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Crystal and Molecular Structure of Hydridotris[bis(trimethylsilyl)amido]uranium(IV)

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New hydride derivatives of thorium(IV) and uranium(IV), $HM[N(SiMe_3)_2]_3$, have been prepared recently.[1] This paper describes the crystal structure of the uranium species, though the hydride ion was not located, and shows that the thorium analogue is isostructural. The reaction chemistry and spectroscopy leave no doubt that these derivatives are authentic examples of four-coordinate, monomeric hydride, compounds.[1,2]

Experimental Section

Hydridotris[bis(trimethylsilyl)amino]thorium(IV), hydridotris[bis(trimethylsilyl)amido]uranium(IV), and tris[bis(trimethylsilyl)amido]uranium(III) were prepared as previously described.[1,3] The crystals used in the X-ray analysis were grown from pentane (−10 °C). The needles were loaded into quartz capillaries under argon, and the capillaries were sealed.

A brown crystal of the uranium hydride, needle-shaped with hexagonal cross section ~0.15 mm across and ~0.4 mm long, was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of several low-angle reflections showed peaks with half-widths of 0.13 and 0.11° for $h00$ and $00l$ type reflections, respectively. The space group is $P\bar{3}1c$. The setting angles of 12 manually centered reflections ($20.0° < 2\theta < 30.3°$) were used to determine by least squares the cell parameters a = 16.402 (8) Å and c = 8.501 (4) Å; V = 1980.6 Å^3. There are two molecules in the unit cell.

Intensity data were collected with use of the θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each peak was scanned from 0.75° before the $K\alpha_1$ peak to 0.75° after the $K\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range, offset by 0.5°. The needle direction of the crystal was approximately parallel to the ϕ axis of the diffractometer. The temperature during data collection was 21 ± 1 °C. Three standard reflections, (300, 060, and 002), were measured after every 200th scan; a decay of about 1% in all three standards was observed, and the data were corrected accordingly. An absorption correction[4] (μ = 41 cm^{-1}) was applied, and values ranged from 1.65 to 1.75. A total of 3569 scans, not including standards, resulted in 897 unique reflections, 521 of which had intensities greater than 3σ.

The atomic positions of U, Si, N, and C were taken from the isomorphous Nd(III) compound[5] and used to start the least-squares refinement of the structure. The full-matrix least-squares program minimizes the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$, and the structure was refined with anisotropic temperature factors to an R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.091 for 608 ($F^2 > 2\sigma$) data. A difference Fourier calculation showed a large peak, 3 e Å^{-3}, with coordinates near 0, 0, 0.3. This peak is in the channel through the origin, parallel to the z axis. No ordered matter has been observed in this channel,[5-8] which is large enough to fit molecules the size of benzene.[8] So that the electron density of the largest peak in the difference Fourier, 3 e Å^{-3} could be compensated for, a pseudoatom, with the scattering power of carbon and an isotropic thermal parameter, was included in the least-squares calculations. The R value after a series of least-squares refinements was 0.071. The methyl hydrogen atoms were not observed in the difference Fourier map, but their estimated positions were calculated with C–H bond distances of 0.95 Å and with the assumption of a staggered arrangement of tetrahedral C–H bonds to the Si–C tetrahedral bonds. The estimated hydrogen atom positions were included in the least-squares refinements but not refined. One isotropic thermal parameter for all nine hydrogen atoms was included and refined. Because of large observed discrepancies among some of the lower 2θ angle data, probably due to inaccurate absorption corrections, all 17 data with $(\sin\theta)/\lambda < 0.14$ were deleted. The final R value for 498 data, $F^2 > 3\sigma$, was 0.044, and for all 897 data it was 0.095. The weighted R_w ($[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) was 0.053 for 48 parameters. The goodness-of-fit was 1.24, and in the last cycle no parameter changed more than 0.01σ.

Table I. Unit Cell Dimensions (Å) of Tris[bis(trimethylsilyl)amido]uranium(III), Hydridotris[bis(trimethylsilyl)amido]uranium(IV), and Hydridotris[bis(trimethylsilyl)amido]thorium(IV)

	U(III)	U(IV)	Th(IV)
color	dark red	brown	white
a, Å	16.56 (5)	16.402 (8)	16.47 (3)
c, Å	8.43 (4)	8.501 (4)	8.53 (3)
V, Å^3	2002	1981	2004

Table II. Positional and Thermal Parameters[a] with Estimated Standard Deviations[b]

atom	x	y	z
U	$^2/_3$	$^1/_3$	0.3100 (1)
N	0.5133 (6)	0.2567	$^1/_4$
Si	0.4575 (2)	0.2881 (2)	0.1105 (3)
C(1)	0.4016 (9)	0.3520 (9)	0.197 (1)
C(2)	0.3660 (8)	0.1863 (9)	−0.002 (1)
C(3)	0.5488 (9)	0.3682 (8)	−0.029 (1)
H(1)[c]	0.4489	0.4084	0.2463
H(2)	0.3565	0.3137	0.2728
H(3)	0.3723	0.3683	0.1162
H(4)	0.3197	0.1433	0.0688
H(5)	0.3948	0.1558	−0.0547
H(6)	0.3383	0.2077	−0.0763
H(7)	0.5773	0.3363	−0.0763
H(8)	0.5946	0.4218	0.0260
H(9)	0.5203	0.3869	−0.1076
X[c]	0.0	0.0	0.313 (2)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U[d]	5.65 (5)	5.65	4.54 (5)	2.825	0.0	0.0
N[e]	5.2 (5)	4.5 (3)	4.5 (4)	2.6	0.0	−0.3 (3)
Si	6.2 (1)	6.3 (1)	5.4 (1)	3.4 (1)	−1.1 (1)	−0.3 (1)
C(1)	10.8 (8)	11.1 (8)	8.5 (6)	7.9 (7)	−0.5 (6)	−0.5 (6)
C(2)	10.2 (8)	9.7 (8)	9.1 (6)	4.1 (7)	−3.8 (6)	−1.9 (6)
C(3)	10.2 (8)	9.3 (7)	6.3 (5)	4.0 (6)	0.9 (5)	1.9 (5)

[a] The anisotropic temperature factor has the form $\exp[-0.25\cdot(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots)]$. [b] In this and the following tables the number in parentheses in the estimated standard deviation of the least significant digit. [c] Isotropic temperature parameters for H and X are 15 (2) and 3.0 (4) Å^2, respectively. X is the pseudoatom introduced to compenstate for the largest electron density peak in the channel; it does not represent any chemically recognizable structure. [d] Symmetry conditions of the special position: $B_{11} = B_{22} = 2B_{12}$ and $B_{13} = B_{23} = 0$. [e] Symmetry conditions of the special position: $x = 2y$, $B_{11} = 2B_{12}$, and $B_{13} = 0$.

The expressions used in processing the data and estimating the weights are given in the supplementary material; the "ignorance factor", p, was set to 0.06. Scattering factors from Doyle and Turner[9] were used, and dispersion corrections[10] were applied. The largest peak

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Table III. Interatomic Distances (Å)

	dist	cor[a]
U-3N	2.237 (9)	2.240
N-2Si	1.727 (5)	1.740
Si-C(1)	1.86 (1)	1.89
Si-C(2)	1.86 (1)	1.90
Si-C(3)	1.84 (1)	1.88

[a] Adjusted for thermal motion with the assumption of the "riding model".

Table IV. Selected Angles (Deg)

N-U-N	115.0 (1)	N-Si-C(2)	113.3 (5)
U-N-Si	127.1 (3)	N-Si-C(3)	106.8 (5)
U-N-Si[a]	106.9 (2)	C(1)-Si-C(2)	107.9 (6)
Si-N-Si[a]	125.3 (6)	C(1)-Si-C(3)	107.8 (6)
N-Si-C(1)	112.5 (4)	C(2)-Si-C(3)	108.3 (5)

[a] Atom at position $x, x - y, {}^1/_2 - z$.

in the final difference Fourier map was ~0.8 e $Å^{-3}$ about 1 Å from the U atom. The second and third peaks were each ~0.3 e $Å^{-3}$ and were in the channel along the z axis; none of the residual density in the hole could be related to any chemically reasonable structure.

Weissenberg photography, using Cu Kα X-rays, was used to determine the cell dimensions of the isomorphous complexes of U(III) and Th(IV). Table I summarizes these results. Unfortunately the crystal quality of these compounds was very poor and crystal structure determinations were not attempted.

Results and Discussion

Atomic parameters, distances, and angles are listed in Tables II–IV; an ORTEP drawing of the structure is shown in Figure 1. The uranium atom is on a crystallographic 3-fold axis and bonded to three nitrogen atoms. It is disordered in the z direction at locations 0.51 Å above and below the plane at $z = {}^1/_4$. The electron density in the channel, that runs parallel to c at the origin, is attributed to pentane solvent molecules in highly disordered arrangements.

Although $[(Me_3Si)_2N]_3UH$ is isostructural with the binary silylamides of the lanthanide derivatives which have been structurally characterized (Nd,[5] Eu,[6] and Yb[7]), the uranium is tetravalent. The uranium–nitrogen bond length of 2.24 Å is very close to those previously found for terminal, tetravalent uranium–nitrogen bond lengths in $[U(NEt_2)_4]_2$, $[U(MeNCH_2CH_2NMe)_2]_3$, $[U(MeNCH_2CH_2NMe)_2]_4$, and $[U(NPh_2)_4]$ which are 2.22,[11] 2.21,[12] 2.27,[13] and 2.24 Å,[14] respectively. The thorium(IV)–nitrogen bond length in the six-coordinate tetrahydroborate derivative $Th[N(SiMe_3)_2]_3BH_4$ is 2.32 Å.[15] The ionic radius of thorium(IV) is estimated to be ca. 0.05 Å larger than that of uranium(IV).[16] Hence, a uranium(IV)–nitrogen bond length of ca. 2.27 Å can be estimated, in good agreement with the observed value. Since the ionic radius of uranium(III) is ca. 0.08 Å longer than that of thorium(IV), a uranium(III)–nitrogen bond length can be estimated to be ca. 2.4 Å, much longer than that observed. Thus, the U–N bond length in $[(Me_3Si)_2N]_3UH$ supports the identification as a compound of tetravalent uranium.

Unfortunately, a suitable crystal for a structure determination of the uranium(III) silylamide $U[N(SiMe_3)_2]_3$ could not be obtained, but it was found to be isostructural with that of the hydride $HU[N(SiMe_3)_2]_3$. However, the larger cell dimensions and volume (Table I) of the trivalent species are consistent with the fact that uranium(III) is larger than uranium(IV). Further, the similarity of the cell dimensions and volume of the isostructural thorium hydride $[(Me_3Si)_2N]_3ThH$ with those of $[(Me_3Si)_2N]_3U$ indicates that uranium(III) is similar in size to thorium(IV).

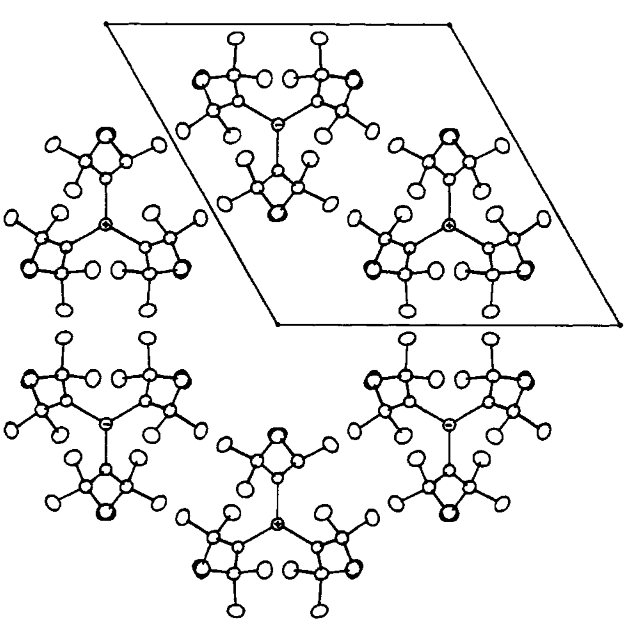

Figure 1. Packing diagram as seen down the c axis.

The hydride ion position could not be located, which is not surprising considering the usual difficulty in finding hydrogen atoms in structures containing very heavy atoms, especially in this case where the considerable disorder degrades the resolving power of the diffraction data.

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Registry No. $[(Me_3Si)_2N]_3UH$, 70605-08-2; $[(Me_3Si)_2N]_3ThH$, 70605-07-1; $U[N(SiMe_3)_2]_3$, 69927-52-2.

Supplementary Material Available: Data processing formulas and the listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Species with a Triple Molybdenum to Molybdenum Bond in Aqueous Solution

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The existence of species containing multiple molybdenum to molybdenum bonds in aqueous solutions was reported by several investigators. Bowen and Taube[1] investigated the product of the reaction between $Ba(TFM)_2$ and $Mo_2(SO_4)_4^{4-}$ in the noncomplexing acid solutions of trifluoromethylsulfonic acid (HTFM). They identified the resulting red ion as $[Mo\overset{4}{-}Mo]^{4+}(aq)$. Pernick and Ardon[2] reported the existence of a stable dimolybdenum species in the 2.5+ oxidation state

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