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Triamidotriazacyclononane Complexes of Group 3 Metals. Synthesis and Crystal Structures

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Reaction of yttrium and lanthanide trichlorides (Ln = La, Eu, Yb) with 1 equiv of the trisodium salt of 1,4,7-tris(dimethylsilylaniline)-1,4,7-triazacyclononane ($Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$) gives good yields of the compounds $[M\{(SiMe_2NPh)_3\text{-tacn}\}]$ (M = Y (**1**), Eu (**3**), Yb (**4**)) and $[La\{(SiMe_2NPh)_3\text{-tacn}\}(THF)]$ (**2**). Reduction of **3** with Na/Hg followed by recrystallization in the presence of diglyme yielded crystals of $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}][Na(diglyme)_2]$ (**5**). Synthesis of the uranium(III) complex $[U\{(SiMe_2NPh)_3\text{-tacn}\}]$ (**6**) is achieved by reaction of 1 equiv of $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$ with uranium triiodide. The U(IV) complexes, $[U\{(SiMe_2NPh)_3\text{-tacn}\}X]$ (X = Cl (**7**); I (**8**)), were prepared via oxidation of **6** with benzyl chloride or I_2, but salt metathesis from UCl_4 provided a higher yield route for **7**. The solid-state structures of **1**–**7** were determined by single-crystal X-ray diffraction. The ligand $[(SiMe_2NPh)_3\text{-tacn}]$ generates a trigonal prismatic coordination environment for the metal center in the neutral complexes **1, 3**, **4**, and **6** and the ionic **5**. In **2** the six nitrogen atoms of the ligand are in a trigonal prismatic configuration with the oxygen atom of the THF capping one of the triangular faces of the trigonal prism. In **7** the coordination geometry around the uranium atom is best described as bicapped trigonal bipyramidal.

Introduction

During the past decade there has been a renewal of interest in the coordination chemistry of lanthanides with macrocyclic ligands. This is due to the diverse array of applications that their metal complexes have found as contrast-enhancing agents in nuclear magnetic resonance imaging,[1] as luminescent probes in medicine and biology,[2] as radiometal-labeled agents for diagnostic imaging,[3] as catalysts[4,5] and in the separation of the lanthanides.[6]

1,4,7-Triazacyclononane-based ligands are becoming increasingly popular due to the ease with which this macrocycle can be derivatized at the nitrogen atoms to yield C_3-symmetric N,N',N''-trisubstituted ligands, which can bind in a facial fashion to a wide range of metals.[7] Although widely used and established as an important class for the main group and transition elements, only a few complexes of tacn-based ligands with group 3 metals have been structurally characterized. Recently, a low-valent uranium(III) complex supported by an aryloxide functionalized triazacyclononane, $[((ArO)_3tacn)U]$, has been synthesized.[8] Attempts to recrystallize this compound from pentane and solutions of Et_2O or THF yielded mono- and dinuclear seven-coordinate uranium(IV) complexes, $[((ArO)_3tacn)U(OAr)]$ and $[\{((ArO)_3tacn)U\}_2(\mu\text{-O})]$, that have been structurally characterized.[8] Other reports include the synthesis of Sc, Y, and Lu complexes with neutral 1,4,7-triazacyclononane ligands

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(1,4,7-tris(carbamoylmethyl)-1,4,7-triazacyclononane (TMCT), M = Y, Lu, and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3-tacn), M = Sc, Y)[4,9] and the X-ray structural characterization of $[Y(TMCT)(CF_3SO_3)_2(H_2O)](CF_3SO_3)$[9] and $[(Me_3\text{-tacn})ScCl_3]$.[4] Two yttrium dialkyl complexes with linked 1,4,7-triazacyclononane−amido monoanionic ancillary ligands, $[\{(R)_2\text{-tacn-}(CH_2)_2NBu^t\}Y(CH_2SiMe_3)_2]$ (R = Me, Pr^i), have also been reported.[5] In addition, the synthesis and structural characterization of lanthanide complexes LnL (Ln = La, Sm, Yb) of a nonadentate ligand derived from 1,4,7-triazacyclononane (L = $[O_2CC(Me)N(CH_2)_2]_3$tacn) have been described.[10] The X-ray crystal structure of a Eu complex, $[Eu(HL)]Cl{\cdot}10H_2O$, where L is a tacn unit incorporating bipyridine arms, with each subunit bearing a negatively charged carboxylate group, is also known.[11] Because of the interesting photophysical properties of the Eu and Tb complexes with this ligand, they have been used as the basis for luminescent probes for bioaffinity assays that rely on TR luminescence measurements.[11]

In recent years, a rich chemistry of f elements involving quadridentate triamidoamine ligands has emerged.[12−19] This stimulated our interest in the use of the somewhat related trianionic 1,4,7-triazacyclononane−amido ligands as ancillaries in the chemistry of group 3 metals. In this paper we report full details on the synthesis and characterization of a range of trivalent $[M\{(SiMe_2NPh)_3\text{-tacn}\}(THF)_x]$ complexes (M = Y, Eu, Yb, U, $x = 0$; La, $x = 1$). The synthesis and characterization of the U(IV) compounds, $[U\{(SiMe_2NPh)_3\text{-tacn}\}X]$ (X = Cl, I) and of the divalent europium compound, $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}][Na(diglyme)_2]$, are also described. The solid-state X-ray structures of several members have been determined, and a detailed structural comparison is provided.

Experimental Section

General Procedures. All preparations and subsequent manipulations were carried out using standard Schlenk line and drybox techniques in an atmosphere of dinitrogen. THF, toluene, and *n*-hexane were dried by standard methods and degassed prior to use. Toluene-d_8 was dried over Na and distilled, and dichloromethane-d_2 was vacuum distilled from P_2O_5. $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$,[20] $LnCl_3(THF)_x$[21] (Y, $x = 2.5$; La, $x = 1.5$), $LnCl_3$ (Ln = Eu, Yb),[22] $UI_3(THF)_4$[23] and UCl_4[24] were prepared by published procedures. The THF content for the yttrium and lanthanum trichlorides and the uranium triiodide was established by elemental analysis. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-300 spectrometer at 300 and 75 MHz, respectively. Spectra were referenced internally using the residual proton resonances relative to tetramethylsilane (toluene-d_8, 2.09 ppm; dichloromethane-d_2, 5.32 ppm). Carbon, hydrogen, and nitrogen analyses were performed in-house using a EA110 CE Instruments automatic analyzer.

Synthetic Procedures. $[Y\{(SiMe_2NPh)_3\text{-tacn}\}]$ (1). $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$ (402 mg, 0.51 mmol) in THF solution was slowly added to a suspension of $YCl_3(THF)_{2.5}$ (192 mg, 0.51 mmol) in THF. After stirring overnight, the NaCl formed was discharged and the solution evaporated to dryness. The beige solid obtained was washed with *n*-hexane. Yield: 80% (270 mg, 0.41 mmol). Elemental anal. Calcd for $YSi_3C_{30}H_{45}N_6$: C, 54.36; H, 6.84; N 12.68. Found: C, 53.75; H, 6.55; N, 12.19.

^1H NMR (toluene-d_8, 20 °C): 7.04 (6H, m, H-*m*), 6.75 (6H, m, H-*o*), 6.72 (3H, *m*, H-*p*), 2.77 (6H, m, CH_2), 2.24 (6H, m, CH_2), 0.27 (18H, s, $SiMe_2$).

^{13}C NMR (toluene-d_8, 20 °C): 153.3 (C_{ipso}), 129.6 (C-*m*), 121.8 (C-*o*), 117.6 (C-*p*), 48.4 (C-ring), 0.0 (C-Si*Me*$_2$).

Crystallization from toluene gives colorless crystals of $\mathbf{1}{\cdot}C_6H_5Me$.

$[La\{(SiMe_2NPh)_3\text{-tacn}\}(THF)]$ (2). The compound was prepared as described for **1**, by adding 363 mg (0.46 mmol) of $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$ to a solution of $LaCl_3(THF)_{1.5}$ (163 mg, 0.46 mmol) in THF. The beige solid was obtained with a yield of 80% (290 mg, 0.37 mmol). Elemental anal. Calcd for $LaSi_3C_{34}H_{53}N_6O$: C, 52.02; H, 6.81; N, 10.71. Found: C, 51.57; H, 6.64; N, 10.57.

^1H NMR (toluene-d_8, 20 °C): 7.15 (6H, *m*, H-*m*), 6.88 (6H, *m*, H-*o*), 6.73 (3H, *m*, H-*p*), 3.33 (4H, THF), 3.03 (6H, *m*, CH_2), 2.38 (6H, *m*, CH_2), 1.10 (4H, THF), 0.29 (18H, $SiMe_2$).

^{13}C NMR (toluene-d_8, 20 °C): 155.7 (C_{ipso}), 129.1 (C-*m*), 124.0 (C-*o*), 117.5 (C-*p*), 68.1 (THF), 48.4 (C-ring), 24.9 (THF), 0.0 (C−Si*Me*$_2$).

Crystallization from toluene gives colorless crystals of **2**.

$[Eu\{(SiMe_2NPh)_3\text{-tacn}\}]$ (3). The compound was synthesized as described for **1** using 101 mg (0.39 mmol) of $EuCl_3$ and 308 mg (0.39 mmol) of $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$. The red compound was isolated in 74% yield (210 mg, 0.29 mmol). Crystallization from toluene gives red-orange crystals of $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}]{\cdot}0.5C_6H_5Me$. Elemental anal. Calcd for $EuSi_3C_{30}H_{45}N_6{\cdot}0.5C_7H_8$: C, 52.62; H, 6.40; N, 10.80. Found: C, 52.19; H, 6.44; N, 10.89.

^1H NMR (toluene-d_8, 20 °C): 36 (6H, vbr, CH_2), 32.8 (6H, H-*o*), 15.2 (3H, H-*p*), 13.8 (6H, *d*, H-*m*), −0.2 (6H, br, CH_2), −16.1 (18H, $SiMe_2$); −60 °C, 89.3 (3H, CH_2), 56.1 (6H, H-*o*), 29.4 (3H, CH_2), 20.0 (9H, H-*p* + H-*o*), 12.7 (3H, CH_2), −13.5 (3H, CH_2), −22.5 (9H, $SiMe_2$), -30.5 (9H, $SiMe_2$).

$[Yb\{(SiMe_2NPh)_3\text{-tacn}\}]$ (4). The compound was prepared as described above for **1** by using 164 mg (0.59 mmol) of $YbCl_3$ and 462 mg (0.59 mmol) of $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$. The yellow solid was obtained with a 68% yield (300 mg, 0.40 mmol).

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Crystallization from toluene gives yellow crystals of $[Yb\{(SiMe_2NPh)_3\text{-tacn}\}]\cdot C_6H_5Me$. Calcd for $YbSi_3C_{30}H_{45}N_6\cdot C_7H_8$: C, 52.96; H, 6.37; N, 10.01. Found: C, 52.32; H, 6.21; N, 9.91.

^1H NMR (toluene-d_8, 40 °C) 82 (6H, vbr, CH_2), 59.6 (6H, H-*o*), 24.6 (6H, H−m), 19.2 (3H, H-*p*), 4.5 (6H, vbr, CH_2), −34.1 (18H, $SiMe_3$); −60 °C, 212.0 (3H, br, CH_2), 109.8 (6H, H-*o*), 74.9 (3H, br, CH_2), 66.4 (3H, br, CH_2), 39.3 (6H, H-*m*), 29.2 (3H, H-*p*), −48.6 (9H, $SiMe_2$), -57.4 (3H, br, CH_2) −74.0 (9H, $SiMe_2$).

$[Eu\{(SiMe_2NPh)_3\text{-tacn}\}][Na(diglyme)_2]$ (5). $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}$ (89 mg) in THF solution was reacted overnight with an equimolar amount of sodium amalgam 0.5% (564 mg). The reddish-brown solution turned gradually to brown. After the mercury had been discharged, the solution was evaporated to dryness and the dark yellow solid washed with hexane. Crystallization from a concentrated THF solution with a few drops of diglyme gave yellow crystals of $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}][Na(diglyme)_2]$. Calcd for $EuNaSi_3C_{42}H_{73}N_6O_6$: C, 49.59; H, 7.23; N, 8.26. Found: C, 49.31; H, 7.41; N, 8.12.

$[U\{(SiMe_2NPh)_3\text{-tacn}\}]$ (6). Addition of 298 mg (0.40 mmol) of $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$ to a solution of $UI_3(THF)_4$ (360 mg, 0.40 mmol) in THF resulted in an immediate color change from blue to purple. The mixture was stirred overnight at room temperature, and then the solvent was removed under vacuum. The residue was extracted with toluene and centrifuged to remove the NaI. Removal of the toluene under vacuum yielded **6** as a brown powder, which was further washed with hexane and vacuum-dried. Yield: 70% (250 mg). Crystallization from toluene solution gives dark brown crystals of $[U\{(SiMe_2NPh)_3\text{-tacn}\}]\cdot 0.5C_6H_5Me$. Calcd for $USi_3C_{30}H_{45}N_6\cdot 0.5C_7H_8$: C, 46.80; H, 5.71; N, 9.79. Found: C, 46.04; H, 5.44; N, 9.45.

^1H NMR (toluene-d_8, 20 °C): 7.3 (18H, $SiMe_2$), 3.0 (6H, H-*m*), 1.3 (3H, H-*p*), −0.5 (6H, CH_2), −6.7 (6H, H-*o*), −29.1 (6H, CH_2); −70 °C, 15.1 (9H, $SiMe_2$), 10.8 (9H, $SiMe_2$), −0.8 (3H, CH_2), −1.3 (6H, H-*m*), −3.00 (3H, H-*p*), −3.4 (3H, CH_2), −21.1 (6H, H-*o*), −43.0 (3H, CH_2), −52.1 (3H, CH_2).

$[U\{(SiMe_2NPh)_3\text{-tacn}\}Cl]$ (7). $[U\{(SiMe_2NPh)_3\text{-tacn}\}Cl]$ was prepared by adding a stoichiometric amount of benzyl chloride (26 mg, 0.20 mmol) to a solution of 180 mg (0.20 mmol) of **6** in toluene. The reaction was immediate with formation of a green precipitate. Stirring was continued for an additional 4 h. The green precipitate was washed twice with toluene and vacuum-dried. Yield: 30% (55 mg, 0.06 mmol)).

Alternatively **7** could be prepared by adding 320 mg (0.39 mmol) of $Na_3[(SiMe_2NPh)_3\text{-tacn}](THF)_2$ to a solution of UCl_4 (150 mg, 0.39 mmol) in THF. The mixture immediately turned from green to green-brownish. Stirring was continued for 4 h. The NaCl was discharged and the solvent removed under vacuum. The solid obtained was washed twice with toluene and extracted in CH_2Cl_2. Yield: 65% (200 mg, 0.23 mmol). Calcd for $UClSi_3C_{30}H_{45}N_6\cdot CH_2Cl_2$: C, 42.52; H, 5.35; N, 9.92. Found: C, 42.44; H, 5.46; N, 9.92.

^1H NMR (CD_2Cl_2, 20 °C): 11.6 (18H, $SiMe_2$), 9.1 (6H, H-*m*), 6.5 (6H, br), 5.6 (3H, t, H-*p*), −11.1 (6H, br), −49.0 (6H, CH_2).

Green crystals of **7** were obtained by slow concentration of a dichloromethane solution.

$[U\{(SiMe_2NPh)_3\text{-tacn}\}I]$ (8). Iodine (26 mg, 0.10 mmol) in toluene was added dropwise to a solution of 180 mg (0.19 mmol) of **6** in toluene. There was an immediate color change from reddish-brown to green. After 2 h of stirring, the mixture was centrifuged. The brown supernatant solution was discharged and the light green solid washed twice with toluene and vacuum-dried. Calcd for $USi_3C_{30}H_{48}N_6I$: C, 38.38; H, 4.83; N, 8.95. Found: C, 37.62; H, 4.79; N, 8.67.

^1H NMR (CD_2Cl_2, 35 °C): 13.6 (18H, br, $SiMe_2$), 9.6 (6H, br), 6.2 (9H, br), −12 (6H, vbr), −49.5 (6H, CH); −70 °C, 86.5 (6H, $SiMe_2$), 83.6 (6H, H-*o*), 32.3 (6H, H-*m*), 19.2 (3H, H-*p*), −10.3 (6H, $SiMe_2$), −18.5 (2H, CH_2), −28.3 (6H, $SiMe_2$), −29.4 (2H, CH_2), −55.5 (2H, CH_2), −77.7 (2H, CH_2), −91.1 (2H, CH_2), −143.3 (2H, CH_2).

Crystallization from CH_2Cl_2 gave thin yellowish-green needles not adequate for X-ray diffraction analysis.

X-ray Crystallographic Analysis. Colorless crystals of $[Y\{(SiMe_2NPh)_3\text{-tacn}\}]\cdot C_6H_5Me$ (**1**$\cdot C_6H_5Me$) and $[La\{(SiMe_2NPh)_3\text{-tacn}\}(THF)]$ (**2**), red-orange crystals of $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}]\cdot 0.5C_6H_5Me$ (**3**$\cdot 0.5C_6H_5Me$), and dark brown crystals of $[U\{(SiMe_2NPh)_3\text{-tacn}\}]\cdot 0.5C_6H_5Me$ (**6**$\cdot 0.5C_6H_5Me$) were grown by slow concentration of toluene solutions. Crystals of $[Yb\{(SiMe_2NPh)_3\text{-tacn}\}]\cdot C_6H_5Me$ (**4**$\cdot C_6H_5Me$) (yellow) were grown from toluene/hexane mixtures and crystals of $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}][Na(diglyme)_2]$ (**5**) (yellow) from a THF/diglyme mixture. Green crystals of $[U\{(SiMe_2NPh)_3\text{-tacn}\}Cl]$ (**7**) were obtained by slow concentration of a dichloromethane solution. Crystals were mounted in thin-walled glass capillaries in a nitrogen-filled glovebox (crystals of **4**$\cdot C_6H_5Me$ and **6**$\cdot 0.5C_6H_5Me$ were immersed in Nujol before mounting). Data were collected at room temperature on an Enraf-Nonius CAD4-diffractometer with graphite-monochromatized Mo Kα radiation. Data were corrected[25] for Lorentz and polarization effects, for linear decay, and for absorption by empirical corrections based on Ψ scans. A summary of the crystallographic data is given in Table 1.[26]

The structures were solved using Patterson methods[27] and successive difference Fourier techniques and refined by full-matrix least squares refinements on F^2 using SHELXL-97.[28] Compounds **1**$\cdot C_6H_5Me$ and **4**$\cdot C_6H_5Me$ are isomorphous, and in their lattice there is one disordered toluene solvent molecule per formula unit. **3**$\cdot 0.5C_6H_5Me$ and **6**$\cdot 0.5C_6H_5Me$ are isomorphous, with half-toluene solvent molecule per formula unit, disordered about an inversion center. Examination of the crystal structure of **7** with the VOID routine of PLATON[29] showed 60.6% of filled space and 14.8% of potential solvent area (~557.3 Å^3), which was an indication of solvent present in the lattice. The five strongest peaks in the difference Fourier map, in the range 5.1−2.1 e Å^{-3}, were introduced as full-occupancy atoms (one oxygen and four carbon atoms), but no chemical identity could be assigned to these solvent peaks. So, they were excluded from the formula, from the molecular weight, and from the calculation of the density in Table 1. All non-hydrogen atoms were refined with anisotropic thermal motion parameters, and the hydrogen atoms were assigned idealized positions based on the geometries of their attached carbon atoms (the solvent atoms in **3**$\cdot 0.5C_6H_5Me$ were refined isotropically, with geometric restraints and H atoms omitted). Atomic scattering factors and anomalous

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(26) Crystal data for **1**$\cdot C_6H_5Me$: $C_{37}H_{53}N_6Si_3Y$, fw = 755.03, monoclinic, space group $P2_1/n$, $a = 10.9430(8)$ Å, $b = 16.3749(14)$ Å, $c = 22.582(3)$ Å, $\beta = 91.195(7)°$, $V = 4045.7(7)$ Å^3, $Z = 4$, $D_{calc} = 1.240$ Mg/m^3. 7084 unique reflections were used in the structure solution and refinement of 425 parameters. Final refinement converged at R1 = 0.109 and wR2 = 0.123 for 2614 reflections with $I > 2\sigma(I)$. Crystal data for **6**$\cdot 0.5C_6H_5Me$: $C_{33.5}H_{49}N_6Si_3U$, fw = 858.09, monoclinic, space group $P2_1/n$, $a = 11.0783(11)$ Å, $b = 15.7081(17)$ Å, $c = 21.187(2)$ Å, $\beta = 97.246(10)°$, $V = 3657.4(6)$ Å^3, $Z = 4$, $D_{calc} = 1.558$ Mg/m^3. 6395 unique reflections were used in the structure solution and refinement of 377 parameters. The refinement converged at R1 = 0.101 and wR2 = 0.167 for 2807 reflections with $I > 2\sigma(I)$.

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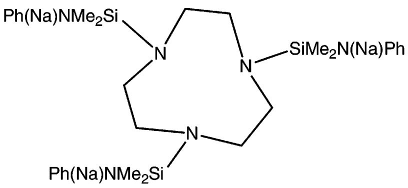
Table 1. Crystallographic Data

	2	**3**·0.5C_6H_5Me	**4**·C_6H_5Me	**5**	**7**
formula	$C_{34}H_{53}N_6Si_3OLa$	$C_{33.5}H_{49}N_6Si_3Eu$	$C_{37}H_{53}N_6Si_3Yb$	$C_{42}H_{73}N_6O_6NaSi_3Eu$	$C_{30}H_{45}N_6Si_3ClU$
fw	785.00	772.02	839.16	1017.28	847.47
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	Cc	$P2_12_12_1$
a, Å	11.752(2)	11.0803(12)	10.9131(10)	21.763(2)	13.267(2)
b, Å	18.536(2)	15.772(2)	16.355(2)	12.6630(13)	16.472(2)
c, Å	18.301(2)	21.081(2)	22.560(3)	19.082(2)	17.285(4)
β, deg	105.082(10)	97.039(9)	91.150(9)	100.240(9)	
V, Å^3	3849.5(9)	3656.2(7)	4025.9(9)	5175.0(10)	3777.5(11)
Z	4	4	4	4	4
ρ_{calc}, g cm^{-3}	1.354	1.403	1.385	1.306	1.490
μ(Mo Kα), mm^{-1}	1.237	1.845	2.445	1.336	4.490
R1	0.0545	0.0738	0.0897	0.0542	0.0671
wR2	0.1098	0.1288	0.1383	0.0649	0.1184

Scheme 1



dispersion terms were taken as in ref 28. The drawings were made with ORTEP 3.[30] Because of the low quality of crystals **1** and **6** and, consequently, poor quality of data/refinement, relevant geometrical parameters will be given, but details regarding structure solution and refinement are available as Supporting Information.

Results and Discussion

Addition of a THF solution of the sodium salt of 1,4,7-tris(dimethylsilylphenylamine)-1,4,7-triazacyclononane (Na_3-[($SiMe_2NPh$)$_3$-tacn](THF)$_2$) (Scheme 1) to a suspension of the trivalent lanthanide chlorides (Ln = Y, La, Eu, Yb) in the same solvent affords the corresponding [M{($SiMe_2NPh$)$_3$-tacn}] (M = Y (**1**), Eu (**3**), Yb (**4**)) and [La{($SiMe_2NPh$)$_3$-tacn}(THF)] (**2**) complexes (eq 1).

$$\mathrm{MCl_3 + Na_3[(SiMe_2NPh)_3\text{-}tacn](THF)_2 \rightarrow}$$
$$\mathrm{[M\{(SiMe_2NPh)_3\text{-}tacn\}(THF)_{\mathit{x}}] + 3NaCl}$$
$$\mathrm{M = Y\ (\mathbf{1}),\ Eu\ (\mathbf{3}),\ Yb\ (\mathbf{4})} \qquad x = 0$$
$$\mathrm{M = La\ (\mathbf{2})} \qquad x = 1 \tag{1}$$

With the objective of synthesizing a Eu(II)−tacn compound, **3** was treated in THF with a stoichiometric amount of 0.5% Na/Hg. The initial red-brown solution gradually changed to brown. The dark yellow solid isolated from the reaction mixture was crystallized from a concentrated THF solution with a few drops of diglyme to give yellow crystals of [Eu{($SiMe_2NPh$)$_3$-tacn}][Na(diglyme)$_2$] (**5**).

Addition of 1 equiv of Na_3[($SiMe_2NPh$)$_3$-tacn](THF)$_2$ in THF to a solution of uranium triiodide in the same solvent resulted in formation of a brown-greenish solution. [U{($SiMe_2NPh$)$_3$-tacn}] (**6**) was separated from the NaI formed in the reaction by extraction in toluene.

$$\mathrm{UI_3(THF)_4 + Na_3[(SiMe_2NPh)_3\text{-}tacn(THF)_2] \rightarrow [U\{(SiMe_2NPh)_3\text{-}tacn\}] + 3NaI} \tag{2}$$

Compounds **1**−**6** were soluble in common aromatic and ethereal solvents and slightly soluble in hexane, with the exception of **6**, which was moderately soluble in this solvent.

Although the NMR spectra showed no evidence for significant impurities, analytically pure samples of **3**−**5** were difficult to obtain probably due to variable amounts of solvent retained in the lattice.

Since the new ligand has been demonstrated to support the trivalent oxidation state of uranium(III), it was of obvious interest to explore the redox chemistry of uranium(III) in this coordination environment. Compound **6** is readily oxidized by benzyl chloride and iodine in toluene to yield the insoluble chloride [U{($SiMe_2NPh$)$_3$-tacn}Cl] (**7**) and iodide [U{($SiMe_2NPh$)$_3$-tacn}I] (**8**) compounds, respectively. However, salt metathesis provides a higher yield route to **7**. Thus, stirring UCl_4 with Na_3[($SiMe_2NPh$)$_3$-tacn](THF)$_2$ in THF results in formation of a white precipitate and a green brownish solution. Removal of the THF followed by addition of toluene yielded a green precipitate and a brown solution (eq 3).

$$\mathrm{UCl_4 + Na_3[(SiMe_2NPh)_3\text{-}tacn(THF)_2] \rightarrow [U\{(SiMe_2NPh)_3\text{-}tacn\}Cl] + 3NaCl} \tag{3}$$

The green precipitate was further extracted with CH_2Cl_2 to separate some unreacted uranium tetrachloride.

Both compounds are insoluble in aromatic solvents, suggesting the presence of ionic compounds. However, determination of the X-ray structure of **7** showed that this was not the case.

The new complexes have been characterized by standard analytical and spectroscopic techniques. Because complexes **1**−**8** represent a complete series of new complexes, single crystals were grown for X-ray diffraction studies.

Solid-State Structures of the Six-Coordinate [Y{($SiMe_2NPh$)$_3$-tacn}]·C_6H_5Me (1·C_6H_5Me), [Eu{($SiMe_2NPh$)$_3$-tacn}]·0.5C_6H_5Me (3·0.5C_6H_5Me), [Yb{($SiMe_2NPh$)$_3$-tacn}]·C_6H_5Me (4·C_6H_5Me),[Eu{($SiMe_2$NPh)$_3$-tacn}][Na(diglyme)$_2$] (5), and [U{($SiMe_2NPh$)$_3$-tacn}]·0.5C_6H_5Me (6·0.5C_6H_5Me) Complexes. Complexes **1** and **4** are isomorphous and crystallize in the monoclinic space group $P2_1/n$[31] with a molecule of toluene contained within the lattice. Complexes **3** and **6** are isomorphous and crystallize in the monoclinic space group $P2_1/n$ with a half-

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(30) Farrugia, L. J. ORTEP-3, *J. Appl. Crystallogr.* **1997**, *30*, 565.

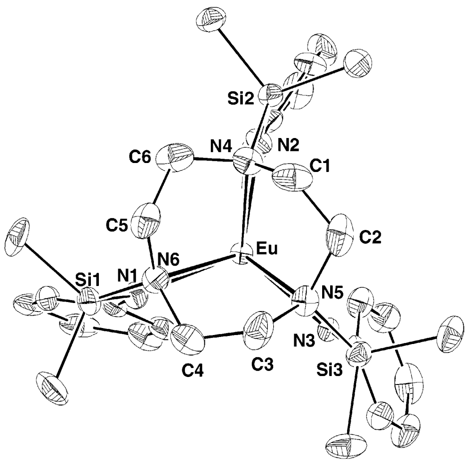

Figure 1. ORTEP diagram of $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}]\cdot 0.5C_6H_5Me$, (**3**·$0.5C_6H_5Me$), using 20% probability ellipsoids.

molecule of toluene included in the crystal lattice. The structure of **5** consists of $[Eu\{(SiMe_2NPh)_3\text{-tacn}\}]^-$ anions and well-separated sodium cations coordinated to two molecules of diglyme, and they crystallize in the monoclinic space group *Cc*. As a representative, the molecular structure of **3** is shown in Figure 1 (**1** and **4**−**6** are not illustrated, but analogous atomic numbering schemes are used for all the molecular structures).

Table 2 summarizes important bond distances and angles.

For all the complexes the metal center is six-coordinate by the three amine nitrogen donors of the 1,4,7-triazacyclononane ring and three amido nitrogen donor atoms of the pendant arms. The resulting N_6M polyhedron is best described as a slightly distorted trigonal prism, the two trigonal planes defined by the two sets of nitrogen donor atoms being nearly parallel (interplanar angles N_{123}/N_{456} in Table 3).

In all compounds the pendant amido groups are oriented around the C_3 symmetry axis in the same direction (Δ or Λ conformation)[32] with average twist angles (φ)[33] of 4.3°, 1.7°, 4.6°, 0.6°, and 0.8° for **1**, **3**, **4**, **5**, and **6**, respectively. The coordinated 1,4,7-triazacyclononane backbone of the amine forms three five-membered chelate rings M−N−C−C−N which adopt a $(\delta\delta\delta)_5$ or $(\lambda\lambda\lambda)_5$ conformation. In crystals of **1** and **4**, the enantiomeric pair of the complexes $(\Delta(\delta\delta\delta)_5/\Lambda(\lambda\lambda\lambda)_5)$ is present in the centric unit cell of the space group $P2_1/n$, while complexes **3** and **6** exhibit the $\Delta(\lambda\lambda\lambda)_5/\Lambda(\delta\delta\delta)_5$ pair.

The metal nitrogen distances reflect the difference in the ionic radii of the metal.[34] The average M−N(amido) distances, **1** (2.279(9) Å), **3** (2.313(11) Å), **4** (2.216(14) Å), are slightly longer than those observed in $[M\{N(SiMe_3)_2\}_3]$ (2.226(6), 2.259(9), and 2.158(13) Å for Y, Eu, and Yb, respectively),[35−37] which is not surprising in view of the higher coordination number of the metal center in the triazacyclononane environment. Thus, the Y−N(amido) distance in **1** is better compared with that of the five-coordinate $[Y\{N(SiMe_2H)_3(THF)_2]$[38] (2.26 Å). **1** can also be compared with the five-coordinate $[Y\{N(CH_2CH_2NSiMe_2Bu^t)_3\}ClLi(thf)_3]$,[12] a compound with both Y−N(amido) and Y−N(amine) bonds. In **1** the Y−N(amido) bond distance (2.279(9) Å) is 0.05 Å longer than that observed in $[Y\{N(CH_2CH_2NSiMe_2Bu^t)_3\}ClLi(thf)_3]$ (2.231 (2) Å), while the average Y−N(amine) bond length of 2.517(15) Å is some 0.07 Å shorter than the corresponding distance of 2.588(4) Å in that compound.[12] This is a consequence of the position of the metal in the two coordination polyhedra. In $[Y\{N(CH_2CH_2NSiMe_2Bu^t)_3\}ClLi(thf)_3]$ the yttrium sits 0.67 Å out of the plane defined by the three amido nitrogen atoms, while in **1** the metal atom is 0.69 Å below the corresponding plane approaching the three nitrogen amine atoms. The average M−N(amine) distances in **3** and **4** (2.563(10) and 2.50(3) Å, respectively) are consistent with those reported in the literature.[39] In **5** the average Eu−N(amido) distance of 2.522(9) Å is slightly longer than the average Eu−N distance of 2.448(4) Å in the ionic $NaEu[N(SiMe_3)_2]_3$,[40] and the average Eu−N(amine) distance of 2.746(12) Å compares with those reported in the literature.[41] In **6** the average U−N(amido) distance of 2.35(2) Å is similar to those of 2.320(4), 2.339(3), and 2.320 Å observed in the uranium(III) complexes $U[N(SiMe_3)_2]_3$,[42] $[(SiMe_3)_2N]_4U_2[\text{-}N(H)(mesityl)]_2$,[43] and $U(N(R)Ar)_3(THF)$ (R = *tert*-butylanilide, Ar = Ph-2,6-Me_2)[44] and to the longer U−N bond distance of 2.358(19) Å in $(\eta\text{-}C_5Me_5)U[N(SiMe_3)_2]_2$[45] (the other U−N distance is 2.23(3) Å). The U−N(amine) distance of 2.66(2) Å is slightly shorter than the corresponding distance of 2.697(4) Å in the ionic $[U(tbpa)I_2]Ipy$ (tbpa = tris[(2,2′-bipyridin-6-yl)methyl]amine).[46]

Solid-State Structures of the Seven-Coordinate [La{(SiMe₂NPh)₃-tacn}(THF)] (2) and [U{(SiMe₂NPh)₃-

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(31) Crystals of **1** and **4** in another crystalline form were isolated during another crystallization process: trigonal space group *R*3, with two molecules per asymmetric unit, one lying on a crystallographic 3-fold axis. **1**·$1.5C_6H_5Me$: $a = 29.733(4)$ Å, $c = 18.204(3)$ Å, $V = 13937(4)$ Å^3, $Z = 12$, $D_{calc} = 1.145$ Mg/m^3. **4**·$1.5C_6H_5Me$: $a = 29.643(4)$ Å, $c = 18.147(3)$ Å, $V = 13809(3)$ Å^3, $Z = 12$, $D_{calc} = 1.277$ Mg/m^3.

(32) The convention adopted assigns Δ and Λ to a structure where the trigonal plane defined by the nitrogen amine atoms is twisted to the right and left, respectively, by reference to the trigonal plane defined by the nitrogen amido atoms when viewed down the C_3 axis.

(33) The twist angles were calculated by taking the average of the angles made by the projections of the vertices of the top and bottom faces along the direction of the two centroids of the trigonal faces. For a regular trigonal prism $\varphi = 0°$.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Six-Coordinate Complexes

	1·C_6H_5Me	**3**·0.5C_6H_5Me	**4**·C_6H_5Me	**5**	**6**·0.5C_6H_5Me
M−N(1)	2.283(9)	2.321(9)	2.205(14)	2.515(9)	2.326(19)
M−N(2)	2.283(9)	2.318(8)	2.227(13)	2.530(9)	2.367(15)
M−N(3)	2.271(8)	2.301(8)	2.216(13)	2.522(9)	2.360(16)
M−N(4)	2.504(8)	2.574(9)	2.473(13)	2.739(8)	2.677(19)
M−N(5)	2.513(9)	2.556(8)	2.520(12)	2.740(8)	2.640(18)
M−N(6)	2.533(8)	2.558(8)	2.517(13)	2.760(9)	2.653(19)
N(1)−M−N(2)	110.6(3)	111.6(3)	110.7(5)	117.2(3)	115.1(7)
N(1)−M−N(3)	111.6(3)	111.0(3)	110.5(5)	114.2(3)	112.3(6)
N(2)−M−N(3)	111.6(3)	115.5(3)	109.7(5)	117.8(3)	118.4(6)
N(4)−M−N(5)	71.5(3)	70.1(3)	72.7(4)	67.8(3)	68.4(6)
N(4)−M−N(6)	70.8(3)	69.2(3)	71.1(4)	67.5(3)	68.8(6)
N(5)−M−N(6)	71.8(3)	70.4(3)	72.6(5)	67.0(3)	67.5(6)

Table 3. Interplanar Angles (deg) between the Amido($N_{1,2,3}$)/Amine($N_{4,5,6}$) Trigonal Planes, Dihedral Angles (deg) between the Amido($N_{1,2,3}$) and the Phenyl Planes, Average Twist Angles (φ) (deg), and Distances (Å) of the Metal to the Trigonal Planes

	1·C_6H_5Me	**2**	**3**·0.5C_6H_5Me	**4**·C_6H_5Me	**5**	**6**·0.5C_6H_5Me
$N_{1,2,3}/N_{4,5,6}$	0.63	1.83	0.81	1.56	0.48	0.26
$N_{1,2,3}/Ph_1$	78.03	50.04	81.59	77.67	88.84	85.01
$N_{1,2,3}/Ph_2$	73.09	43.29	88.57	72.32	79.89	88.48
$N_{1,2,3}/Ph_3$	78.40	60.26	74.26	77.69	77.44	76.28
φ	4.3	12.5	1.7	4.6	0.6	0.8
$d(M/N_{1,2,3})$	0.69	0.31	0.64	0.71	0.48	0.52
$d(M/N_{4,5,6})$	1.86	2.16	1.92	1.84	2.11	2.02

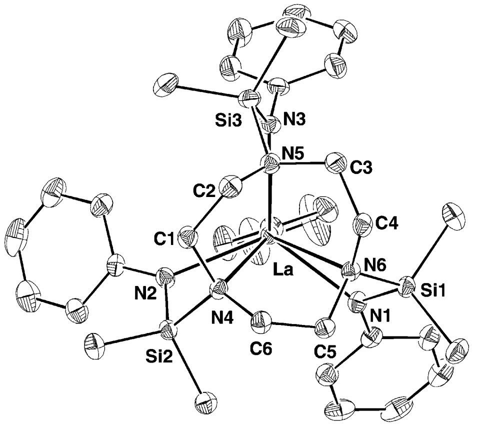

Figure 2. ORTEP diagram of [La{(SiMe$_2$NPh)$_3$-tacn}(THF)] (**2**), using 20% probability ellipsoids.

tacn}Cl] (7) Complexes. Complex **2** crystallizes in the monoclinic space group $P2_1/n$. The lanthanum ion is seven-coordinate by the six nitrogen atoms of the ligand and the oxygen atom of the THF molecule, which is capping the trigonal face defined by the three nitrogen atoms of the amido groups (Figure 2).

Relevant metrical parameters are collected in Tables 3 and 4.

The coordination of the THF molecule results in a higher distortion from the trigonal prismatic geometry. The phenyl rings are pushed away from the trigonal plane N_{123} as shown by the dihedral angles between the trigonal plane N_{123} and the planes of the phenyl rings (N_{123}/Ph) that average 51.2° to be compared with the values of approximate 80° in the six-coordinate complexes. Also, the nitrogen amine atoms are much twisted by reference to the nitrogen amido atoms (Table 3). The enantiomorphous pair identified as $\Delta(\delta\delta\delta)_5/\Lambda(\lambda\lambda\lambda)_5$ is observed in the crystals of **2**. The average La−N(amido) bond length of 2.45(3) Å is slightly longer than the corresponding distance in the four-coordinate [La{N(SiMe$_3$)$_2$}$_3$(PPh$_3$O)][47] (2.41(2) Å) and in the five-coordinate [La{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$][48] (2.402(5) Å). The average La−N(amine) of 2.75(2) Å compares with the distance of 2.728(4) Å in [La(tbpa)(H$_2$O)(ClO$_4$)][ClO$_4$]$_2$·2CHCl$_3$·MeOH (tbpa = tris[(2,2′-bipyridin-6-yl)methyl]-amine),[46] and the La−O distance of 2.598(4) Å is very similar to that of 2.573(4) Å in [La{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$].[48]

Complex **7** crystallized from a CH_2Cl_2 solution in the orthorhombic space group $P2_12_12_1$. The uranium ion is seven-coordinate by the six nitrogen donor atoms and the chlorine atom. Selected bond distances and angles are summarized in Tables 3 and 4. An analysis of the metal geometry showed that the structure could not be assigned to the usual polyhedral forms for seven-coordinate complexes. The best way to visualize the structure is to consider the geometry around the metal as a bicapped trigonal bipyramid (Figure 3).

The nitrogen atoms N(2), N(5), and N(6) define the equatorial plane, while the chlorine atom and N(4) define the apexes (Cl−U−N(4) = 170.5(3)°). The two nitrogen atoms N(1) and N(3) cap two of the triangular faces of the bipyramid making N−U−Cl angles of 79.5 (4)° and 78.8 (3)°, respectively. The U−N(2) distance of 2.249(13) Å is within the range (2.20−2.28 Å) of amido U−N distances in [UN{CH$_2$CH$_2$N(SiMe$_3$)}$_3$Cl]$_2$,[15] [UN(CH$_2$CH$_2$NSiMe$_2$Bu^t)$_3$],[19]

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for Seven-Coordinate Complexes (X = O (**2**), Cl (**7**))

	2	**7**		**2**	**7**
M−X	2.598(4)	2.668(4)	M−N(4)	2.739(4)	2.632(11)
M−N(1)	2.475(5)	2.324(13)	M−N(5)	2.773(5)	2.626(13)
M−N(2)	2.460(4)	2.249(13)	M−N(6)	2.741(4)	2.651(12)
M−N(3)	2.423(5)	2.327(13)			
N(1)−M−N(2)	118.90(15)	97.5(5)	N(4)−M−N(6)	64.58(13)	67.4(4)
N(1)−M−N(3)	124.70(17)	158.3(5)	N(5)−M−N(6)	64.77(13)	65.7(4)
N(2)−M−N(3)	111.62(16)	93.7(5)	N(2)−M−N(5)	105.03(15)	124.2(5)
N(4)−M−N(5)	65.13(14)	67.7(4)	N(2)−M−N(6)	121.67(14)	119.7(5)
X−M−N(1)	78.10(14)	79.5(4)	X−M−N(4)	146.97(13)	170.5(3)
X−M−N(2)	89.52(14)	121.8(4)	X−M−N(5)	142.11(13)	102.8(3)
X−M−N(3)	81.42(15)	78.8(3)	X−M−N(6)	135.30(13)	109.3(3)

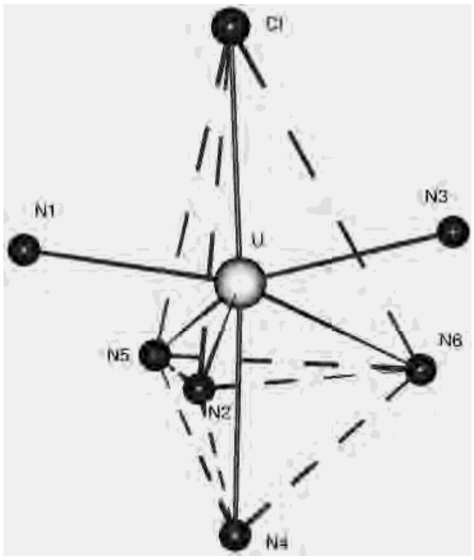

Figure 3. View of the bicapped triangular bypiramidal coordination polyhedron of **7**.

and *cis*-$UCl_2[N(SiMe_3)_2]_2$·DME.[49] The distances of the capping nitrogen atoms to uranium (U−N(1) = 2.324(13) Å and U−N(3) = 2.327(13) Å) are about 0.08 Å longer than the corresponding distance of the nitrogen amido atom lying in the equatorial plane. The U−N amine bond distances are similar and average 2.636(13) Å, a value that is in line with those found in the trisamidoamine uranium(IV) complexes $[UN\{CH_2CH_2N(SiMe_3)\}_3Cl]_2$[15] (2.567(9) Å) and $[UN(CH_2CH_2NSiMe_2Bu^t)_3X]$[18] (2.67(2) Å, X = Cl; 2.67(1) Å, X = Br; 2.685(6) Å, X = I) and the tacn-based ligands, $[((ArO)_3tacn)U(OAr)]$ (2.703(15) Å) and $[\{((ArO)_3tacn)U\}_2(\mu\text{-}O)]$ (2.75(2) Å).[8] The U−Cl distance of 2.668(4) Å is similar to the corresponding distance in $[U(N(CH_2CH_2NSiMe_2Bu^t)_3)Cl]$[18] (2.641(5) Å) and in other tetravalent systems with nitrogen chelating ligands.[50]

A noteworthy feature of the structure of **7** is the presence of the two short Cl···N(1) and Cl···N(3) contacts of 3.20 and 3.18 Å, respectively. We believe that the unusual coordination geometry adopted by the ligands in **7** is not electronic in origin but caused by the crowded environment of the small U(IV) ion. As noted above, distortions of the trigonal prismatic geometry are seen in the lanthanum complex, and it is is not surprising that greater distortions have to occur in **7** since the U(IV) has an ionic radius 0.05 Å smaller than La. It is noteworthy that the U(III) ion, with an ionic radius only 0.007 Å smaller than La, has no room to accommodate a THF ligand. In order to minimize severe Cl···N contacts, the N(1) and N(3) atoms are pulled away from the chlorine as shown by the increase in the N(1)−U−N(3) angle to 158.3° vs 97.5° for N(1)−U−N(2) and 93.7° for N(2)−U−N(3). N(1) and N(3) are twisted in opposite directions by reference to N(6) and N(5), while N(2) is slightly twisted by reference to N(4) (Figure 4).

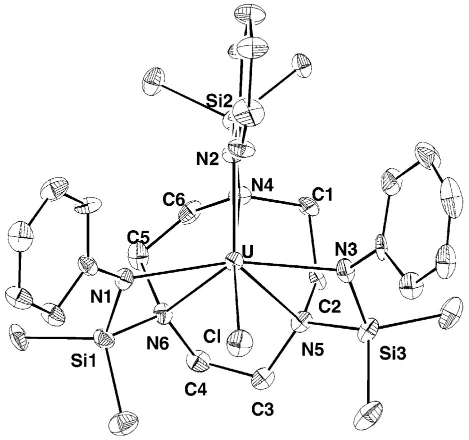

Figure 4. ORTEP diagram of $[U\{(SiMe_2NPh)_3\text{-tacn}\}Cl]$ (**7**), using 20% probability ellipsoids.

Dynamic Behavior of Complexes 1−8 in Solution. As pointed out above, complexes **1**−**6** have approximate C_3 symmetry. This symmetry should give rise to four signals for the diastereotopic methylene protons of the amine ligand (two equatorial and two axial) and two signals for the diastereotopic methyl protons of the $SiMe_3$ groups in the ^1H NMR spectra. In accordance two signals should be expected for the six carbons of the amine backbone in the ^{13}C spectra.

The ^1H NMR spectra of the diamagnetic complexes of Y (**1**) and La (**2**) showed one single signal for the methyl protons of the $SiMe_2$ groups and three peaks for the ortho, meta, and para protons of the phenyl groups with the expected integration and peak multiplicities. Two resonances due to the ethylenic protons of the cyclic amine ligand appeared as AA′BB′ spin systems. In addition there were two resonances due to the THF protons in the spectrum of **2**. This pattern is consistent with a C_{3v} symmetry in solution,

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(49) McCullogh, L. G.; Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 2869.

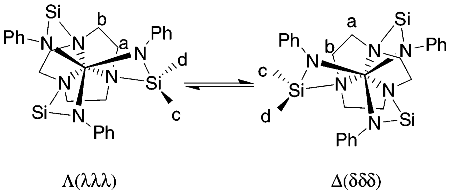
(50) Ball, R. G.; Edelmann, F.; Matisons, G. J.; Takats, J.; Marques, N.; Marçalo, J.; Pires de Matos, A.; Bagnall, K. W. *Inorg. Chim. Acta* **1987**, *132*, 137.

which is not in accordance with the symmetry found in the solid. The ^{13}C NMR spectra at room temperature gave analogous information: one single signal for the ethylene carbon atoms of the 1,4,7-triazacyclononane backbone, four signals for the carbon atoms of the phenyl rings, and one signal for the methyls of the $SiMe_3$ groups was consistent with a C_{3v} symmetrical structure. Cooling the samples to −80 °C resulted in broadening and collapsing of the ^{1}H NMR signals associated with the CH_2 and $SiMe_2$ groups, but a static spectrum was not reached before the solvent froze. The resonances due to the protons on the phenyl ring suffered only minimal line broadening, indicating fast rotation of the phenyl groups.

Spectra were also recorded for the paramagnetic Eu (**3**), Yb (**4**), and U (**5**) complexes. One single resonance for the 18 protons of the $SiMe_2$ groups and two resonances for the six H-*m* and three H-*p* protons of the anilide could be immediately assigned. In addition there were three resonances accounting for six protons each. Because these resonances were broadened and very shifted from the diamagnetic position, it was not possible to assign them to the H-*o* protons and to the ethylenic protons the cyclic amine.[51] This ambiguity could be solved by variable-temperature NMR experiments. When the samples were cooled, the resonances assigned to the $SiMe_2$ groups and to the methylenic protons shifted due to the temperature dependence of the magnetic susceptibility, broadened, and collapsed. By −60 °C the spectra of **3**−**5** had begun to sharpen, and four broad resonances in a 1:1:1:1 intensity ratio assigned to the CH_2 groups and two in a 9:9 intensity ratio owing to the methyl protons of the $SiMe_2$ groups appeared, consistent with C_3 symmetrical structures. While these changes occurred, the resonances of the aromatic protons of the amido groups shifted and broadened, especially that of the ortho protons, but they did not collapsed, indicating that rotation of the phenyl groups is still fast at −80 °C.

Exchange processes are common in macrocyclic lanthanide compounds and have been studied in detail for $Ln(DOTA)^-$ complexes. Exchange between isomers which reflects arm rotation and/or exchange between enantiomers which reflects ethylene ring inversion plus arm rotation have been invoked to explain the NMR data.[52] As mentioned above, the complexes exhist as pairs of enantiomers. An intramolecular isomerization ($\Delta(\delta\delta\delta)_5 \leftrightarrow \Lambda(\delta\delta\delta)_5$) or ring inversion ($\Delta(\delta\delta\delta)_5 \leftrightarrow \Delta(\lambda\lambda\lambda)_5$) would not lead to an increase in symmetry from C_3 to C_{3v}, but a $\Delta \leftrightarrow \Lambda$ interconversion of the MN_6 polyhedra and simultaneous concerted inversion of the five-membered chelate rings ($(\lambda\lambda\lambda)_5 \leftrightarrow (\delta\delta\delta)_5$) can explain the increase in the symmetry observed in solution. An illustrative diagram of this process is presented in Scheme 2.

Scheme 2



At room temperature the ^{1}H NMR spectrum of **7** in CD_2Cl_2 displayed one resonance at 11.6 ppm for the protons of the $SiMe_2$ groups and two resonances assigned to the H-*m* and H-*p* of the phenyl rings at 9.1 and 5.6 ppm, respectively. In addition, the spectrum exhibited three resonances accounting for six protons each at 6.5, −11.1, and −49.0 ppm. Assignment of these resonances to the H-*o* protons of the phenyl rings and to the ethylenic protons of the amine backbone was not possible. A 2D COSY spectrum was run, but cross peaks were only observed for the H-*m* and H-*p* protons. It has been noticed by others that, presumably due to effective transverse relaxation, cross peaks were not observed in the COSY spectra of other heavy paramagnetic chelates.[52d] Homonuclear decoupling experiments were also unsuccessful. Variable-temperature ^{1}H NMR spectra were obtained for the compound. Cooling of the sample resulted in progressive broadening and shifting of the ^{1}H NMR signals, and by −80 °C all the resonances had disappeared into the baseline. Thus, the ^{1}H NMR spectrum of **7** is rather structurally uninformative and is suggestive of a complex with a fluxional coordination sphere.

The room temperature ^{1}H NMR spectrum of **8** in CD_2Cl_2 displayed several broad overlapping resonances between 14 and 6 ppm and one resonance at −52.0 ppm. Warming of the sample to 35 °C resulted in sharpening of the resonances. At this temperature the spectrum displayed one resonance centered at 13.6 ppm for the methyl protons of the $SiMe_2$ groups, two broad resonances centered at 9.7 and 6.2 ppm, one almost collapsed into the baseline at −12 ppm, and one at −49.5 ppm. Hence, the spectrum is similar to that of **7**, suggesting that **8** is a molecular compound with a structure similar to that of **7**, with the larger iodide ligand giving rise to a more rigid structure in solution. In fact the broadness of the signals indicated that in the case of **8** the process responsible for the fluxionality of the molecule was slower on the NMR time scale. Cooling of the sample results in progressive broadening and shifting of the signals, and by −30 °C all the resonances had collapsed. By −70 °C the spectrum had began to sharpen again: five resonances accounting for six protons at 86.6, 83.0, 32.3, −10.3, and −28.3 ppm, one at 19.2 ppm accounting for three protons, and six at −18.5, −29.4, −55.5, −77.7, −91.1, and −143.3 ppm integrating for two protons were observed (Figure 5).

These last six resonances are certainly due to the ethylenic protons of the amine, but the assignment of the other resonances remains speculative. Since there is only one resonance accounting for the para protons of the phenyl

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(51) In the spectrum of **4** only one broad resonance assigned to the protons of the cyclic amine was observed at room temperature. Upon warming of the sample to 40 °C the second resonance appeared as a broad signal centered at 4.5 ppm.

(52) (a) Aime, S.; Botta, M.; Fasano, M.; Marques, M. P. M.; Geraldes, C. F. G. C.; Pubanz, D.; Merbach, A. E. *Inorg. Chem.* **1997**, *36*, 2059. (b) Zhang, S.; Kovacs, Z.; Burgess, S.; Aime, S.; Terreno, E.; Sherry, A. D. *Chem. Eur. J.* **2001**, *7*, 288. (c) Pittet, P. A.; Früh, D.; Tissières, V.; Bünzli, J. C. *J. Chem. Soc., Dalton Trans.* **1997**, 895. (d) Forsberg, J. H.; Delaney, R. M.; Zhao, Q.; Harakas, G.; Chandran, R. *Inorg. Chem.* **1995**, *34*, 3705.

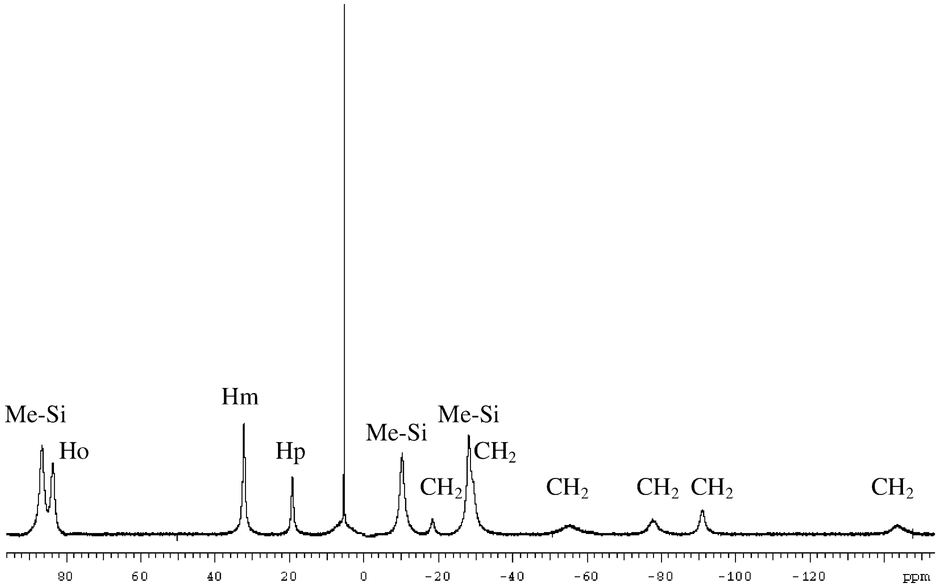

Figure 5. ^{1}H NMR spectrum of [U{(SiMe$_2$NPh)$_3$-tacn}Cl] (**7**), recorded in CD_2Cl_2 at −70 °C.

groups, two of the five resonances accounting for six protons may be due to the H-*o* and H-*m* of the phenyl rings, the three remaining resonances being due to the split of the methyl protons of the SiMe$_2$ groups.

At −80 °C the resonances due to the ethylenic protons begin to broad again, indicating that inversion of the ethylenic chain might be slowing. However, the slow exchange limit was not reached before the solvent froze.

In the low-temperature spectrum of **8** the presence of three resonances with an intensity ratio 6:6:6 due to the methylic protons of the SiMe$_2$ groups and six resonances with an intensity ratio 2:2:2:2:2:2 assigned to the ethylenic protons of the amine is reminiscent of a C_s symmetry. In the solid **7** has C_1 symmetry (Figure 4), but in solution, if inversion of the ethylenic backbone of the amine is fast in the NMR time scale, the symmetry raises to C_s, with U, Cl, N2, and N4 contained in the mirror plane. This symmetry is consistent with the low-temperature NMR spectrum of **8**.

Conclusions

A series of group 3 metal complexes with the hexadentate (SiMe$_2$NPh)$_3$-tacn)$^{3-}$ ligand has been prepared. The yttrium, europium, ytterbium, and uranium(III) complexes are six-coordinate by the tacn ligand with identical coordination geometries. The compounds display trigonal prismatic structures with the six nitrogen atoms of the ligand defining parallel planes. The higher ionic radius of La allows coordination of a THF ligand, with the metallic center retaining a C_3 coordination sphere since the oxygen atom of the THF is capping a trigonal face of the prism. The compounds are fluxional at room temperature, but variable-temperature ^{1}H NMR studies sustain a dynamic process involving a change in conformation of the ethylenic units in concert with movement of the pendant arms. Tetravalent uranium halides can be prepared either by redox methods or in the case of the chloride by metathesis. The uranium(IV) halides are seven-coordinate molecular complexes, but contrary to the La compound, the coordination geometry is better described as bicapped trigonal bipyramidal. Both compounds are fluxional, but a different dynamics than that observed for the six-coordinate complexes seems to be responsible for the fluxionality of these molecules. Work to develop this chemistry continues, namely, replacement of the halide by other ligands with different electronic and steric properties in order to get a better insight into the molecular structure and the dynamic behavior of these compounds.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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