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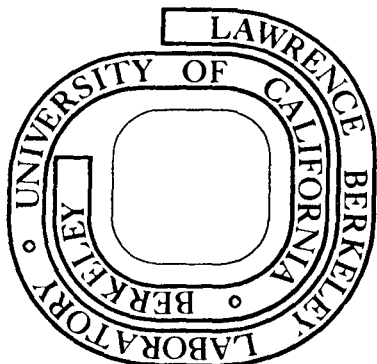
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PREPARATION AND COORDINATION CHEMISTRY

Richard A. Anderson

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Contribution from:  
Chemistry Department and  
Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

Tris(hexamethyldisilylamido) Uranium(III);  
Preparation and Coordination Chemistry

by

Richard A. Andersen

## Abstract

Red, monomeric, volatile tris(hexamethyldisilylamido) uranium(III) has been prepared from uranium trichloride [prepared from uranium tetrachloride and one molar equivalent of sodium naphthalene in tetrahydrofuran] and sodium hexamethyldisilylamide in tetrahydrofuran. The geometry of this three coordinate amide is thought to be pyramidal, analogous to that of its congener, neodymium. The tris-silylamide does not form coordination complexes with a variety of Lewis bases, though the analogous neodymium compound affords 1:1 complexes with *t*-BuNC and *t*-BuCN. The uranium amide is oxidized by molecular oxygen or trimethylamineoxide to a uranium(V) species,  $OU[N(\text{SiMe}_3)_2]_3$ . The neodymium tris-silylamide reacts with the dimethylsulfide complex of borane affording  $Nd(\text{BH}_4)_3(\text{thf})_3$ .

The trivalent oxidation state of uranium is not well known. The majority of compounds in this class are neutral or anionic complexes with ligands such as halide, carbonate, etc.<sup>1,2</sup> These are generally insoluble in common organic solvents, nonvolatile, and they are doubtless coordination polymers of some type.<sup>3</sup> The insoluble  $\eta\text{-C}_6\text{H}_6$  complex,  $(\eta\text{-C}_6\text{H}_6)\text{U}(\text{AlCl}_4)_3$ , prepared by the classic Fischer  $\pi$ -arene synthesis, has been characterized by X-ray crystallography.<sup>4</sup> The tricyclopentadienide,  $\text{Cp}_3\text{U}$ , is volatile and soluble in benzene and forms coordination complexes with tetrahydrofuran and cyclohexylisocyanide.<sup>5</sup> Dicyclopentadienideuranium cyanide has also been briefly described.<sup>6</sup>

A principal difficulty in preparation of trivalent uranium compounds is the time-consuming preparation of uranium trichloride.<sup>7</sup> This problem has been solved by reducing commercially available uranium tetrachloride with one molar equivalent of sodium naphthalene in tetrahydrofuran. The red suspension was not isolated nor further characterized, but it was used for preparation of compounds of this understudied oxidation state of uranium.

Reaction of the red suspension from uranium tetrachloride and sodium naphthalene with three molar equivalence of sodium hexamethyldisilylamide in tetrahydrofuran followed by removal of tetrahydrofuran and naphthalene yields red  $U[N(SiMe_3)_2]_3$ . The three coordinate amide is paramagnetic, monomeric and easily soluble in aliphatic hydrocarbon solvents. Physical properties of this and other compounds are shown in Table I.

Unfortunately, we have not been able to grow single crystals which are satisfactory for X-ray analysis. This is most unfortunate since tris-silylamide-metal compounds are of two structural types, viz., planar or pyramidal. The Group IIIA main group elements and the trivalent first row transition elements (titanium, vanadium, chromium, and iron) have been characterized crystallographically and are examples of planar  $MN_3$  coordination. In contrast, the trivalent Group IIIB (scandium) and 4f-series elements (neodymium, europium, and ytterbium) are examples of pyramidal  $MN_3$  coordination.<sup>8,9</sup> The volatility of the uranium and neodymium compounds, 80-100°C and 80-90°C in vacuum, respectively, and the monomer molecular ions in gas phase mass spectra strongly suggests that these compounds are isostructural in gas phase. The great similarity of the infrared absorption spectra in the solid phase

of these two compounds further suggests that they are isostructural in solid. Thus a pyramidal  $UN_3$  skeleton is implicated. Table II lists some infrared vibrational frequencies assigned by Bradley for scandium through iron using a previous analysis by Bürger for the Group IIIA metal compounds.<sup>10,11</sup> The absorptions for neodymium, europium, and uranium have been assigned by analogy with these earlier assignments. It is apparent that the  $\nu_{asy} MNSi_2$  stretching frequencies for the tris-silylamides which are pyramidal lie ca. 50-100  $cm^{-1}$  greater than those for the amides which are planar. This further strengthens our contention that  $U[N(SiMe_3)_2]_3$  is pyramidal.

Since  $M[N(SiMe_3)_2]_3$ ,  $M = La, Eu, \text{ or } Lu$ , form 1:1 coordination complexes with triphenylphosphineoxide, the coordination chemistry of the uranium analogue was of interest.<sup>15</sup> Much to our surprise  $U[N(Me_3Si)_2]_3$  has no coordination chemistry. It does not yield isolatable complexes with carbon monoxide, trimethylphosphine, trimethylphosphine oxide, tetrahydrofuran, trimethylamine, pyridine, t-butylisocyanide, nor t-butylcyanide at room temperature and atmospheric pressure. The coordination behavior of  $Nd[N(SiMe_3)_2]_3$  provides a useful comparison since neodymium lies directly above uranium in Periodic Table. It has a meager coordination chemistry, forming 1:1 complexes only with t-butylcyanide and t-butylisocyanide of the Lewis bases listed. The general lack of Lewis acidity of these two metals is most readily accounted for by steric effects, the metal being effectively surrounded by voluminous silylamide ligands. The existence of complexes with the cyanide and isocyanide ligands, where the bulky t-butyl groups are far

removed from the coordinating atom, for neodymium and their inability to yield coordination complexes with uranium cannot be due to steric hindrance. Indeed, uranium should be a better acceptor since it is larger than neodymium, the trivalent ionic radii being 102 nm and 98 nm, respectively, and therefore better able to increase its coordination number.<sup>16</sup> Hence, an alternative explanation must be found. We would like to suggest that the difference in coordinative affinity is due to the difference in electronegativity of the metal atoms. Regardless what scale is used, the electronegativity of neodymium is less than that of uranium. For example, a scale devised by Allred shows the electronegativity of neodymium to be 1.1 and that of uranium to be 1.4.<sup>17</sup> The neodymium atom is more electropositive and, accordingly, a better acid to a reference base, like t-BuNC.

The Lewis base, trimethylamine oxide, reacts with  $U[N(\text{SiMe}_3)_2]_3$ , yielding the pentavalent amide,  $OU[N(\text{SiMe}_3)_2]_3$ . The oxide does not sublime but is readily soluble in aromatic solvents. The oxo-amide can be rather more conveniently prepared from molecular oxygen and the tris-silylamide. Not surprisingly the neodymium compound is stable to oxidation.

The neodymium amide provides a convenient route to the tetrahydroborate,  $\text{Nd}(\text{BH}_4)_3(\text{thf})_3$ , on reaction with  $\text{BH}_3(\text{SMe}_2)$ . The complex is insoluble in hydrocarbon and ethereal solvents, except tetrahydrofuran, from which it crystallizes. Curiously, the tetrahydroborate has not been described previously, as it could not be obtained from lithium tetrahydroborate and neodymium trichloride.<sup>18</sup> The infrared spectrum (Table I) is essentially identical to that of the analogous erbium complex<sup>19</sup> and indicative of tridentate



coordination.<sup>20</sup> However, care must be used when deducing denticity from infrared data when more than one tetrahydroborate group is present in a molecule. This is well illustrated by  $Y(BH_4)_3(thf)_3$ , which contains one bidentate and two tridentate tetrahydroborate groups.<sup>21</sup> The uranium silylamide does not yield a isolatable substance with  $BH_3SMe_2$ .

### Experimental Section

Analyses were by the microanalytical laboratory of this department. Solution magnetic susceptibilities were measured on a Varian T-60 machine operating at 37°C by Evans' method.<sup>22</sup> Solid state magnetic susceptibility measurements were obtained on a PAR model 155 vibrating sample magnetometer employing a homogeneous magnetic field capable of a maximum field strength of 12.5 K G. The magnetometer was calibrated with  $HgCo(NCS)_4$ .<sup>23</sup> All operations were performed under nitrogen.

Tris(Hexamethyldisilylamido) Uranium(III). Naphthalene (1.50 g, 0.0117 mol) dissolved in tetrahydrofuran (30 mL) was added to sodium (0.270 g, 0.0117 mol) suspended in tetrahydrofuran (10 mL). After stirring the green solution for 8 h, it was added to a solution of uranium tetrachloride (4.10 g, 0.0108 mol) in tetrahydrofuran (50 mL). The bright red suspension was stirred for 24 h. Sodium hexamethyldisilylamide (5.93 g, 0.0324 mol) in tetrahydrofuran (50 mL) was added to the suspension which was stirred for 12 h. The volatile material was removed in vacuum and the residue was extracted with pentane (3 x 100 mL). The combined extracts were evaporated to dryness and naphthalene was sublimed (40°C/10<sup>-2</sup> torr). Pentane (150 mL) was added to the residue and the red solution

was filtered, concentrated to ca. 50 mL in vacuum, and cooled (-10°C). The red prisms, 4.5 g (76%) were collected and dried in vacuum. The compound sublimed at 80-100°C/10<sup>-3</sup> torr. Anal. Calcd. for C<sub>18</sub>H<sub>56</sub>N<sub>3</sub>Si<sub>6</sub>U: C, 30.1; H, 7.52; N, 5.85. Found: C, 29.8; H, 7.58; N, 5.77.

Oxo Tris(Hexamethyldisilylamido) Uranium(V). (a) From Trimethylamineoxide. Tris(hexamethyldisilylamido) uranium (1.9 g, 0.0027 mol) dissolved in pentane (30 mL) was added to anhydrous trimethylamine oxide (0.20 g, 0.0027 mol) suspended in pentane (20 mL). The smell of trimethylamine was readily detected. The brown-red solution was stirred for 24 h, evaporated to dryness in vacuum, and residue was crystallized from toluene (-10°C) as green-yellow prisms. Yield was 1.0 g (51%). Anal. Calcd. for C<sub>18</sub>H<sub>54</sub>N<sub>3</sub>OSi<sub>6</sub>U: C, 29.4; H, 7.36; N, 5.72. Found: C, 29.4; H, 6.95; N, 5.72.

(b) From Molecular Oxygen. Molecular oxygen was passed (ca. 5 min) through a solution of tris(hexamethyldisilylamido) uranium (1.0 g, 0.0014 mol) in toluene (30 mL). The brown-red solution was evaporated to dryness in vacuum and the residue was crystallized as green-yellow prisms from toluene, yield 0.50 g (50%). The mp, ir, and NMR spectra were identical to those of the authentic specimen.

Tris(Hexamethyldisilylamido)Neodymium(III)-t-Butylcyanide. t-Butylcyanide (0.16 g, 0.0019 mol) in pentane (5 mL) was added to a solution of tris(hexamethyldisilylamido)neodymium (1.0 g, 0.0016 mol) in pentane (30 mL). The blue solution was stirred for 24 h, evaporated to dryness and residue was crystallized from pentane as pale blue prisms in quantitative yield. Anal. Calcd. for C<sub>23</sub>H<sub>63</sub>N<sub>4</sub>NdSi<sub>6</sub>: C, 39.0; H, 8.91; N, 7.92. Found: C, 39.6; H, 8.61; N, 7.93.

Tris(Hexamethyldisilylamido)Neodymium(III)-t-Butylisocyanide.

t-Butylisocyanide (0.15 g, 0.0018 mol) in pentane (5 mL) was added to a solution of tris (hexamethyldisilylamido)neodymium (0.90 g, 0.0014 mol) in pentane (30 mL). The blue solution was stirred for 24 h, evaporated to dryness in vacuum, and residue was crystallized from pentane as light blue prisms in quantitative yield. Anal. Calcd. for  $C_{23}H_{63}N_4NdSi_6$ : C, 39.0; H, 8.91; N, 7.92. Found: C, 39.5; H, 8.03; N, 8.03.

Tris(Tetrahydroborato)Neodymium(III)-Tris(Tetrahydrofuran).

The dimethylsulfide complex of borane (0.40 g, 0.0053 mol) in pentane (30 mL) was added to tris(hexamethyldisilylamido)neodymium (0.70 g, 0.001 mol), dissolved in pentane (30 mL). A pale blue precipitate formed immediately. The suspension was stirred for 24 h, evaporated to dryness in vacuum, and residue was crystallized from tetrahydrofuran (-10°C) as light blue needles. Yield was 0.40 g. Anal. Calcd. for  $C_{12}H_{36}B_3NdO_3$ : C, 35.6; H, 8.90. Found: C, 35.9; H, 8.76.

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Table I

Physical Properties

<u>Compound</u>	<u>m.p. (°C)</u>	<u><math>\mu_{\text{eff}}</math> (B.M.)</u>	<u><math>^1\text{H}</math> NMR</u>	<u>Area Ratio</u>	<u>Infrared<sup>j</sup></u>
$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{U}$	137-140	2.51 <sup>a</sup>	$\delta$ -18.1 <sup>b</sup>	--	--
$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{UO}$	157-159	1.82 <sup>c</sup>	$\delta$ 0.44 <sup>d</sup>	--	$\nu_{\text{UO}}$ , 930
$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{NdNC-t-Bu}$	143-144	3.3 <sup>e</sup>	$\delta$ 1.45 <sup>f</sup> , -8.11 <sup>g</sup>	54:9	$\nu_{\text{NC}}$ , 2250
$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{NdCN-t-Bu}$	140-141	3.2 <sup>e</sup>	$\delta$ 2.30 <sup>h</sup> , -7.70 <sup>i</sup>	54:9	$\nu_{\text{CN}}$ , 2195
$(\text{BH}_4)_3\text{Nd}(\text{thf})_3$	161-163	--	--	--	$\nu_{\text{BH}_4}$ , 2440s, 2310w, 2220s, 2170m

(a) Follows Curie-Weiss Law ( $\chi = \frac{C_M}{T+\theta}$ ,  $C_M = 1.64$ ,  $\theta = -10.5\text{K}$ ) from 10 to 70K.

(b) In benzene, width at half-height 9 Hz.

(c) Follows Curie-Weiss Law ( $\chi = \frac{C_M}{T+\theta}$ ,  $C_M = 0.413$ ,  $\theta = -7.6\text{K}$ ) from 10 to 50K.

(d) In benzene.

(e) Evans' method in benzene.

(f) In benzene, width at half-height 14 Hz.

(g) In benzene, width at half-height 4 Hz.

(h) In benzene, width at half-height 11 Hz.

(i) In benzene, width at half-height 3 Hz.

(j) Nujol mulls, in  $\text{cm}^{-1}$ .

Table II. Selected Infrared Absorptions in Compounds of Type  $M[N(\text{SiMe}_3)_2]_3$

Metal	$\nu_{\text{asy}}^{\text{MNSi}_2}$ (a)	$\nu_{\text{sym}}^{\text{MNSi}_2}$ (a,b)	$\nu_{\text{MN}_3}$ (a)	Crystallographic Reference	Infrared Reference
Al	906	840	390,392	12	11
Ga	913	825	388,375	8	11
Ti	899	820,787	422,380	8	10
V	902	820,790	418	8	10
Cr	902	820,790	420,376	8	10
Fe	902	820,790	420,376	13	10
Sc	950	820,780	420,382	14	10
Nd	995	810,765	381,369	9	<del>this work</del>
Eu	985	815,770	383,371	14	<del>this work</del>
U	990	812,765	380,366	not known	<del>this work</del>

(a)  $\text{cm}^{-1}$

(b) First number is a shoulder, second a strong absorption.

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