Communications

Uranium−Group 14 Element Single Bonds: Isolation and Characterization of a Uranium(IV) Silyl Species

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*Summary: A uranium silyl compound, (Ar[^{t}Bu]N)$_3$USi(SiMe$_3$)$_3$ (**1**; Ar = 3,5-C$_6$H$_3$Me$_2$), has been synthesized, isolated, and characterized structurally and theoretically; compound **1** crystallizes in the space group $P\bar{3}$ and its U−Si interatomic distance was found to be 3.091(3) Å. Geometry optimizations were carried out for the model systems $H_3EU(NH_2)_3$ (E = C, Si, Ge, Sn) with a set of reasonable constraints; calculated U−E distances and bond energies are in good accord with experimental data.*

Molecules incorporating actinide−silicon single bonds have been described, but such silyl species are quite scarce. The compounds Cp_3USiPh_3[1] and $Cp^*{}_2Th(SiR_3)Cl$ (SiR_3 = $SiPh_3$, Si^{t}BuPh$_2$, Si(SiMe$_3$)Ph$_2$)[2] have been obtained with difficulty[2] and found to react readily with isocyanides[1] or CO.[2] Given the paucity of structural and thermodynamic data relevant to actinide−silicon bonds, the synthesis, isolation, and structural and theoretical characterization of a representative compound became a target objective. In addition, since such an investigation may be deemed prerequisite to the eventual uncovering of systems featuring actinide−silicon multiple bonds, the synthesis of a silyluranium(IV) complex was undertaken and is described herein.

Chosen for purposes of kinetic stabilization was the tris(trimethylsilyl)silyl substituent popularized by Tilley and co-workers,[3,4] in conjunction with the tris(*N-tert*-butylanilide)uranium motif described previously.[5,6] Accordingly, the reaction between IU(N[^{t}Bu]Ar)$_3$[5] (Ar = 3,5-C$_6$H$_3$Me$_2$) and (THF)$_3$LiSi(SiMe$_3$)$_3$[7] (diethyl ether, −100 to 25 °C, 10.5 h) was found to give a red solid in ca. 80% yield after filtration, concentration, and recrystallization.[8] Further recrystallization from a saturated diethyl ether solution at −35 °C provided single crystals suitable for an X-ray diffraction study.

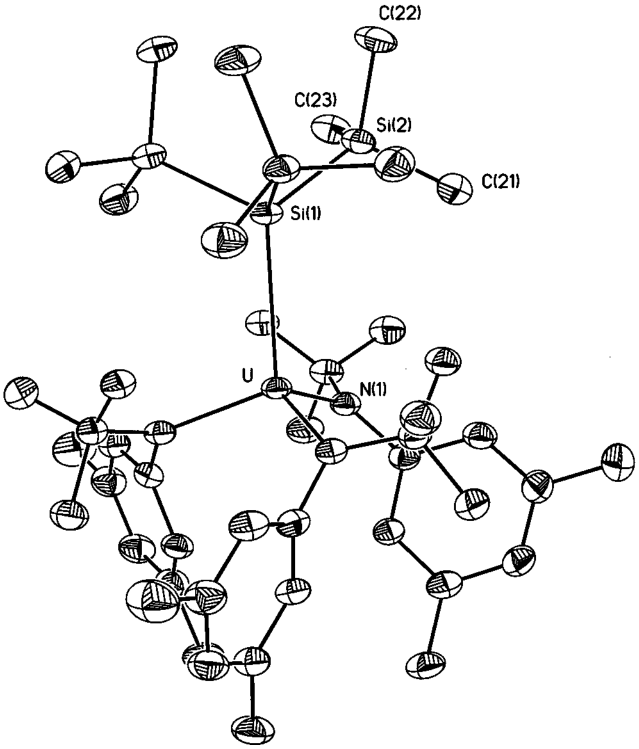

Figure 1. Structural representation of compound **1** with thermal ellipsoids at the 35% probability level. Selected interatomic distances (Å) and angles (deg): U−Si, 3.091(3); U−N, 2.210(5); Si−Si, 2.354(2); N−U−N, 109.56(12); N−U−Si, 109.38(12).

The red compound, formulated as (Ar[^{t}Bu]N)$_3$USi(SiMe$_3$)$_3$ (**1**), crystallizes in the space group $P\bar{3}$ in such a way as to enforce molecular C_3 symmetry (Figure 1). Attention should be drawn to the most salient metrical parameter, namely the U−Si interatomic distance of

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(1) Porchia, M.; Brianese, N.; Casellato, U.; Ossola, F.; Rossetto, G.; Zanella, P.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1989**, 677.

(2) Radu, N. S.; Engeler, M. P.; Gerlach, C. P.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 3621.

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(4) Burckhardt, U.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 6328.

(5) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836.

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(7) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

(8) A 0.5300 g portion of IU(N[^{t}BuAr)$_3$ (0.5935 mmol, 1 equiv) and 0.2789 g of (THF)$_3$LiSi(SiMe$_3$)$_3$ (0.5935 mmol, 1 equiv) were dissolved in 30 mL and 10 mL of diethyl ether, respectively, and the solutions were frozen. The thawing (THF)$_3$LiSi(SiMe$_3$)$_3$ solution was added dropwise to the thawing solution of IU(N[^{t}BuAr)$_3$. The reaction mixture was stirred for 10.5 h at room temperature. The volatiles were removed, and the red solid obtained was extracted with diethyl ether and the solution filtered through Celite and concentrated. Recrystallization at −35 °C allowed the isolation of 0.4785 g of product **1** (79.6% yield) in two crops. ^{1}H NMR (300 MHz, C$_6$D$_6$, 22 °C): δ 19.926 (s, 9H, *Me*−Si based on NOE difference experiment results), 3.431 (s, 2H, *o*-Ar), 0.233 (s, 1H, *p*-Ar), −2.3 (vb s, 6H, *Me*−Ar), −5.520 (s, 9H, *t-Bu*). Anal. Calcd for $C_{45}H_{81}N_3Si_4U$: C, 53.27; H, 8.05; N, 4.14. Found: C, 53.58; H, 8.46; N, 3.53.

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Table 1. Calculated[a] U−E Bond Lengths, Energies, Polarity, and Orbital Composition for $H_3E-U(NH_2)_3$ Compounds (E = C, Si, Ge, Sn)

E	d_{U-E}	$d_{U-E} - r_E$[b]	$\delta_U^+ + \delta_E^-$[c]	U−E bond orbital[d]	D_{U-E}[e]
C	2.432	1.662	1.077	56% C p_z, 15% U d_{z^2}	58
Si	2.992	1.814	0.693	49% Si p_z, 15% U d_{z^2}	45
Ge	3.018	1.803	0.722	51% Ge p_z, 14% U d_{z^2}	46
Sn	3.202	1.810	0.649	42% Sn p_z, 16% U d_{z^2}, 12% U s	44

[a] See text for computational details; distances given in Å. [b] This quantity should equal the uranium covalent radius (r_U); values of r_E used are those calculated for the four E_2H_6 compounds using the same method as for the uranium derivatives. Additionally, independent geometry optimization of the hypothetical singly bonded D_{3d} quintet $U_2(NH_2)_6$ gave r_U = 1.812 Å. [c] Measure of the bond ionicity from calculated Hirshfeld charges. [d] C and U atomic orbitals contributing ≥10% are shown. [e] Bond dissociation enthalpy in kcal/mol.

3.091(3) Å. Binary uranium silicides such as U_3Si have been characterized structurally and found to contain mainly U−Si distances close to 3.05 Å.[9,10] No Si−U bond distances appear to have been measured previously for molecular systems, and values of the uranium covalent radius[11] are very scarce in the literature.[12,13] Density functional theory (DFT) calculations therefore were carried out on a set of representative model systems in order to obtain an estimate of the uranium single bond covalent radius (r_U).

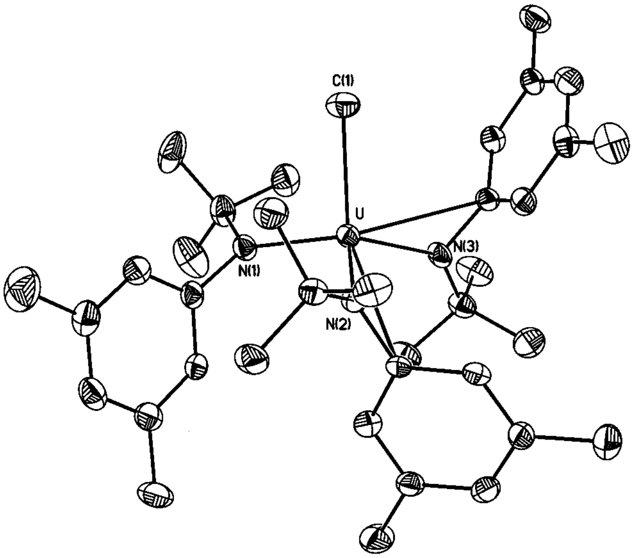

Figure 2. Structural representation of compound **2** with thermal ellipsoids at the 35% probability level. Selected interatomic distances (Å): U−C(1), 2.446(7); U−N(1), 2.211(4); U−N(2), 2.237(4); U−N(3), 2.231(4).

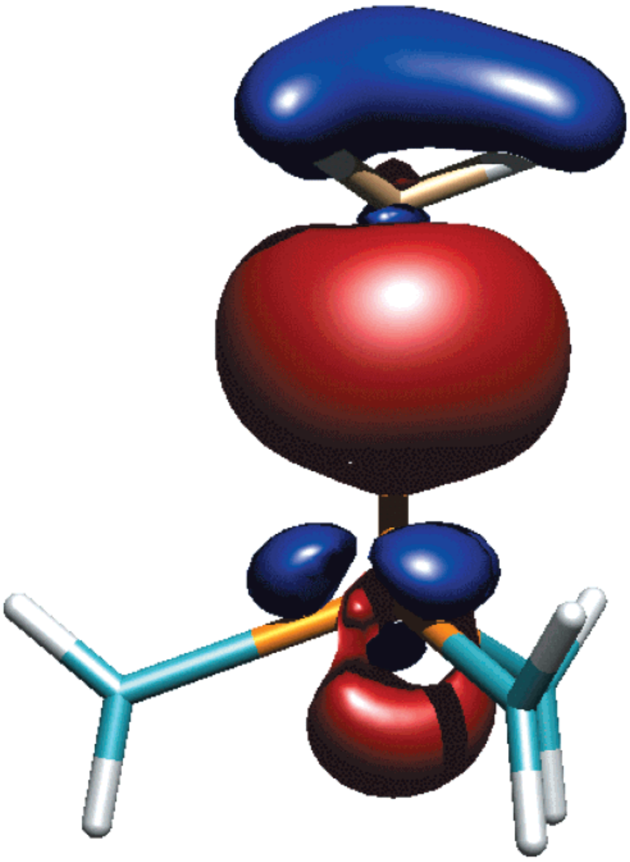

Figure 3. Uranium−silicon bonding molecular orbital for the $H_3SiU(NH_2)_3$ system.

Geometry optimizations were carried out for the model systems $H_3EU(NH_2)_3$ (E = C, Si, Ge, Sn) with a set of reasonable constraints.[14] Most interesting is that the distances d_{U-E} (Table 1) are predictable if r_U is taken to be 1.8 Å, with the exception of d_{U-C}, which experiences a contraction as anticipated[11] on the basis of the relatively large ionic contribution to the bonding for E = C.[15] This U−C distance is also in accord with the experimental value of 2.446(7) Å determined for MeU(N[^{t}Bu]Ar)$_3$ (**2**) by X-ray crystallography (Figure 2 and Supporting Information).[16−19] In addition, the U−Sn calculated distance compares well to the value of 3.166(1) Å determined for Cp_3USnPh_3.[20] In each case the U−E bonding molecular orbital is comprised mainly of valence E p_z and U d_{z^2} contributing atomic orbitals, as represented graphically in Figure 3. Also of interest

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(9) Kimmel, G.; Sharon, B.; Rosen, M. *Acta Crystallogr. Sect. B: Struct. Science* **1980**, *36*, 2386.

(10) Remschnig, K.; Lebihan, T.; Noel, H.; Rogl, P. *J. Solid State Chem.* **1992**, *97*, 391.

(11) Pauling, L. C. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals; An Introduction to Modern Structural Chemistry*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(12) The crystallographic program SHELX-97 by G. M. Sheldrick and co-workers uses 1.8 Å as the covalent radius for uranium. Following is a quote from the SHELX-97 manual (http://shelx.uni-ac.gwdg.de/SHELX/): “The covalent radii stored in the program are based on experience rather than taken from a specific source, and are deliberately overestimated for elements which tend to have variable coordination numbers so that ‘bonds’ are not missed.”

(13) Pyykko, P. *Chem. Rev.* **1988**, *88*, 563.

(14) The ADF program suite (http://www.scm.com/) was utilized for geometry optimizations. All-electron ZORA type V basis sets were used for all atoms, VWN and PW91 functionals were employed for all calculations, and the spin-unrestricted option was utilized together with the ZORA relativistic formalism. Preliminary calculations were carried out on the set of E_2H_6 (E = C, Si, Ge, and Sn) compounds in D_{3d} symmetry to establish the E covalent radii and E−H bond distances. Geometry optimization on $H_3CU(NH_2)_3$, carried out in C_{3v} symmetry, was used to define the U−N distance for the uranium systems. The constraints of C_{3v} molecular symmetry and tetrahedral angles at the U and E centers were imposed for all four $H_3EU(NH_2)_3$ molecules, which were treated as spin triplets. See the SI for sample input files and for ADF literature citations.

(15) Terminal uranium(IV) methyl derivatives were found to present U−C distances of 2.465(7), 2.42(2), 2.41(1), and 2.498(5) Å (see the next four references).

(16) Stewart, J. L.; Andersen, R. A. *J. Chem. Soc., Chem. Commun* **1987**, 1846.

(17) Lukens, W. W., Jr.; Beshouri, S. M.; Blosch, L. L.; Stuart, A. L.; Andersen, R. A. *Organometallics* **1999**, *18*, 1235.

(18) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293.

are the U−E bond energies, which fall in two groups: the relatively strong (58 kcal/mol) U−C bond and the weaker (44−46 kcal/mol) bonds to Si, Ge, and Sn. Thermodynamic measurements made by Marks and coworkers on $Cp_3USi(SiMe_3)_3$ ($D_{U-Si} = 37(3)$ kcal/mol) and on Cp_3USiPh_3 ($D_{U-Si} = 35(4)$ kcal/mol) are relevant.[21] The values are consistent also with the thermal stability of **1**: storing a benzene-d_6 solution at 60 °C for 2 days elicited no detectable decomposition. While the Si−Si bond lengths (2.354(2) Å) in compound **1** are normal, the Si−Si−Si angles (102.91(9)°) are moderately compressed and the Si−Si−U angles (115.43(8)°) are slightly enlarged relative to the tetrahedral value. Such a bending of the Me_3Si groups away from the *tert*-butyl substituents *could* signify a stressed U−Si contact, perhaps consistent with the 0.1 Å disparity in U−Si distances in **1** as compared with the computational model. Adopted by the $U(N[^tBu]Ar)_3$ moiety is a three-bladed propeller conformation accommodating the silyl substituent in a tightly geared fashion. Compound **1** is a rare case of uranium(IV) exhibiting only four close interatomic contacts, and it is instructive that the angles at uranium (109.38(12) and 109.56(12)°) describe a near-perfect tetrahedron. The U−N distances (2.210(5) Å) are typical for a uranium(IV) derivative supported by the *N*-*tert*-butylanilide ligand[5,6] and compare well with the 2.230 Å calculated value.

In solution at 25 °C compound **1** is found to be unreactive toward a range of reagents, including CO, H_2, nitriles, isocyanates, and isonitriles, with the exception of ^iPrNC.[22] Given the low U−Si bond strength and the affinity of both U and Si for ligation by electronegative atoms, it can be inferred that the low observed reactivity is sterically imposed. Future structural work on compounds containing uranium−group 14 element single bonds will be of interest to explore further the size of uranium in its covalent compounds.

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Supporting Information Available: Text, figures, and tables giving full synthetic details and spectroscopic data for **2**, full X-ray structural details for **1** and **2**, and details of computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Porchia, M.; Casellato, U.; Ossola, F.; Rossetto, G.; Zanella, P.; Graziani, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1034.

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(22) The reaction between compound **1** and 1.5−2 equiv of ^iPrNC gave, after 36 h, a mixture of compounds, as determined by ^1H NMR spectroscopy. The reaction mixture contained a major product and small amounts of some decomposition products (identified by comparison of their chemical shifts in the ^1H NMR spectrum of the reaction mixture). Attempts to isolate and characterize the major product formed have been unsuccessful so far.