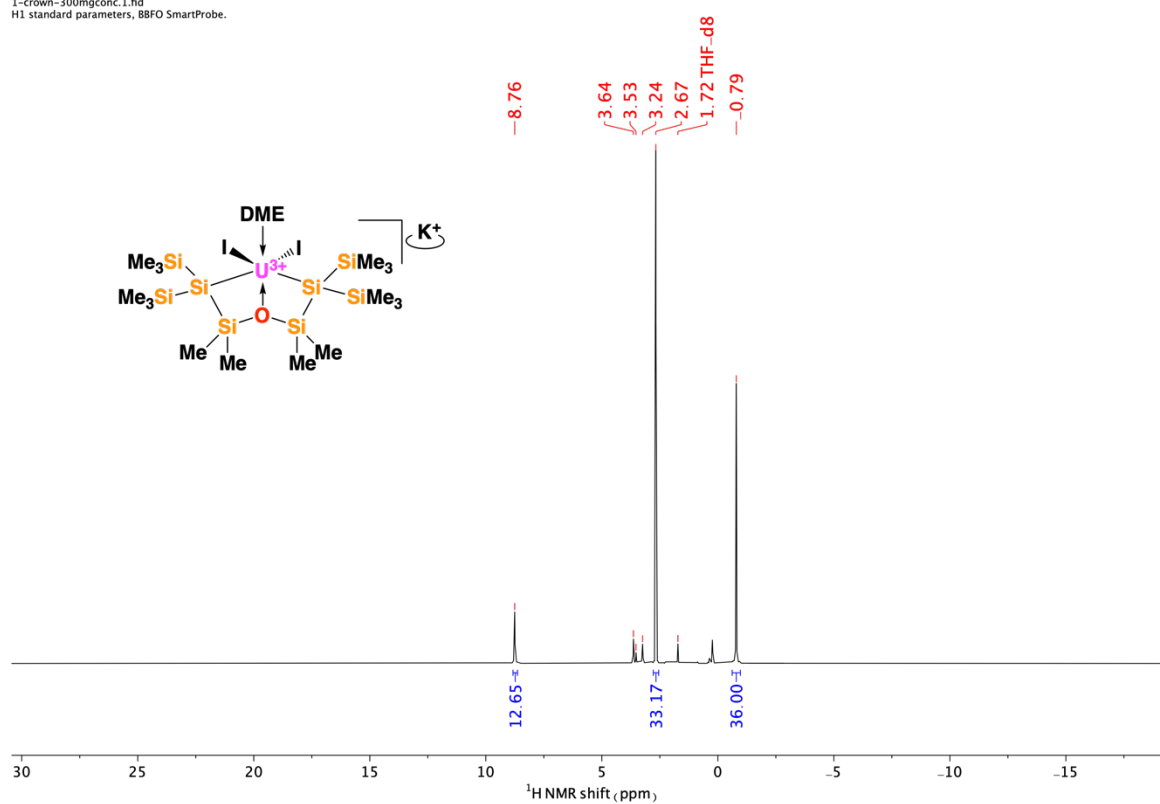


Figure S4. ^1H NMR Spectrum (400 MHz, 25 °C, $\text{THF-}d_8$) of **1-crown**.

1-crown-300mgconc.1.fid
H1 standard parameters, BBFO SmartProbe.

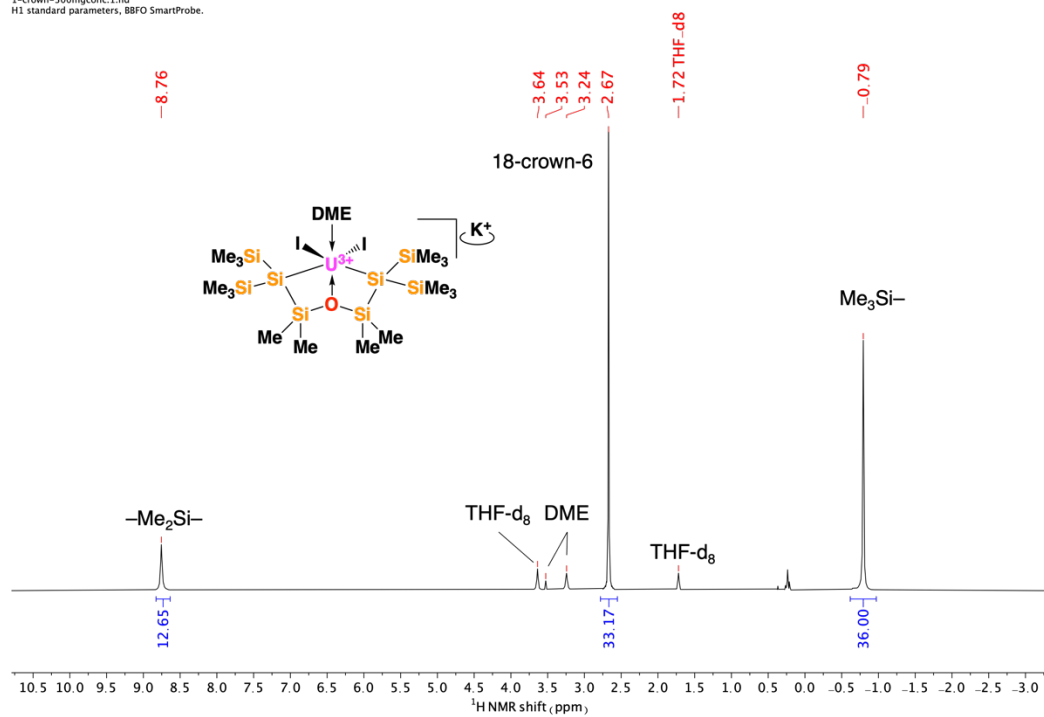


Figure S5. ¹H NMR Spectrum (zoomed-in) (400 MHz, 25 °C, THF-d₈) of **1-crown**.

1-crown-300mgconc.8.fid
C13 standard parameters, BBFO SmartProbe.

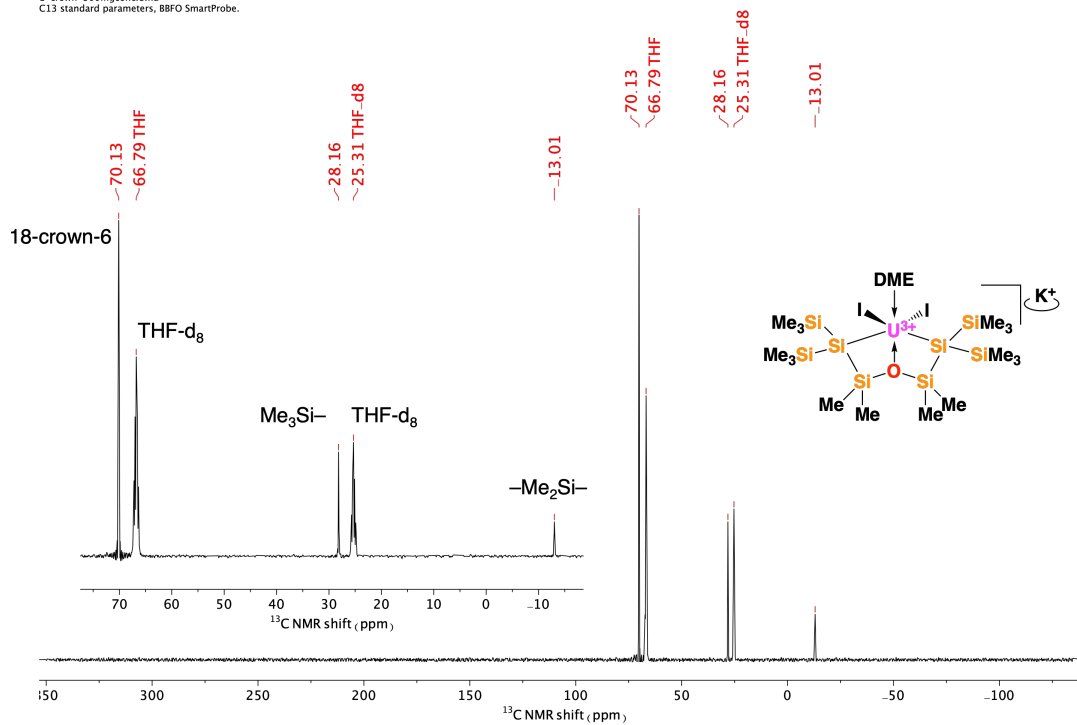


Figure S6. ¹³C NMR spectrum (and zoom) (100.62 MHz, 25 °C, THF-d₈) of **1-crown**.

1-crown-300mgconc.2.fid
S129 INEPTD standard parameters with 1H decoupling, J(Si-H) = 7 Hz., BBFO SmartProbe.
at=0.5
d1=1
INEPT

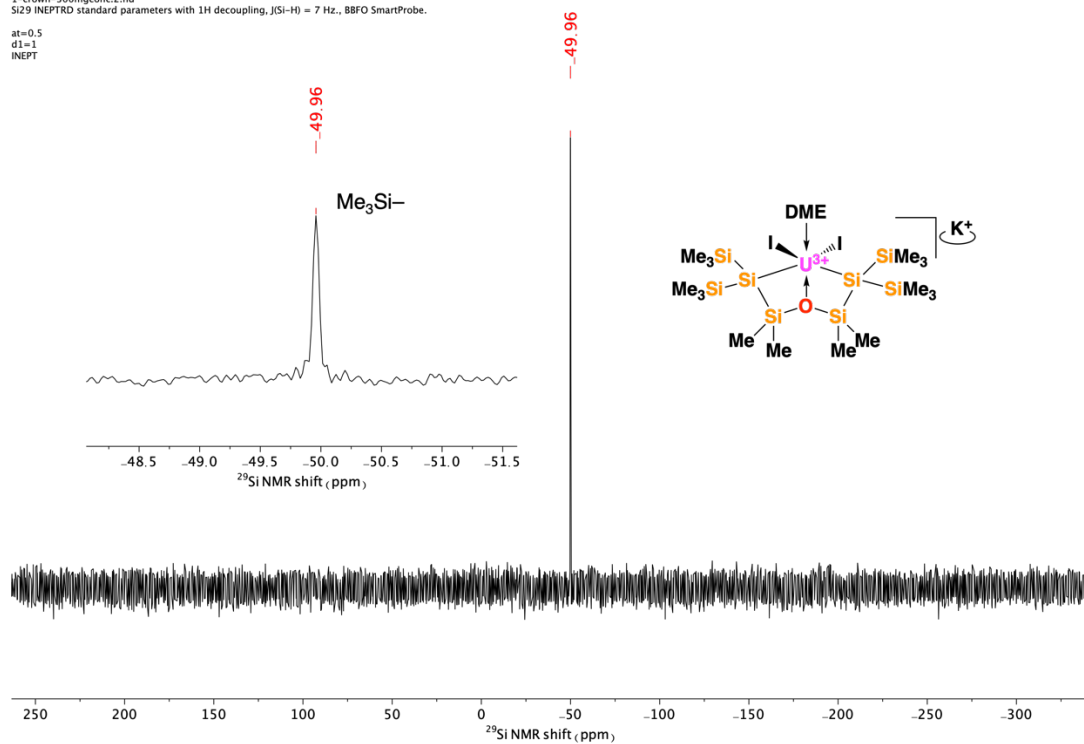


Figure S7. ^{29}Si INEPT NMR Spectrum (79.49 MHz, 25 °C, $\text{THF-}d_8$) of **1-crown**. (External Standard = $\text{Si}(\text{SiMe}_3)_4$ = -9.8 ppm)

1-crown-300mgconc.3.fid
S129 standard parameters with inverse-gated 1H decoupling, BBFO SmartProbe.

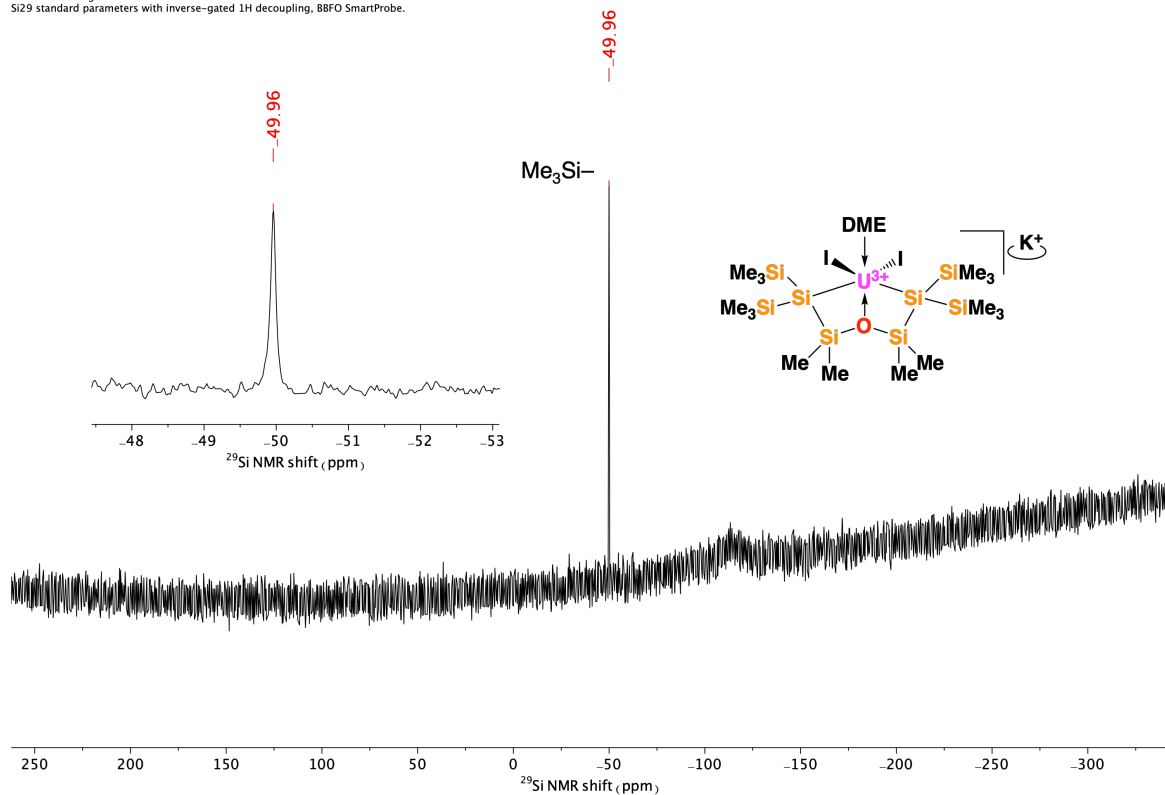


Figure S8. $^{29}\text{Si}\{^1\text{H}\}$ NMR Spectrum (79.49 MHz, 25 °C, $\text{THF-}d_8$) of **1-crown**. (External Standard = $\text{Si}(\text{SiMe}_3)_4$ = -9.8 ppm)

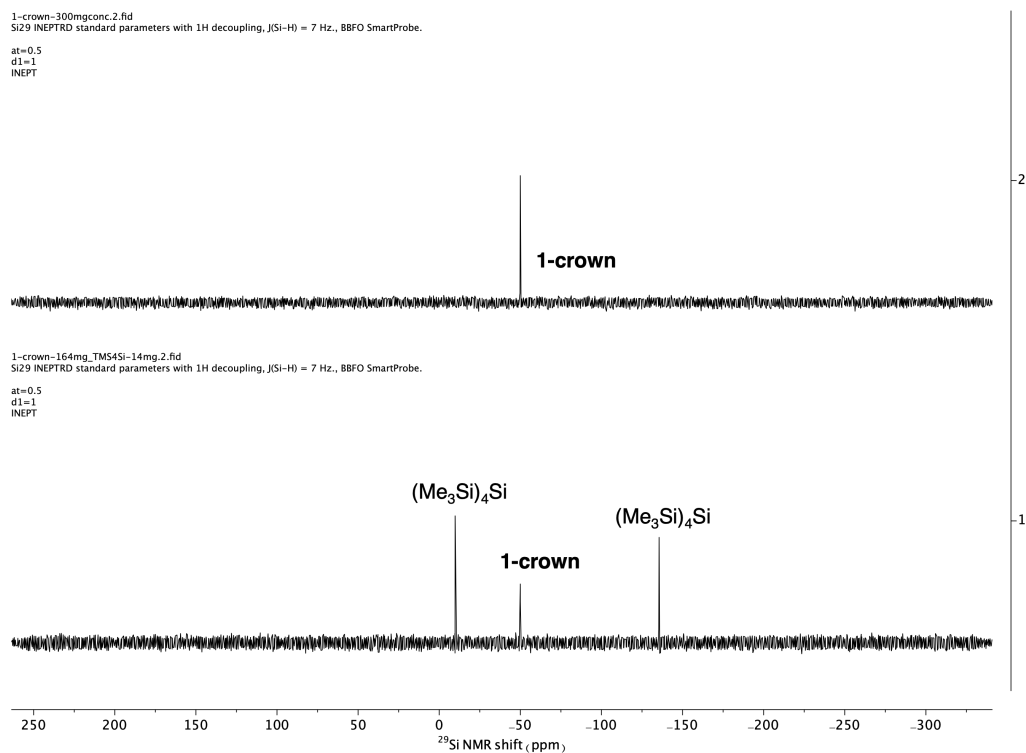


Figure S9. Comparison of ²⁹Si{¹H}NMR Spectra (79.49 MHz, 25 °C, THF-*d*₈) of a purified sample of **1-crown** (top) and a sample of 0.164 g of **1-crown** doped with 0.014 g of Si(SiMe₃)₄ (a common byproduct) (bottom). (Internal Standard = Si(SiMe₃)₄ = -9.8 ppm).

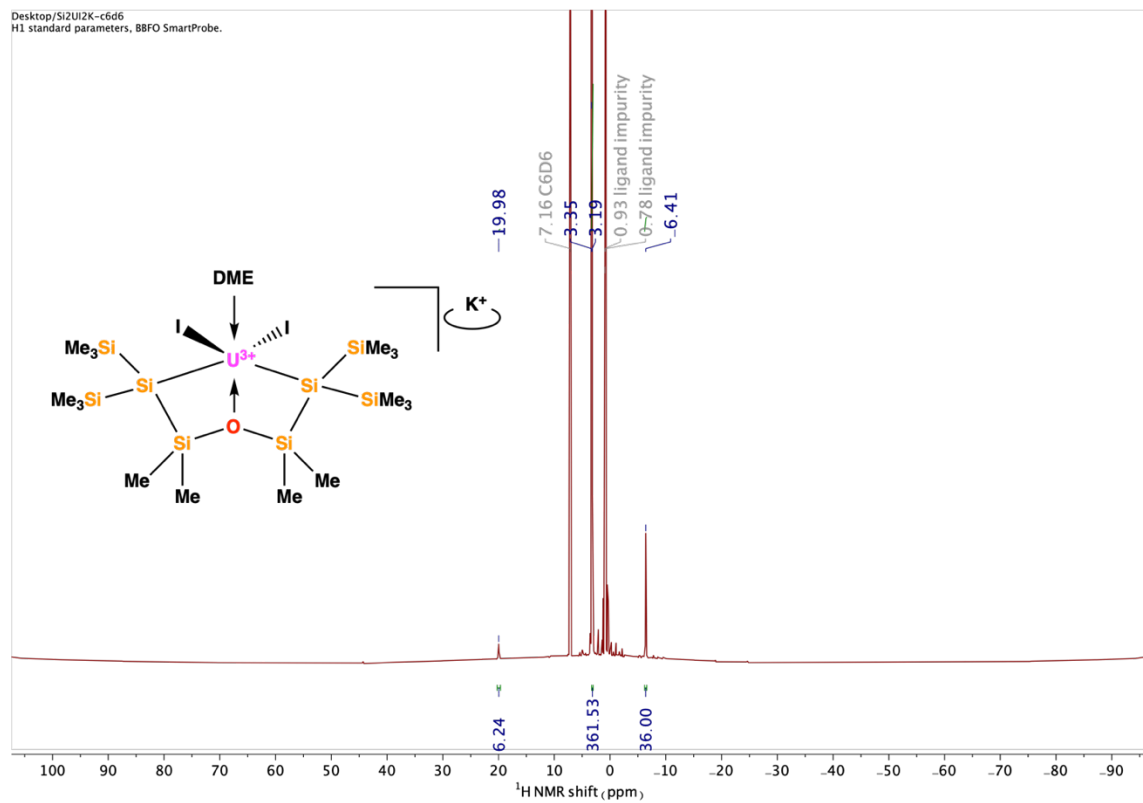
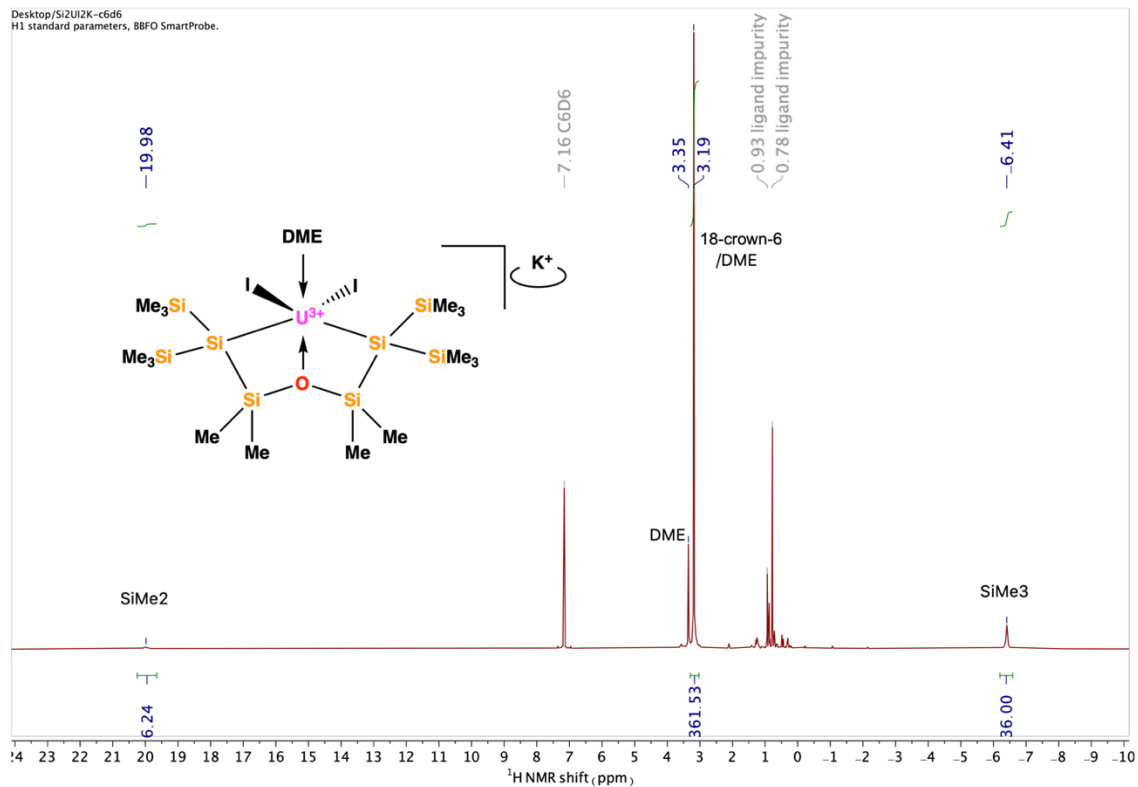
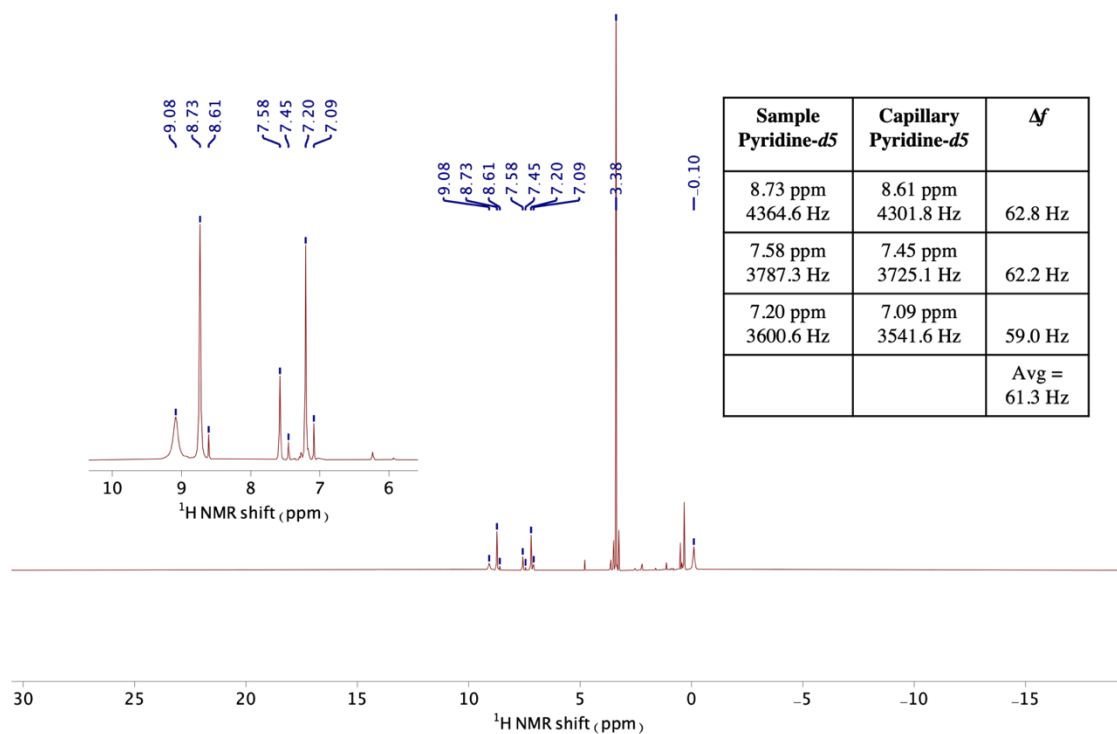


Figure S10. ¹H NMR Spectrum (400 MHz, 26 °C, C₆D₆) of **1-crown**.



Si2UI2K-pyridined5-Evansmethod.1.fid
H1 standard parameters, cryoprobe prodigy.



Evans' Method Calculation for 1-crown

Mass of sample (m) = 0.007 g

Molecular weight of **1-crown** = 1366.62 g/mol

Mass of solvent (pyridine- d_5) = 0.615 g density = 1.05 g/mL

Volume of solvent = 0.586 mL

Sample Concentration (c) = 0.008741 M

Magnet Strength (f) = 499.83 MHz

Average Δf = 61.3 Hz

$$\chi_{molar} = \left| \frac{-3 \cdot \Delta f}{4\pi \cdot f \cdot c} \right| = \left| \frac{-3 \cdot [61.3 \text{ Hz}]}{4\pi \cdot [499.83 \text{ MHz}] \cdot [0.008741 \text{ M}]} \right| = 3.3496 \mu_B$$

Infrared Spectra

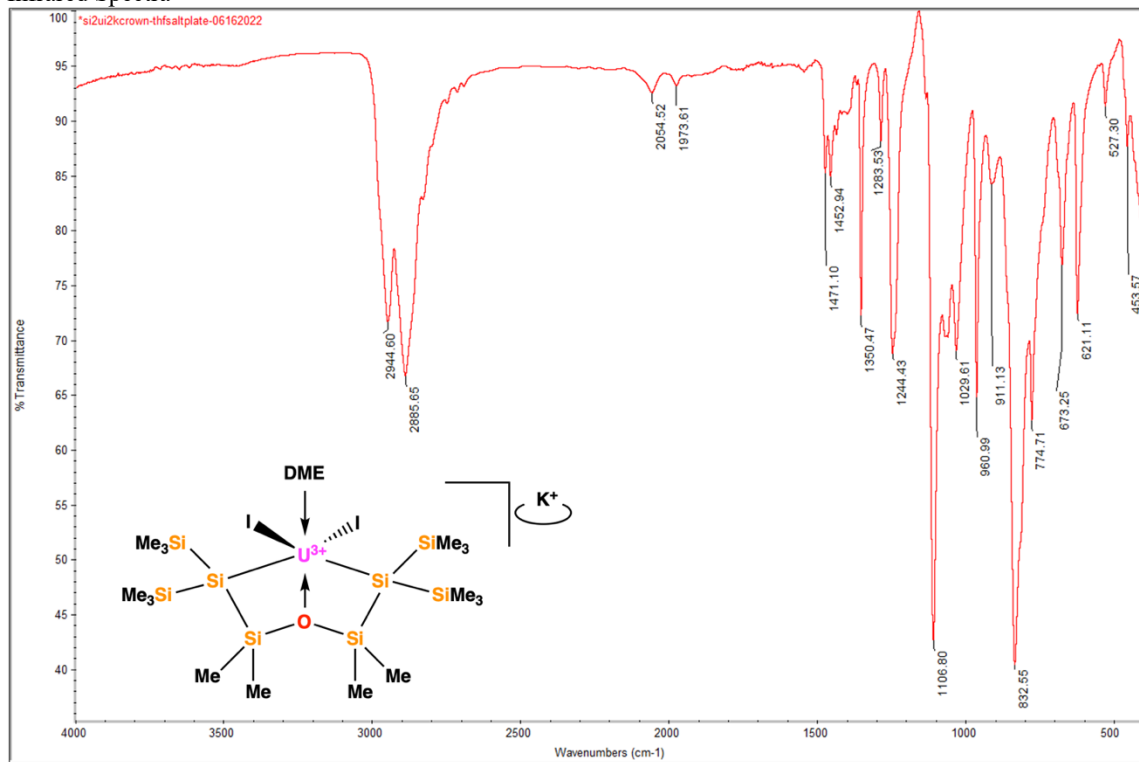


Figure S13. FTIR spectrum (KBr Salt Plate, THF solution) of **1-crown**.

Crystallographic Details

Table S1. Crystallographic data for compound **1** and **1-crown**.

Entry	1	2	3
Internal Name	NL_3_122_crown_0m	NL_3_99_UI3_t2_0m_a	NLguest3_0m_a
Crystal data	1-crown (18-crown-6, DME adduct)	1 (no 18-crown-6, DME adduct)	1-crown (18-crown-6, THF adduct)
Chemical formula	C ₃₂ H ₈₂ I ₂ KO ₉ Si ₈ U·C ₄ H ₁₀ O	C ₂₀ H ₅₈ I ₂ O ₃ Si ₈ U·C ₁₆ H ₄₀ KO ₈	C ₃₆ H ₈₈ I ₂ KO ₉ Si ₈ U·C ₄ H ₁₀ O
M_r	1440.74	1462.79	1494.83
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2/c$	Monoclinic, $C2/c$
Temperature (K)	150	150	150
a, b, c (Å)	13.4213 (5), 15.8641 (6), 16.3965 (6)	14.8717 (5), 15.8095 (5), 28.9025 (9)	49.049 (13), 13.108 (5), 21.124 (7)
α, β, γ (°)	104.442 (2), 102.934 (2), 96.066 (2)	103.785 (2)	90.054 (19)
V (Å ³)	3246.4 (2)	6599.7 (4)	13581 (8)
Z	2	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	3.7	3.64	3.54
Crystal size (mm)	0.23 × 0.20 × 0.10	0.05 × 0.05 × 0.01	0.24 × 0.08 × 0.04
Data collection			
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., <i>J. Appl. Cryst.</i> 48 (2015) 3-10	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). <i>J. Appl. Cryst.</i> 48, 3-10.	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., <i>J. Appl. Cryst.</i> 48 (2015) 3-10
T_{\min}, T_{\max}	0.573, 0.747	0.595, 0.747	0.566, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	74723, 23927, 19239	127091, 25260, 12924	179769, 20794, 13797
R_{int}	0.042	0.095	0.1
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.77	0.771	0.716
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.029, 0.060, 1.02	0.051, 0.128, 1.01	0.043, 0.115, 1.02
No. of reflections	23927	25260	20794
No. of parameters	591	611	687
No. of restraints	133	118	300
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 0.5905P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 5.5493P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 40.3862P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.98, -1.40	1.70, -1.53	1.54, -1.59

Crystallographic References

- 1) Computer programs: Apex4 v2021.4-0 (Bruker, 2021), *SAINTE* V8.40B (Bruker, 2020), *SHELXT* (Sheldrick, 2015), *SHELXL2018/3* (Sheldrick, 2015, 2018), SHELXLE Rev1275(Hübschle *et al.*, 2011).
- 2) Computer programs: Apex4 v2021.4-0 (Bruker, 2021), *SAINTE* V8.40B (Bruker, 2020), *SHELXT* (Sheldrick, 2015), *SHELXL2018/3* (Sheldrick, 2015, 2018), SHELXLE Rev1275(Hübschle *et al.*, 2011).
- 3) Computer programs: Apex4 v2021.4-0 (Bruker, 2021), *SAINTE* V8.40B (Bruker, 2020), *SHELXT* (Sheldrick, 2015), *SHELXL2019/3* (Sheldrick, 2015, 2019), SHELXLE Rev1275(Hübschle *et al.*, 2011).

Special Refinement Details

- 1) Co-crystallized solvent diethyl ether was positionally disordered and refined as two separate ether molecules (O1E > C4E and O1EB > C4EB). The 1,2 and 1,3 bond distances were restrained to be similar to each other. The U_{ij} components of the anisotropic displacement parameters for the disordered atoms closer to each other than 2.0 Å were restrained to be similar within a standard deviation of 0.01 Å². Subject to these conditions, the occupancy ratio of the positionally disordered moiety refined to 0.721(11) : 0.279(11).
- 2) There is one coordinating 1,2-dimethoxyethane (DME) molecule per uranium center, each with the central C-C bond on a 2-fold axis coincident with the uranium and silyl-ether oxygen atom (EQIV \$1 2-x, +y, 3/2-z).

The DME molecule with C9, C10, and O2 is disordered about the 2-fold axis and their 1,2 and 1,3 bond distances were restrained to be similar to the well-resolved DME molecule of the potassium countercation C29, O11, C30, C31, O12, and C32.

The DME molecule with C19, C20, and O4 is positionally disordered over two positions and the 1,2 and 1,3 bond distances of the disordered DME were restrained to be similar to half of another well-resolved DME molecule, O5 C22 C21.

In addition, the central C-C bond of each DME molecule (C10A-C10B, C19-C19_\$1, and C19b-C19b_\$1) was restrained to 1.49 Å (of a typical central C-C bond of a DME molecule) with an esd of 0.01 Å, resulting in bond lengths of 1.481(8), 1.489(9), and 1.485(10) Å, respectively.

The U_{ij} components of the anisotropic displacement parameters for disordered atoms closer to each other than 2.0 Å were restrained to be similar within a standard deviation of 0.01 Å².

Subject to these conditions, the occupancy ratio of the positionally disordered moiety refined to 0.743(13) : 0.257(13).

- 3) Six reflections were obstructed by the beamstop and were omitted from refinement.

A mild anti-bumping restraint (BUMP -0.02) was applied to prevent atoms of minor disordered moieties approaching each other too closely.

THF molecule disorder:

One of the two THF molecules on the uranium center was found to be disordered (O2). The 1,2 and 1,3 distances for disordered moieties were restrained to be similar to each other. The position and U_{ij} of the anisotropic displacement parameters (ADPs) were constrained to be the same for atoms O2 and O2B.

The THF molecule containing O3 was initially modelled as disordered. However, the second disordered moiety was found to be < 5% and thus was omitted from further disorder modelling (FVAR 3 = 0.96824) and was refined to be fully occupied during the final refinement process.

The U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar with an esd of 0.01 Å².

Under these conditions, the THF O2/O2B disorder was found to have an occupancy ratio of 0.613(11) : 0.387(11).

Diethyl ether molecule disorder:

There is an outersphere diethyl ether molecule that was found to be disordered over two positions over an inversion center, defining four different positions for one ether molecule. The 1,2 and 1,3 distances for disordered ether molecules were restrained to be similar to those of a well-defined ether molecule (which has O10 on an inversion center).

The U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar with an esd of 0.01 Å².

Under these conditions, the diethyl ether molecule O11/O11B was found to have an occupancy ratio of 0.291(13) : 0.209(13). Thus, a PART ratio of 0.582(26) : 0.418(26).

Tables of Geometric Parameters

Table S2. Selected geometric parameters of compound **1** (Å, °)

U1—O2A	2.553 (18)	U2—Si6	3.1457 (13)
U1—O1	2.587 (4)	Si1—O1	1.6971 (19)
U1—O2B	2.71 (2)	Si1—Si2	2.3084 (18)
U1—I1	3.1065 (4)	Si2—Si4	2.3299 (18)
U1—Si2	3.1281 (12)	Si2—Si3	2.3445 (19)
U2—O3	2.528 (4)	Si5—O3	1.7163 (19)
U2—O4B	2.61 (3)	Si5—Si6	2.3197 (18)
U2—O4	2.622 (10)	Si6—Si7	2.3352 (18)
U2—I2	3.1319 (3)	Si6—Si8	2.3463 (18)
O2A—U1—O2B	62.3 (2)	O4B—U2—O4B ⁱⁱ	62.4 (13)
O1—U1—I1 ⁱ	100.422 (10)	O4—U2—I2 ⁱⁱ	88.88 (19)
O1—U1—I1	100.421 (10)	I2—U2—I2 ⁱⁱ	162.177 (16)
I1 ⁱ —U1—I1	159.157 (19)	Si6 ⁱⁱ —U2—Si6	129.96 (5)
Si2 ⁱ —U1—Si2	128.94 (5)		
Si2—Si1—O1—U1	23.17 (6)	Si6—Si5—O3—U2	23.70 (6)

Symmetry code(s): (i) $-x+1, y, -z+1/2$; (ii) $-x+2, y, -z+3/2$.

Table S3. Selected geometric parameters of compound **1-crown (DME adduct)** (Å, °).

U1—O1	2.5613 (13)	U1—I1	3.1256 (2)
U1—O2'	2.6149 (17)	U1—Si2'	3.1276 (6)
U1—O2	2.6384 (16)	Si1—O1	1.7041 (15)
U1—I1'	3.1125 (2)	O1—Si1'	1.7078 (15)
U1—Si2	3.1149 (6)	I1'—K1	3.4608 (5)
Si2—U1—Si2'	130.014 (16)	O2'—U1—O2	62.83 (6)
O1—U1—Si2	64.83 (3)	O2'—U1—I1'	87.61 (5)
O1—U1—O2'	149.64 (6)	O2—U1—Si2	83.11 (4)
O1—U1—O2	147.51 (6)	O2—U1—I1'	79.16 (4)
O1—U1—I1'	96.82 (3)	I1'—U1—I1	164.321 (6)
O2'—U1—Si2	145.13 (5)	U1—I1'—K1	135.435 (11)

Table S4. Selected geometric parameters of compound **1-crown (THF adduct)** (Å, °).

U1—O1	2.553 (3)	U1—Si1	3.1713 (14)
U1—O3	2.578 (3)	I2—K1 ⁱ	3.3535 (13)
U1—O2B	2.579 (3)	Si1—Si2	2.3123 (18)
U1—O2	2.579 (3)	Si2—O1	1.703 (3)
U1—I2	3.0845 (10)	Si3—O1	1.709 (3)
U1—I1	3.1086 (11)	Si3—Si4	2.3080 (19)
U1—Si4	3.1377 (15)		
O1—U1—O3	144.61 (10)	O2B—U1—Si4	147.54 (9)
O1—U1—O2B	147.15 (11)	O2—U1—Si4	147.54 (9)
O1—U1—O2	147.15 (11)	I2—U1—Si4	89.83 (3)
O3—U1—O2	68.06 (12)	I1—U1—Si4	99.25 (3)
O1—U1—I2	94.13 (7)	O1—U1—Si1	64.82 (7)
O3—U1—I2	85.41 (9)	O3—U1—Si1	150.52 (8)
O2B—U1—I2	83.53 (10)	O2B—U1—Si1	82.46 (10)
O2—U1—I2	83.53 (10)	O2—U1—Si1	82.46 (10)
O1—U1—I1	99.34 (7)	I2—U1—Si1	91.46 (3)
O3—U1—I1	85.78 (9)	I1—U1—Si1	90.88 (3)
O2B—U1—I1	83.11 (10)	Si4—U1—Si1	129.59 (4)
O2—U1—I1	83.11 (10)	U1—I2—K1 ⁱ	158.24 (2)
I2—U1—I1	166.017 (13)	Si2—Si1—U1	78.92 (5)
O1—U1—Si4	64.83 (7)	Si3—Si4—U1	79.88 (5)
O3—U1—Si4	79.78 (9)		
Si1—Si2—O1—Si3	155.7 (3)	Si4—Si3—O1—Si2	162.7 (3)
Si1—Si2—O1—U1	-20.94 (15)	Si4—Si3—O1—U1	-20.71 (15)

Symmetry code(s): (i) x, -y+1, z-1/2.

SolidG of Complex 1

Ligand	% shielding
Silyl ligand (tridentate)	45.24
DME (bidentate)	22.25
Iodide #1	10.98
Iodide #2	10.97
SUM:	89.44 (0.73% overlap)
Without DME:	67.19

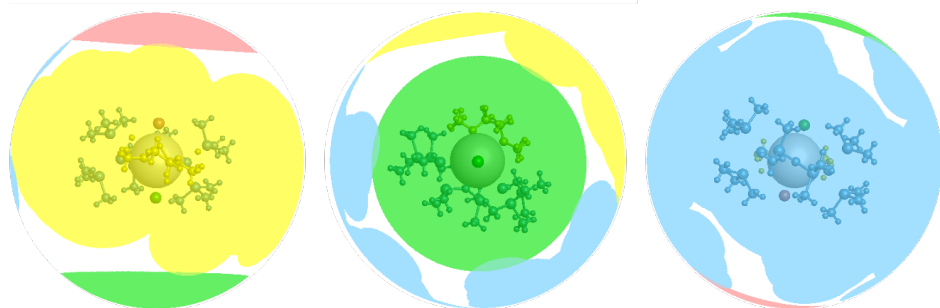


Figure S14. **1-crown (DME adduct) 18-crown-6(K⁺)** and solvent molecules removed from the .xyz file.^[5]

```

+-----+
|               Program Solid-G. Ver 0.25, October 09, 2006.               |
|               The Molecular Structure Laboratory                          |
|               Chemistry Department, University of Wisconsin-Madison      |
+-----+
| Structure from Si2UI2K_nocrown.xyz                                     on 9/26/2023 9:11:55 AM |
+-----+

```

Table 1. Complex composition, atomic coordinates and radii

Atom	L	X	Y	Z	Cov	vdW	ZER
U1	0	-0.0000	0.0000	-0.0000	1.713	3.050	2.285
Si8	1	-4.4426	-1.3730	-1.8644	0.900	2.205	1.834
Si7	1	-1.4646	-1.7709	-4.0847	0.900	2.205	1.834
Si6	1	-2.1128	-1.3480	-1.8717	0.900	2.205	1.834
Si5	1	-1.4641	-3.1777	-0.6226	0.900	2.205	1.834
Si4	1*	4.4427	-1.3730	1.8644	0.900	2.205	1.834
Si3	1	1.4646	-1.7709	4.0848	0.900	2.205	1.834
Si2	1	2.1129	-1.3480	1.8717	0.900	2.205	1.834
Si1	1*	1.4641	-3.1777	0.6226	0.900	2.205	1.834
O1	1*	-0.0000	-2.5872	-0.0000	0.620	1.697	1.471
H9	1	-0.2042	-3.4878	3.8782	0.371	1.675	1.000
H8	1	-0.4973	-2.6145	5.1868	0.371	1.675	1.000
H7	1	-0.8975	-2.0518	3.7431	0.371	1.675	1.000
H6	1	1.9651	-5.1618	1.8584	0.371	1.675	1.000
H58	1	-4.6796	-0.3067	0.2582	0.371	1.675	1.000
H57	1	-6.0967	-0.8801	-0.2153	0.371	1.675	1.000
H56	1	-5.0001	-1.8679	0.4034	0.371	1.675	1.000
H55	1	-6.2207	-2.8648	-2.4085	0.371	1.675	1.000
H54	1	-4.9722	-3.1439	-3.3700	0.371	1.675	1.000
H53	1	-4.9660	-3.6988	-1.8690	0.371	1.675	1.000
H52	1	-4.6347	0.8577	-2.7090	0.371	1.675	1.000
H51	1	-4.8715	-0.1870	-3.8980	0.371	1.675	1.000

H50	1	-6.0425	0.1096	-2.8483	0.371	1.675	1.000
H5	1	0.4375	-4.7510	2.1008	0.371	1.675	1.000
H49	1	-3.4825	-2.3955	-5.2123	0.371	1.675	1.000
H48	1	-2.2339	-3.1057	-5.9178	0.371	1.675	1.000
H47	1	-2.8184	-3.6910	-4.5478	0.371	1.675	1.000
H46	1	-0.7516	0.4656	-4.5592	0.371	1.675	1.000
H45	1	-1.0514	-0.3024	-5.9309	0.371	1.675	1.000
H44	1	-2.2611	0.2695	-5.0530	0.371	1.675	1.000
H43	1	0.2043	-3.4878	-3.8782	0.371	1.675	1.000
H42	1	0.4974	-2.6145	-5.1868	0.371	1.675	1.000
H41	1	0.8976	-2.0518	-3.7430	0.371	1.675	1.000
H40	1	-1.9650	-5.1618	-1.8584	0.371	1.675	1.000
H4	1	0.8624	-5.4880	0.7453	0.371	1.675	1.000
H39	1	-0.4374	-4.7510	-2.1008	0.371	1.675	1.000
H38	1	-0.8623	-5.4880	-0.7453	0.371	1.675	1.000
H37	1	-2.7075	-2.6500	1.3310	0.371	1.675	1.000
H36	1	-3.3900	-3.8841	0.5743	0.371	1.675	1.000
H35	1	-2.0836	-4.1173	1.4689	0.371	1.675	1.000
H3	1	2.7076	-2.6500	-1.3310	0.371	1.675	1.000
H24	1	4.6797	-0.3067	-0.2582	0.371	1.675	1.000
H23	1	6.0968	-0.8801	0.2153	0.371	1.675	1.000
H22	1	5.0002	-1.8679	-0.4034	0.371	1.675	1.000
H21	1	6.2208	-2.8648	2.4085	0.371	1.675	1.000
H20	1	4.9723	-3.1439	3.3700	0.371	1.675	1.000
H2	1	3.3901	-3.8841	-0.5743	0.371	1.675	1.000
H19	1	4.9660	-3.6988	1.8690	0.371	1.675	1.000
H18	1	4.6347	0.8577	2.7090	0.371	1.675	1.000
H17	1	4.8716	-0.1870	3.8980	0.371	1.675	1.000
H16	1	6.0426	0.1096	2.8483	0.371	1.675	1.000
H15	1	3.4826	-2.3955	5.2124	0.371	1.675	1.000
H14	1	2.2340	-3.1057	5.9178	0.371	1.675	1.000
H13	1	2.8184	-3.6910	4.5478	0.371	1.675	1.000
H12	1	0.7517	0.4656	4.5592	0.371	1.675	1.000
H11	1	1.0514	-0.3024	5.9309	0.371	1.675	1.000
H10	1	2.2612	0.2695	5.0531	0.371	1.675	1.000
H1	1	2.0837	-4.1173	-1.4688	0.371	1.675	1.000
C8	1	5.1374	-1.0711	0.1488	0.670	1.825	1.539
C7	1	5.2456	-2.9587	2.4477	0.670	1.825	1.539
C6	1	5.0734	0.0182	2.9614	0.670	1.825	1.539
C5	1	2.6405	-2.8733	5.0582	0.670	1.825	1.539
C4	1	1.3712	-0.1383	5.0189	0.670	1.825	1.539
C3	1	-0.2390	-2.5793	4.2414	0.670	1.825	1.539
C20	1	-5.1373	-1.0711	-0.1488	0.670	1.825	1.539
C2	1	1.1442	-4.8432	1.4282	0.670	1.825	1.539
C19	1	-5.2455	-2.9587	-2.4477	0.670	1.825	1.539
C18	1	-5.0734	0.0182	-2.9614	0.670	1.825	1.539
C17	1	-2.6405	-2.8733	-5.0582	0.670	1.825	1.539
C16	1	-1.3711	-0.1383	-5.0189	0.670	1.825	1.539
C15	1	0.2391	-2.5793	-4.2414	0.670	1.825	1.539
C14	1	-1.1442	-4.8432	-1.4282	0.670	1.825	1.539
C13	1	-2.5378	-3.4947	0.8637	0.670	1.825	1.539
C1	1	2.5379	-3.4947	-0.8637	0.670	1.825	1.539
O3	2*	-1.0212	2.3327	-0.9291	0.620	1.697	1.471
O2	2*	0.9131	2.1699	0.9881	0.620	1.697	1.471
H68	2	0.7225	2.6273	2.8651	0.371	1.675	1.000
H67	2	0.7321	3.1975	-1.5153	0.371	1.675	1.000
H66	2	-2.7498	2.6795	-1.2990	0.371	1.675	1.000
H65	2	1.7960	1.4852	2.5426	0.371	1.675	1.000
H64	2	2.1906	3.0263	2.3687	0.371	1.675	1.000
H63	2	-0.4743	3.6697	1.0249	0.371	1.675	1.000
H62	2	0.9222	4.3021	0.5522	0.371	1.675	1.000
H61	2	-0.5573	4.1277	-1.2730	0.371	1.675	1.000
H60	2	-1.7156	3.2295	-2.3894	0.371	1.675	1.000
H59	2	-2.1417	1.6870	-2.3972	0.371	1.675	1.000

H34	2	-1.7960	1.4852	-2.5426	0.371	1.675	1.000
H33	2	-2.1905	3.0263	-2.3687	0.371	1.675	1.000
H32	2	-0.7224	2.6273	-2.8651	0.371	1.675	1.000
H31	2	0.4743	3.6697	-1.0249	0.371	1.675	1.000
H30	2	-0.9222	4.3021	-0.5522	0.371	1.675	1.000
H29	2	-0.7321	3.1975	1.5153	0.371	1.675	1.000
H28	2	0.5574	4.1277	1.2730	0.371	1.675	1.000
H27	2	1.7157	3.2295	2.3894	0.371	1.675	1.000
H26	2	2.1418	1.6870	2.3972	0.371	1.675	1.000
H25	2	2.7499	2.6795	1.2990	0.371	1.675	1.000
C9	2	1.9550	2.4624	1.8274	0.670	1.825	1.539
C12	2	-1.4671	2.3707	-2.2821	0.670	1.825	1.539
C11	2	-0.3296	3.5137	-0.4688	0.670	1.825	1.539
C10	2	0.0669	3.3319	0.9460	0.670	1.825	1.539
I2	3*	2.0043	0.5619	-2.3059	1.233	2.291	1.941
I1	4*	-2.0043	0.5619	2.3060	1.233	2.291	1.941

Legend:

L - ligand #, atoms connected to U1 are marked with a *,
X,Y,Z, - Cartesian coordinates,
Cov - covalent radius,
vdW, - van der Waals radius,
ZER - Zero Energy Radius, at R(E=0)

Table 2. Ligand Composition and Coordination

Ligand	H	Atoms	Formula	U1-L	Coordinated atoms
1	3	73	H48C16O1Si8	3.198	Si4 Si1 O1
2	2	26	H20C4O2	2.252	O3 O2
3	1	1	I1	3.106	I2
4	1	1	I1	3.107	I1

Legend:

Ligand - ligand number,
H - ligand hapticity,
Atoms - number of atoms in the ligand,
U1-L - distance between U1 and the geometrical center of the shape formed by the coordinated atoms,
CA - list of atoms coordinated to U1.

Table 3. Coordinated Atom Data

Atom	U1 -Atom Distance Angstroms	Atom Solid Angle Steradians	Atom Cone Angle Degrees
Si4	5.0099	0.44	42.95
Si1	3.5537	0.90	62.14
O1	2.5872	1.11	69.30
O3	2.7106	1.01	65.73
O2	2.5531	1.15	70.36
I2	3.1065	1.38	77.34
I1	3.1065	1.38	77.34

Table 4. Ligand Angle Calculations

Ligand #	Omega(L) Steradians	G(L) Percent	Equivalent Cone Angle (ECA) Degrees
----------	------------------------	-----------------	--

1	5.68	45.24	169.07
2	2.80	22.25	112.58
3	1.38	10.98	77.40
4	1.38	10.97	77.37

SUM(G(L))	11.24	89.44	
G(complex)	11.15	88.71	
G(gamma)	0.09	0.73	

G(U1)	6.80	54.09	Si4 Si1 O1 O3 O2 I2 I1

S(U1)	6.21	49.41	Si1 O1 O3 O2 I2 I1

Legend:

Ligand - Ligand #,
Omega(L) - Solid Angle of the Ligand,
G(L) - The percentage of the sphere shielded by the ligand,
ECA - Cone angle corresponding to the Omega(L) and not Tolman's cone angle for the ligand. The ECA is usually smaller than Tolman's cone angle since this program does not assume free rotation about the M-L axis.

SUM(G(L)) - The sum of all individual ligand G(L) values,
G(complex) - The G value for the complex, all ligands treated as one,
G(gamma) - The percentage of the sphere shielded by more than one ligand.
G(U1) - The percentage of U1 's surface shielded by the ligated atoms only,
S(U1) - The percentage of U1 's surface "in contact" with the ligated atoms.

Table 5. Unfavorable Close Contacts Between Atoms

No Unfavorable Interligand Interactions Found.

Table 6. Normalization to M-L=2.28 Angstroms

Ligand	Omega(L) Steradians	G2.28(L) Percent	Equivalent Cone Angle (ECA) Degrees
1	6.87	54.64	190.65
2	2.76	21.94	111.74
3	2.99	23.78	116.73
4	2.99	23.78	116.74

Legend:

Ligand - Ligand #,
Omega(L) - Solid Angle of the Ligand normalized to M-L=2.28 A,
G2.28(L) - The normalized percentage of the sphere shielded by the ligand,
ECA - Cone angle corresponding to the Omega(L) and not Tolman's cone angle for the ligand. The ECA is always smaller than Tolman's cone angle since this program does not assume free rotation about the M-L axis.

+-----+
| Output written to Si2UI2K_nocrown.out. |
| Computation Time: 4.17 seconds. Completed on 9/26/2023 9:12:00 AM |
+-----+

References

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15* (5), 1518–1520. <https://doi.org/10.1021/om9503712>.
- (2) Monreal, M. J.; Thomson, R. K.; Cantat, T.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L. UI4(1,4-dioxane)2, [UCl4(1,4-dioxane)]2, and UI3(1,4-dioxane)1.5: Stable and Versatile Starting Materials for Low- and High-Valent Uranium Chemistry. *Organometallics* 2011, *30*, 2031–2038. [dx.doi.org/10.1021/om200093q](https://doi.org/10.1021/om200093q)
- (3) Zitz, R.; Hlina, J.; Aghazadeh Meshgi, M.; Krenn, H.; Marschner, C.; Szilvási, T.; Baumgartner, J. Using Functionalized Silyl Ligands To Suppress Solvent Coordination to Silyl Lanthanide(II) Complexes. *Inorg. Chem.* **2017**, *56* (9), 5328–5341. <https://doi.org/10.1021/acs.inorgchem.7b00420>.
- (4) Blinka, T. A.; Helmer, B. J.; West, R. Polarization Transfer NMR Spectroscopy for Silicon-29: The INEPT and DEPT Techniques. In *Advances in Organometallic Chemistry*; Elsevier, 1984; Vol. 23, pp 193–218. [https://doi.org/10.1016/S0065-3055\(08\)60611-5](https://doi.org/10.1016/S0065-3055(08)60611-5).
- (5) Guzei, I. A.; Wendt, M. An Improved Method for the Computation of Ligand Steric Effects Based on Solid Angles. *Dalton Trans.* **2006**, No. 33, 3991–3999. <https://doi.org/10.1039/B605102B>.