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

Tris((hexamethyldisilyl)amido)uranium(III): Preparation and Coordination Chemistry

RICHARD A. ANDERSEN

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Red, monomeric, volatile tris((hexamethyldisilyl)amido)uranium(III) has been prepared from uranium trichloride (prepared from uranium tetrachloride and 1 molar equiv of sodium naphthalene in tetrahydrofuran) and sodium (hexamethyldisilyl)amide 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 trimethylamine oxide to a uranium(V) species, $OU[N(SiMe_3)_2]_3$. The neodymium tris(silylamide) reacts with the dimethyl sulfide complex of borane affording $Nd(BH_4)_3(THF)_3$.

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.[1,2] These are generally insoluble in common organic solvents, are nonvolatile, and are doubtless coordination polymers of some type.[3] The insoluble η-C_6H_6 complex $(\eta\text{-}C_6H_6)U(AlCl_4)_3$, prepared by the classic Fischer π-arene synthesis, has been characterized by X-ray crystallography.[4] The tricyclopentadienide, Cp_3U, is volatile and soluble in benzene and forms coordination complexes with tetrahydrofuran and cyclohexyl isocyanide.[5] Dicyclopentadienyluranium cyanide has also been briefly described.[6]

A principal difficulty in preparation of trivalent uranium compounds is the time-consuming preparation of uranium trichloride.[7] This problem has been solved by reducing commercially available uranium tetrachloride with 1 molar equiv of sodium naphthalene in tetrahydrofuran. The red suspension was not isolated nor further characterized, but it was used for the preparation of compounds of this understudied oxidation state of uranium.

Reaction of the red suspension from uranium tetrachloride and sodium naphthalene with 3 molar equiv of sodium (hexamethyldisilyl)amide 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 3A 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 3B (scandium) and 4f-series (neodymium, europium, and ytterbium) elements are examples of pyramidal MN_3 coordination.[8,9] The volatility of the uranium and neodymium compounds, 80–100 °C and 80–90 °C under vacuum, respectively, and the monomeric molecular ions in gas-phase mass spectra strongly suggest 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 form. Thus a pyramidal UN_3 skeleton is implicated. Table II lists some infrared vibrational frequencies assigned by Bradley for scandium through iron by using a previous analysis by Bürger for the group 3A metal compounds.[10,11] The absorptions for neodymium, europium, and uranium have been assigned by analogy with these earlier assignments. It is apparent that the $\nu_{as}(MNSi_2)$ stretching frequencies for the tris(silylamides) which are pyramidal lie ca. 50–100 cm^{-1} higher 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, or Lu, forms 1:1 coordination complexes with triphenylphosphine oxide, the coordination chemistry of the uranium analogue was of interest.[15] Much to our surprise, $U[N(Me_3Si)_2]_3$ has no coordination chemistry. It does not yield isolable complexes with carbon monoxide, trimethylphosphine, trimethylphosphine oxide, tetrahydrofuran, trimethylamine, pyridine, *tert*-butyl isocyanide, nor *tert*-butyl cyanide 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 the periodic table. It has a meager coordination chemistry, forming 1:1 complexes only with *tert*-butyl cyanide and *tert*-butyl isocyanide, 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 *tert*-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 and 98 nm, respectively, and therefore better able to increase its coordination number.[16] 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.[17] 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 $U[N(SiMe_3)_2]_3$, yielding the pentavalent amide $OU[N(SiMe_3)_2]_3$. The oxide does not sublime but is readily soluble in aromatic solvents. The oxoamide 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 $Nd(BH_4)_3(THF)_3$ on reaction with $BH_3(SMe_2)$. 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.[18] The infrared spectrum (Table I) is essentially identical to that of the analogous erbium complex[19] and indicative of tridentate coordination.[20] However, care must be used when deducing

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Table I. Physical Properties

compd	mp, °C	μ_{eff}, μ_B	^{1}H NMR, δ	area ratio	IR[j]
$[(Me_3Si)_2N]_3U$	137–140	2.51[a]	−18.1[b]		
$[(Me_3Si)_2N]_3UO$	157–159	1.82[c]	0.44[d]		ν_{UO} 930
$[(Me_3Si)_2N]_3Nd(NC\text{-}t\text{-}Bu)$	143–144	3.3[e]	1.45,[f] −8.11[g]	54:9	ν_{NC} 2250
$[(Me_3Si)_2N]_3Nd(CN\text{-}t\text{-}Bu)$	140–141	3.2[e]	2.30,[h] −7.70[i]	54:9	ν_{CN} 2195
$(BH_4)_3Nd(THF)_3$	161–163				ν_{BH_4} 2440 s, 2310 w, 2220 s, 2170 m

[a] Follows Curie–Weiss law ($\chi = C_M/(T + \Theta)$; $C_M = 1.64$; $\Theta = -10.5$ K) from 10 to 70 K. [b] In benzene; width at half-height 9 Hz. [c] Follows Curie–Weiss law ($\chi = C_M/(T + \Theta)$; $C_M = 0.413$; $\Theta = -7.6$ K) from 10 to 50 K. [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 cm^{-1}.

Table II. Selected Infrared Absorptions in Compounds of Type $M[N(SiMe_3)_2]_3$

metal	ν_{as}[a] $(MNSi_2)$	ν_s[a,b] $(MNSi_2)$	ν_{MN_3}[a]	crystallogr ref	IR ref
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	this work
Eu	985	815, 770	383, 371	14	this work
U	990	812, 765	380, 366	not known	this work

[a] cm^{-1}. [b] First number is a shoulder and second a strong absorption.

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.[21] The uranium silylamide does not yield an isolable 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.[22] 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 kG. The magnetometer was calibrated with $HgCo(NCS)_4$.[23] All operations were performed under nitrogen.

Tris((hexamethyldisilyl)amido)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 the green solution was stirred 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 (hexamethyldisilyl)amide (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 under vacuum, and the residue was extracted with pentane (3 × 100 mL). The combined extracts were evaporated to dryness and naphthalene was sublimed (40 °C (10^{-2} torr)). Pentane (150 mL) was added to the residue, and the red solution was filtered, concentrated to ca. 50 mL under vacuum, and cooled (−10 °C). The red prisms, 4.5 g (76%), were collected and dried under vacuum. The compound sublimed at 80–100 °C (10^{-3} torr). Anal. Calcd for $C_{18}H_{56}N_3Si_6U$: C, 30.1; H, 7.52; N, 5.85. Found: C, 29.8; H, 7.58; N, 5.77.

Oxotris((hexamethyldisilyl)amido)uranium(V). (a) From Trimethylamine Oxide. Tris((hexamethyldisilyl)amido)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 and evaporated to dryness under vacuum, and the residue was crystallized from toluene (−10 °C) as green-yellow prisms, yield 1.0 g (51%). Anal. Calcd for $C_{18}H_{54}N_3OSi_6U$: 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((hexamethyldisilyl)amido)uranium (1.0 g, 0.0014 mol) in toluene (30 mL). The brown-red solution was evaporated to dryness under vacuum, and the residue was crystallized as green-yellow prisms from toluene; yield 0.50 g (50%). The melting point and IR and NMR spectra were identical to those of the authentic specimen.

Tris((hexamethyldisilyl)amido)neodymium(III)–*tert*-Butyl Cyanide. *tert*-Butyl cyanide (0.16 g, 0.0019 mol) in pentane (5 mL) was added to a solution of tris((hexamethylsilyl)amido)neodymium (1.0 g, 0.0016 mol) in pentane (30 mL). The blue solution was stirred for 24 h and evaporated to dryness, and the residue was crystallized from pentane as pale 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, 39.6; H, 8.61; N, 7.93.

Tris((hexamethyldisilyl)amido)neodymium(III)–*tert*-Butyl Isocyanide. *tert*-Butylisocyanide (0.15 g, 0.0018 mol) in pentane (5 mL) was added to a solution of tris((hexamethyldisilyl)amido)neodymium (0.90 g, 0.0014 mol) in pentane (30 mL). The blue solution was stirred for 24 h and evaporated to dryness under vacuum, and the 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, 8.93; N, 8.03.

Tris(tetrahydroborato)neodymium(III)–Tris(tetrahydrofuran). The dimethyl sulfide complex of borane (0.40 g, 0.0053 mol) in pentane (30 mL) was added to tris((hexamethyldisilyl)amido)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 and evaporated to dryness under vacuum, and residue was crystallized from tetrahydrofuran (−10 °C) as light blue needles, yield 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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Registry No. $[(Me_3Si)_2N]_3U$, 69927-52-2; $[(Me_3Si)_2N]_3UO$, 69927-53-3; $[(Me_3Si)_2N]_3Nd(NC\text{-}t\text{-}Bu)$, 69942-15-0; $[(Me_3Si)_2N]_3Nd(CN\text{-}t\text{-}Bu)$, 69942-16-1; $(BH_4)_3Nd(THF)_3$, 69942-17-2; $[(Me_3Si)_2N]_3Nd$, 41836-23-1; $[(Me_3Si)_2N]_3Eu$, 35789-02-7; uranium tetrachloride, 10026-10-5; sodium (hexamethyldisilyl)amide, 1070-89-9.

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Contribution from the Michael Faraday Laboratories, Department of Chemistry,
Northern Illinois University, DeKalb, Illinois 60115

Fluoro-Containing Complexes of Chromium(III). 9. Resolution and Some Anation Reactions of the *cis*-Fluoroaquobis(ethylenediamine)chromium(III) Cation[1]

JOE W. VAUGHN* and GARY J. SEILER

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The racemic cation *cis*-fluoroaquobis(ethylenediamine)chromium(III) was resolved into its chiral forms by the use of the $(+)_{5890}$-bromocamphor-π-sulfonate anion. The absolute configurations of the chiral forms were established by use of optical rotatory dispersion spectral studies. For the least soluble product, anation of the optical isomers with thiocyanate or fluoride ion in the solvent methyl alcohol takes place with retention of absolute configuration.

Introduction

The *cis*-fluoroaquobis(ethylenediamine)chromium(III) cation was first isolated as a solid salt in 1976.[2] The arrangement of the fluoro and aquo ligands in this complex was deduced from the method of synthesis and from electronic spectral studies. The purpose of this investigation was to provide unequivocal evidence for the cis geometry by resolving the complex into its optical forms. In addition, some anation reactions of the optical isomers were to be studied to determine if such reactions took place with retention of absolute configuration, isomerization, or racemization.

Experimental Section

cis-[Cr(en)$_2$F(OH$_2$)]I$_2$·H$_2$O. This complex was prepared as described.[2] The entire sample, 8.5 g (17.5 mmol), was dissolved in 7 mL of water at room temperature. The resulting solution was filtered to remove a small amount of insoluble material, and the filtrate was cooled in an ice bath for 1 h. The cooled filtrate was stirred frequently during this time. At the end of 1 h the orange solid was collected, washed with acetone, and air-dried; yield 2.7 g, 32%. Anal. Calcd for cis-[Cr(en)$_2$F(OH$_2$)]I$_2$·H$_2$O: C, 9.99; H, 4.20; N, 11.65; Cr, 10.8. Found: C, 9.94; H, 4.22; N, 11.45; Cr, 11.2. The electronic absorption spectrum was in good agreement with the literature values.[2]

A rapidly stirred solution of 1.11 g (2.3 mmol) of recrystallized cis-[Cr(en)$_2$F(OH$_2$)]I$_2$·H$_2$O in 10 mL of water was diluted in a dropwise fashion with a filtered solution of 1.62 g (4.75 mmol) of sodium tetraphenylborate in 5 mL of water. A pink precipitate formed at once when the tetraphenylborate solution was added. Another 20 mL of water was added to the reaction mixture, and the stirring was continued for an additional 10 min. The product was collected, washed with 10 mL of ice water, and air-dried for 2 h; yield 1.59 g, 79%. Anal. Calcd for cis-[Cr(en)$_2$F(OH$_2$)][(C$_6$H$_5$)$_4$B]$_2$·1.5H$_2$O: C, 71.2; H, 6.95; N, 6.40; Cr, 5.95; F, 2.16. Found: C, 72.0; H, 7.20; N, 6.48; Cr, 5.85; F, 2.21. This synthesis has produced some erratic results in that the amount of hydrated water varies greatly depending on the drying conditions.

Resolution of cis-[Cr(en)$_2$F(OH$_2$)]I$_2$·H$_2$O. A 4.85 g (10 mmol) sample of recrystallized (±)-cis-[Cr(en)$_2$F(OH$_2$)]I$_2$·H$_2$O in 5–6 mL of water was added with constant stirring to a filtered solution of 6.57 g (20 mmol) of ammonium d-α-bromocamphor-π-sulfonate in 30 mL of water. The reaction mixture was allowed to stand overnight at room temperature; the pink precipitate was collected, washed with acetone, and air-dried; yield 3.0 g, 71%. The entire sample of crude material was recrystallized from 35 mL of water at 60 °C; yield 1.08 g, 36%. Anal. Calcd for [Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O: C, 34.00; H, 5.67; N, 6.61; Cr, 6.13; F, 2.24. Found: C, 33.87; H, 5.60; N, 6.47; Cr, 6.20; F, 2.29. The optical rotatory dispersion spectrum of the complex was determined by using the following conditions: 0.2% aqueous solution of the complex, 0.100-dm cell, room temperature. The optical rotatory dispersion spectrum was characterized by α_x (α = specific rotation, x = wavelength in nm): α_{589} 57°; α_{553} 0°; α_{546} −38.0°; α_{520} −93°; α_{495} 0°. The entire sample was recrystallized from 9 mL of water at 60 °C. The optical rotations and elemental analysis did not change upon recrystallization. The electronic absorption spectrum of an aqueous solution of the complex was characterized by λ_{max} 503 nm (ϵ 72.5 M^{-1} cm^{-1}), λ_{min} 428 (ϵ 16.8), and λ_{max} 373 (ϵ 33.2).

A sample of recrystallized $(-)_{5461}$-cis-[Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O lost no weight when dried over anhydrous magnesium perchlorate at room temperature and 0.05 torr for 18 h. In addition, the electronic spectra, molar absorptivities, and optical rotatory dispersion spectra of the undried and dried samples were identical within experimental error. However, the complex did lose 2 mol of water/formula weight of the complex when the material was dried at 120 °C for 18 h. Anal. Calcd for [Cr(en)$_2$F(C$_{10}$H$_{14}$O$_4$BrS)](C$_{10}$H$_{14}$O$_4$BrS): C, 35.4; H, 5.45; N, 6.90; H$_2$O, 4.25. Found: C, 35.50; H, 5.50; N, 6.74; H$_2$O, 4.30. The optical rotatory dispersion spectrum of an aqueous solution of the heated material was nearly identical with that of an aqueous solution of pure ammonium d-α-bromocamphor-π-sulfonate of comparable concentration. The electronic spectrum of an aqueous solution of the dehydrated complex was characterized by λ_{max} 505 nm (ϵ 74.5), λ_{min} 430 (ϵ 20.7), and λ_{max} 373 (ϵ 38.6).

A 0.71-g (0.83-mmol) sample of recrystallized $(-)_{5461}$-cis-[Cr(en)$_2$F(OH$_2$)][(+)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O was dissolved in 25 mL of water at room temperature. The solution was filtered, and the filtrate was treated with a filtered solution of 1.32 g (3.85 mmol) of sodium tetraphenylborate as described previously; yield 0.40 g, 55%. Anal. Calcd for $(-)_{5461}$-cis-[Cr(en)$_2$F(OH$_2$)][(C$_6$H$_5$)$_4$B]$_2$·1.5H$_2$O: C, 71.2; H, 6.95; N, 6.40; Cr, 5.95; F, 2.16. Found: C, 72.0; H, 7.29; N, 6.22; Cr, 6.07; F, 1.75. The optical rotatory dispersion spectrum of a 0.3% solution of the complex in acetone was determined as described previously: α_{589} 0°; α_{546} −186°; α_{520} −162°; α_{500} 0°; α_{535} −200°; α_{460} 172°.

The resolution was repeated by using 1.0 g (2.06 mmol) of (±)-cis-[Cr(en)$_2$F(OH$_2$)]I$_2$·H$_2$O and 1.41 g (4.3 mmol) of the ammonium salt of l-α-bromocamphor-π-sulfonic acid as the resolving agent. The method was a scaled-down version of that described previously; yield 0.372 g, 43%. Anal. Calcd for $(+)_{5461}$-cis-[Cr(en)$_2$F(OH$_2$)][(−)-C$_{10}$H$_{14}$O$_4$BrS]$_2$·H$_2$O: C, 34.00; H, 5.67; N, 6.61; F, 2.24. Found: C, 34.10; H, 5.80; N, 7.08; F, 2.22. The entire sample was recrystallized from 3.5 mL of water at 60 °C; yield 0.103 g, 28%. The optical rotatory dispersion spectrum of 0.3% aqueous solution of the compound was characterized by α_{589} −49°, α_{556} 0°, α_{546} 39.0°, α_{520} 97°, and α_{494} 0°.

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