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Synthesis and Characterization of Thorium *tert*-Butoxide Complexes: X-ray Crystal Structures of $Th(O\text{-}t\text{-}Bu)_4(py)_2$ and $NaTh_2(O\text{-}t\text{-}Bu)_9$

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Two synthetic procedures have been employed for the preparation of thorium *tert*-butoxide complexes. Reaction of $ThI_4(THF)_4$ with 4 equiv of KO-*t*-Bu in THF/pyridine solution provides $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (**1**) in moderate yield. Alcoholysis of the thorium metallacycle $[\{(Me_3Si)_2N\}_2\overline{Th(CH_2SiMe_2N}SiMe_3)]$ with >4 equiv of HO-*t*-Bu produces the dimeric alcoholate $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ (**2**) in 70% isolated yield. The coordinated alcohol in **2** is readily deprotonated by employing $NaN(SiMe_3)_2$ in hexane solution to provide hexane-soluble $NaTh_2(O\text{-}t\text{-}Bu)_9$ (**3**) in ca. 70% yield. Formation of the trimeric complex $Th_3O(O\text{-}t\text{-}Bu)_{10}$ (**4**) occurs upon addition of stoichiometric amounts of H_2O to refluxing toluene solutions of **2**. Compounds **1**–**4** have been characterized by elemental analysis, ^1H NMR, infrared spectroscopy, and, for **1** and **3**, single-crystal X-ray diffraction. In **1**, the Th atom is coordinated to four alkoxide and two pyridine ligands in a cis pseudo-octahedral fashion with average Th–O and Th–N distances of 2.182(6) and 2.752(7) Å, respectively. In **3**, the $NaTh_2(O\text{-}t\text{-}Bu)_9$ unit is closely related to the well-known M_3X_{11} cluster and is best described as $NaTh_2(\mu_3\text{-}O\text{-}t\text{-}Bu)_2(\mu_2\text{-}O\text{-}t\text{-}Bu)_3(O\text{-}t\text{-}Bu)_4$. Averaged Na–$\mu_3$-O and Na–$\mu_2$-O distances are 2.399(17) and 2.607(10) Å, respectively. Th–O distances are 2.155(8), 2.280(10), 2.464(7), and 2.491(7) Å for terminal, doubly bridging to sodium, doubly bridging to thorium, and triply bridging alkoxides, respectively. Crystal data for **1** (at 25 °C): Monoclinic space group $C2/c$, with $a = 12.656(3)$ Å, $b = 15.326(3)$, $c = 16.803(3)$ Å, $\beta = 96.43(3)°$, $V = 3238.7(12)$ Å^3, $d_{calc} = 1.363$ g cm^{-3}, and $Z = 4$. Crystal data for **3** (at 25 °C): Orthorhombic space group $Pnma$, with $a = 11.170(2)$ Å, $b = 25.408(5)$, $c = 17.195(3)$ Å, $V = 4880.1(16)$ Å^3, $d_{calc} = 1.559$ g cm^{-3}, and $Z = 4$.

Introduction

Alkoxide complexes of the actinides were first reported in the mid 1950's, during the search for volatile complexes for uranium isotope separation. Several reviews have summarized the experimental work on thorium alkoxides from the 1950's, with a few publications on *aliphatic* thorium alkoxides originating from the 1960's.[1] Much of the early work on these complexes is due to the pioneering efforts of D. C. Bradley, whose group prepared a number of homoleptic thorium alkoxide complexes.[2-9] The key starting material in Bradley's work was thorium isopropoxide, $Th(O\text{-}i\text{-}Pr)_4$, which was prepared from the reaction of $ThCl_4(HO\text{-}i\text{-}Pr)_4$ with NaO-*i*-Pr in 2-propanol solvent as outlined in eq 1.[2] Other thorium alkoxides were then conveniently prepared by alcohol interchange as outlined in eq 2.[3-9] While these complexes were described nearly 40 years ago, their characterization is still limited to elemental analysis and solution molecular weight determination. Ebullioscopic molecular weight measurements in benzene indicated that aggregation of $Th(OR)_4$ units was occurring in solution. For thorium *tert*-butoxide, $Th(O\text{-}t\text{-}Bu)_4$, a molecular complexity of 3.4 suggested a trimeric or tetrameric complex.[2]

$$ThCl_4(HO\text{-}i\text{-}Pr)_4 + 4NaO\text{-}i\text{-}Pr \xrightarrow{HO\text{-}i\text{-}Pr} Th(O\text{-}i\text{-}Pr)_4 + 4NaCl \quad (1)$$

$$Th(O\text{-}i\text{-}Pr)_4 + 4HOR \xrightarrow{HOR} Th(OR)_4 + 4HO\text{-}i\text{-}Pr \quad (2)$$

$$R = Me, Et, i\text{-}Pr, n\text{-}Pr, t\text{-}Bu, etc.$$

More recent studies of thorium alkoxides have shown that treatment of the thorium metallacycle $[\{(Me_3Si)_2N\}_2\overline{Th(CH_2SiMe_2N}SiMe_3)]$ with 4 equiv of di-isopropylmethanol in toluene yields colorless crystals of $[Th(OCH\text{-}i\text{-}Pr_2)_4]_2$ in high yield.[10] The bulky di-isopropylmethoxide dimer was shown to exist in a dynamic equilibrium at ambient temperature in hydrocarbon solution between monomeric $Th(OCH\text{-}i\text{-}Pr_2)_4$ and its dimer $Th_2(OCH\text{-}i\text{-}Pr_2)_8$ as outlined in eq 3.[10]

$$Th_2(OCH\text{-}i\text{-}Pr_2)_8 \rightleftharpoons 2Th(OCH\text{-}i\text{-}Pr_2)_4 \quad (3)$$

We wished to extend these studies of *aliphatic* thorium alkoxide chemistry to include somewhat less sterically demanding ligands and thus began an investigation of thorium complexes employing primarily *tert*-butoxide ligation. We report here the synthesis, physicochemical properties, and molecular structures of a series of new thorium *tert*-butoxide complexes prepared by a combination of metathetical and alcoholysis techniques. The relationship between these compounds and those described by Bradley in the early 1950's will be discussed.

Results and Discussion

Synthesis and Reactivity. One of the most general synthetic routes for preparation of metal alkoxide complexes is the

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metathesis reaction of a metal halide and an alkali metal alkoxide. While this strategy has great utility in transition metal chemistry, retention of the alkali metal and formation of "ate" or "double alkoxide" complexes can be a pervasive problem in the chemistry of actinide and lanthanide metals.[11] Following the methodology described previously,[12] we find that the metathesis reaction of thorium tetra*iodide*, $ThI_4(THF)_4$,[13] or tetra*bromide*, $ThBr_4(THF)_4$,[13] with *potassium* alkoxide salts at room temperature results in complete metathesis of the iodide or bromide ligands and provides the convenient preparation of a series of thorium alkoxide complexes and their Lewis base adducts. Since the metathesis reactions are carried out in donor solvents such as THF, any vacant coordination sites in the resulting $Th(OR)_4$ unit are likely to be filled by solvent molecules to produce mononuclear $Th(OR)_4(THF)_x$ species. Thus we also employ alcoholysis reactions of thorium amide complexes in nondonor solvents (toluene or hexane) as a route to base-free $Th(OR)_4$ units, which are then able to oligomerize until coordinative saturation is obtained.

The reaction of $ThI_4(THF)_4$ with 4 equiv of potassium *tert*-butoxide in THF solution in the presence of excess pyridine produces the mononuclear bis(pyridine) adduct $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (**1**), as outlined in eq 4. The reaction proceeds smoothly at room

$$ThI_4(THF)_4 + 4KO\text{-}t\text{-}Bu \xrightarrow{THF/py} Th(O\text{-}t\text{-}Bu)_4(py)_2 + 4KI \quad (4)$$

temperature and appears to be complete within several hours. Recrystallization from hexane/pyridine gives the white, crystalline product in 22% yield based on eq 4. We note the earlier preparation by Bradley of a bis(pyridine) complex $Th(OCMe_2CCl_3)_4(py)_2$ [6] and the preparation by Andersen of the related uranium complexes $U[OCH(CF_3)_2]_4(THF)_2$, and $U[OC(CF_3)_3]_4(THF)_2$.[14]

Treatment of the thorium metallacycle $[\{(Me_3Si)_2N\}_2Th(CH_2SiMe_2NSiMe_3)]$[15] with greater than 4 equiv of *tert*-butanol in toluene solution at room temperature results in the complete substitution of alkoxide for amide and produces the dimeric alcoholate of formula $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ (**2**). ^1H NMR spectra of the products obtained by stripping the filtered reaction mixture *in vacuo* show that formation of **2** is essentially quantitative. Recrystallization from a cooled hexane solution at -40 °C gives **2** as a white, crystalline product in 70% yield based on eq 5. The uranium analog of **2**, $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$, has

$$[\{(Me_3Si)_2N\}_2Th(CH_2SiMe_2NSiMe_3)] + {>}4HO\text{-}t\text{-}Bu \xrightarrow{toluene} {}^1/_2Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + 3HN(SiMe_3)_2 \quad (5)$$

been prepared in a similar fashion by Sattelberger and coworkers following the alcoholysis of either $[U(NEt_2)_4]_2$ or $[\{(Me_3Si)_2N\}_2U(CH_2SiMe_2NSiMe_3)]$.[16] Compound **2** is stable in toluene-d_8 or benzene-d_6 solution at room temperature as judged by ^1H NMR spectroscopy. The coordinated alcohol in **2** is readily deprotonated by reaction with sodium bis(trimethylsilyl)amide in toluene or hexane solution to generate $NaTh_2(O\text{-}t\text{-}Bu)_9$ (**3**), which may be isolated as a white crystalline solid in ca. 70% yield as outlined in eq 6.

$$Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + NaN(SiMe_3)_2 \xrightarrow{toluene} NaTh_2(O\text{-}t\text{-}Bu)_9 + HN(SiMe_3)_2 \quad (6)$$

Addition of stoichiometric quantities of water ($^2/_3$ equiv of H_2O/mol of **2**) to a refluxing toluene solution of **2** leads to the formation of the oxo-capped trimeric species $Th_3O(O\text{-}t\text{-}Bu)_{10}$ (**4**) in somewhat variable yield as outlined in eq 7. Examination

$$3Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu) + 2H_2O \xrightarrow{toluene} 2Th_3O(O\text{-}t\text{-}Bu)_{10} + 7HO\text{-}t\text{-}Bu \quad (7)$$

of a crude reaction product mixture by ^1H NMR revealed the presence of **4** and unreacted **2** as the *only* observable species. The trimeric species **4** may be separated from **2** by crystallization due to its lower solubility in hexane. Addition of larger quantities of water to **2** at room temperature results in the formation of a highly insoluble, flocculent white precipitate which we presume to contain thorium oxide/hydroxide species. Sattelberger has shown that the uranium analog to **4** can be prepared in a similar fashion,[16] and somewhat related behavior has been observed in the cerium *tert*-butoxide system described by Evans, who found that both $Ce(O\text{-}t\text{-}Bu)_4(THF)_2$ and $NaCe_2(O\text{-}t\text{-}Bu)_9$ slowly convert to $Ce_3O(O\text{-}t\text{-}Bu)_{10}$ in toluene solution over a period of days to weeks.[17]

Solid-State and Molecular Structures. Two thorium *tert*-butoxide compounds have been examined by single-crystal X-ray diffraction studies during this work: $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (**1**) and $NaTh_2(O\text{-}t\text{-}Bu)_9$ (**3**). In each case, the unit cell revealed discrete molecules. A summary of data collection and crystallographic parameters is given in Table I. Atomic positional parameters are given in Tables II and III.

$Th(O\text{-}t\text{-}Bu)_4py_2$ (1). Single crystals of **1** suitable for an X-ray diffraction study were grown from a hexane solution by slow cooling to -40 °C. A ball and stick drawing giving the atom-numbering scheme used in the tables is shown in Figure 1. Selected bond distances and bond angles are given in Tables IV and V, respectively. Compound **1** crystallizes in the monoclinic space group $C2/c$ with the central thorium atom lying on a 2-fold axis. The central thorium atom is coordinated to four oxygen atoms of *tert*-butoxide ligands and two nitrogen atoms of the pyridine ligands in a cis pseudo-octahedral arrangement as shown in Figure 1. Two different Th–O bond lengths are seen in the molecule, 2.161(6) Å for the *tert*-butoxide ligands trans to pyridine and 2.204(6) Å for the *tert*-butoxide ligands trans to one another. These Th–O distances are similar to the averge terminal Th–O distance of 2.154 Å seen in $Th_2(OCH\text{-}i\text{-}Pr_2)_8$[10] and to the Th–O distance [2.154(8) Å] observed for the 2-butene-2,3-diolate ligand in the X-ray structure of $\{[(\eta^5\text{-}C_5Me_5)_2Th(\mu\text{-}O_2C_2Me_2)]_2\}$.[18] The pyridine ligand exhibits a Th–N distance of 2.752(7) Å and can be compared to the Th–N distance of 2.61(1) Å found for the 2-(6-methylpyridyl)methyl ligand of $Th(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2(CH_2\text{-}py\text{-}6\text{-}Me)_2$[19] and 2.754 Å (av) found for the quinolinato ligands in $Th(C_3H_7NO)(C_9H_6NO)_4$.[20] The Th–O–C angles are relatively large for aliphatic alkoxide ligands; the *tert*-butoxide ligand trans to pyridine exhibits a Th–O–C angle of 171.6(6)°, while those trans to one another are found to be 160.8(6)°.

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Table I. Summary of Crystallographic Data[a]

compound	**1**	**3**
empirical formula	$C_{26}H_{28}N_2O_4Th$	$C_{36}H_{81}O_9NaTh_2$
fw	664.5	1145.1
cryst dimens, mm^{-1}	0.15 × 0.15 × 0.25	0.35 × 0.25 × 0.65
space group	C2/c	Pnma
cell dimens		
a, Å	12.656(3)	11.170(2)
b, Å	15.326(3)	25.408(5)
c, Å	16.803(3)	17.195(3)
β, deg	96.43(3)	
V, Å^3	3238.7(12)	4880.1(16)
Z (molecules/cell)	**4**	**4**
d_{calc}, g cm^{-3}	1.363	1.559
abs coeff, cm^{-1}	47.89	63.49
F(000)	1280	2240
λ(Mo Kα)	0.710 73	0.710 73
T, °C	25	25
2θ range, deg	4.0–50.0	4.0–50.0
measd reflcns	6188	4795
unique intensities	2827	3707
obsd reflcns	2570 ($F > 4.0\sigma(F)$)	2448 ($F > 6.0\sigma(F)$)
R(*F*)	0.0404	0.0376
$R_w(F)$	0.0554	0.0540
goodness-of-fit	1.44	1.47

[a] **1** = $Th(OBu^t)_4(py)_2$; **3** = $NaTh_2(OBu^t)_9$.

Table II. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients[a] (Å^2) for Th(O-*t*-Bu)$_4$(py)$_2$

	10^4x	10^4y	10^4z	10^3U(eq)
Th(1)	0*	1974(1)	2500*	46(1)
O(1)	1681(4)	1680(4)	2387(4)	66(2)
C(1)	2755(8)	1796(8)	2269(7)	81(4)
C(2)	3137(15)	2628(16)	2484(14)	244(15)
C(3)	2860(3)	1658(16)	1392(10)	185(11)
C(4)	3386(12)	1046(17)	2698(11)	261(15)
O(2)	275(6)	2836(4)	3520(4)	75(3)
C(5)	412(10)	3494(7)	4101(6)	80(4)
C(6)	–281(24)	4290(20)	3755(17)	138(3)
C(7)	1624(26)	3745(20)	4243(19)	138(3)
C(8)	–20(30)	3186(18)	4841(20)	138(3)
N(1)	305(6)	557(5)	3506(4)	65(3)
C(9)	1219(9)	486(8)	3952(6)	86(4)
C(10)	1479(11)	–231(10)	4423(7)	113(6)
C(11)	764(13)	–890(9)	4419(9)	126(7)
C(12)	–202(12)	–807(7)	3974(7)	109(6)
C(13)	–406(10)	–63(7)	3502(7)	93(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. Parameters marked by an asterisk were not varied.

NaTh$_2$(O-*t*-Bu)$_9$ (2). Single crystals of **2** suitable for an X-ray diffraction study were grown from hexane solution by slow cooling to –40 °C. A ball and stick drawing giving the atom-numbering scheme used in the tables is given in Figure 2. Selected bond distances and bond angles are given in Tables VI and VII, respectively. Compound **2** crystallizes in the orthorhombic space group *Pnma*, with Na(1) and three bridging alkoxide oxygen atoms [O(1), O(2), O(6)] lying in the mirror plane relating the two halves of the molecule. Crystals of **2** consist of a regular array of NaTh$_2$(O-*t*-Bu)$_9$ molecular units, with no intermolecular interactions between the Na atom of one molecule and O atoms of adjacent molecules. The view of the structure shown in Figure 2 was chosen to emphasize a heterometallic NaTh$_2$ triangle with two μ_3-OR groups. Viewed in this fashion, the molecule is readily described as NaTh$_2$(μ_3-O-*t*-Bu)$_2$(μ_2-O-*t*-Bu)$_3$(O-*t*-Bu)$_4$, and this triangular representation provides a conceptual link to homometallic M$_3$ cluster units, including the Th$_3$O(O-*t*-Bu)$_{10}$ cluster described in this work.

Table III. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients[a] (Å^2) for NaTh$_2$(O-*t*-Bu)$_9$

	10^4x	10^4y	10^4z	10^3U(eq)
Th(1)	2255(1)	1766(1)	69(1)	42(1)
O(1)	3673(9)	2500*	237(6)	46(4)
C(1)	4934(14)	2500*	344(9)	48(6)
C(2)	5281(12)	2013(6)	820(8)	85(6)
C(3)	5548(19)	2500*	–421(11)	82(9)
O(2)	1771(10)	2500*	–844(5)	50(4)
C(4)	1813(17)	2500*	–1674(9)	55(6)
C(5)	3160(17)	2500*	–1909(10)	72(8)
C(6)	1193(15)	2015(6)	–1989(7)	100(7)
O(3)	3239(8)	1273(3)	–724(5)	63(3)
C(7)	3830(17)	865(6)	–1112(9)	87(7)
C(8)	5041(20)	877(11)	–1014(21)	363(31)
C(9)	3637(36)	926(11)	–1965(13)	337(29)
C(10)	3305(20)	351(7)	–935(15)	178(14)
O(4)	346(9)	1505(4)	–196(5)	84(4)
C(11)	–595(13)	1166(8)	–336(10)	98(7)
C(12)	–1096(20)	908(9)	366(11)	158(11)
C(13)	–1611(19)	1507(9)	–752(14)	163(12)
C(14)	–241(22)	792(8)	–1006(14)	183(14)
O(5)	2561(7)	1281(3)	1079(4)	58(3)
C(15)	2782(14)	877(5)	1628(8)	68(5)
C(16)	2507(17)	1045(6)	2436(9)	134(10)
C(17)	2039(23)	402(7)	1421(12)	233(17)
C(18)	4102(20)	712(8)	1604(12)	177(13)
O(6)	1222(10)	2500*	746(5)	54(4)
C(19)	842(17)	2500*	1542(11)	61(7)
C(20)	41(13)	2028(5)	1661(7)	85(6)
C(21)	1966(20)	2500*	2073(10)	85(10)
Na(1)	–212(12)	2500*	–273(9)	168(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. Parameters maked by an asterisk were not varied.

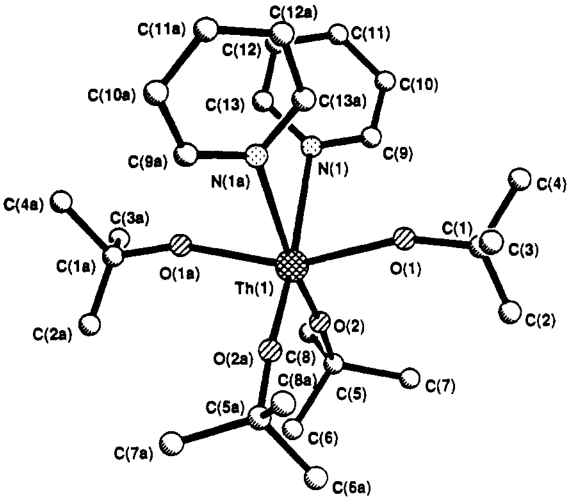

Figure 1. Ball-and-stick drawing of the solid-state molecular structure of Th(O-*t*-Bu)$_4$(py)$_2$ (**1**), emphasizing the cis-pseudo-octahedral geometry and giving the atom-numbering scheme used in the tables.

Table IV. Selected Bond Distances (Å) for the Th(O-*t*-Bu)$_4$(py)$_2$ Molecule

Th(1)–O(1)	2.204(6)	Th(1)–O(2)	2.161(6)
Th(1)–N(1)	2.752(7)	O(2)–C(5)	1.401(12)
O(1)–C(1)	1.407(12)	C(5)–C(6)	1.576(32)
N(1)–C(9)	1.310(13)	C(12)–C(13)	1.396(16)
N(1)–C(13)	1.308(14)	C(11)–C(12)	1.366(21)
C(10)–C(11)	1.355(21)	C(9)–C(10)	1.374(18)

The sodium atom is linked to the thorium atoms by two triply bridging and two doubly bridging oxygen atoms of alkoxide ligands at Na–O distances of 2.399(17) Å (av) and 2.607(10) Å, respectively. If one views O(4) and O(4a) as occupying axial coordination sites on sodium, then the local coordination environment around sodium is essentially that of a distorted trigonal bipyramid with one missing equatorial ligand, yet the "axial" and "equatorial" angles are distorted away from the idealized values due to constraints of the M$_3$ cluster framework. Within the

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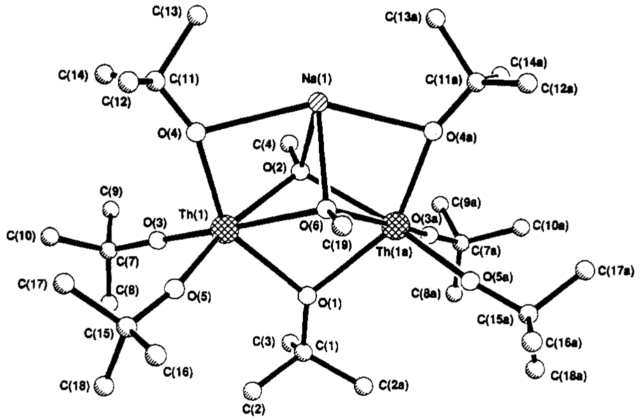


Figure 2. Ball-and-stick drawing of the solid-state molecular structure of $NaTh_2(O\text{-}t\text{-}Bu)_9$ (**3**), emphasizing the trimetallic $NaTh_2$ unit. For clarity, *tert*-butyl carbon atoms are omitted from C(4) and C(19).

Table V. Selected Bond Angles (deg) for the $Th(O\text{-}t\text{-}Bu)_4(py)_2$ Molecule

O(1)–Th(1)–O(2)	97.0(3)	O(1)–Th(1)–N(1)	79.7(2)
O(2)–Th(1)–N(1)	89.8(2)	O(1)–Th(1)–O(1A)	156.4(3)
O(2)–Th(1)–O(1A)	97.3(3)	O(2)–Th(1)–O(2A)	104.7(3)
N(1)–Th(1)–O(2A)	165.5(2)	Th(1)–O(1)–C(1)	160.8(6)
O(1)–Th(1)–N(1A)	81.7(2)	O(1)–C(1)–C(3)	108.1(9)
N(1)–Th(1)–N(1A)	75.8(3)	O(1)–C(1)–C(2)	113.0(12)
Th(1)–O(2)–C(5)	171.6(6)	O(1)–C(1)–C(4)	107.5(10)
O(2)–C(5)–C(7)	108.9(14)	O(2)–C(5)–C(6)	106.3(12)
O(2)C(5)–C(8)	109.0(14)	N(1)–C(9)–C(10)	122.4(11)
Th(1)–N(1)–C(13)	121.4(6)	N(1)–C(13)–C(12)	120.5(11)
Th(1)–N(1)–C(9)	118.1(7)		

Table VI. Selected Bond Distances (Å) for the $NaTh_2(O\text{-}t\text{-}Bu)_9$ Molecule

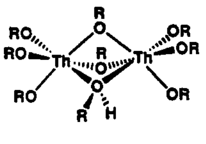
Th(1)–O(1)	2.464(7)	Th(1)–O(2)	2.498(6)
Th(1)–O(3)	2.152(8)	Th(1)–O(4)	2.280(10)
Th(1)–O(5)	2.157(7)	Th(1)–O(6)	2.484(7)
Th(1)–Na(1)	3.380(11)	Th(1)–Th(1A)	3.731(1)
O(1)–C(1)	1.420(19)	O(2)–C(4)	1.428(18)
O(2)–Na(1)	2.423(17)	O(4)–Na(1)	2.607(10)
O(3)–C(7)	1.401(17)	O(6)–Na(1)	2.375(17)
O(4)–C(11)	1.381(20)	O(6)–C(19)	1.432(21)
O(5)–C(15)	1.416(15)		

Table VII. Selected Bond Angles (deg) for the $NaTh_2(O\text{-}t\text{-}Bu)_9$ Molecule

O(1)–Th(1)–O(2)	69.4(3)	O(1)–Th(1)–O(3)	100.7(3)
O(2)–Th(1)–O(3)	98.4(3)	O(1)–Th(1)–O(4)	147.6(3)
O(2)–Th(1)–O(4)	83.6(3)	O(3)–Th(1)–O(4)	100.5(3)
O(1)–Th(1)–O(5)	103.7(3)	O(2)–Th(1)–O(5)	165.3(3)
O(3)–Th(1)–O(5)	95.6(3)	O(4)–Th(1)–O(5)	98.2(3)
O(1)–Th(1)–O(6)	71.1(3)	O(2)–Th(1)–O(6)	68.5(3)
O(3)–Th(1)–O(6)	166.2(3)	O(4)–Th(1)–O(6)	82.9(3)
O(5)–Th(1)–O(6)	97.2(3)	C(4)–O(2)–Na(1)	115.8(10)
Th(1)–O(1)–Th(1A)	98.4(4)	O(2)–C(4)–C(5)	106.9(13)
Th(1)–O(2)–C(4)	128.4(3)	O(3)–C(7)–C(9)	108.9(16)
Th(1)–O(1)–C(1)	130.7(2)	O(3)–C(7)–C(10)	111.9(15)
Th(1)–O(2)–Na(1)	86.8(4)	O(4)–C(11)–C(12)	114.9(14)
Th(1)–O(2)–Th(1A)	96.7(3)	O(5)–C(15)–C(16)	112.3(11)
Na(1)–O(2)–Th(1A)	86.8(4)	Th(1)–O(6)–C(19)	125.8(4)
O(2)–C(4)–C(6)	110.0(9)	C(19)–O(6)–Na(1)	120.3(10)
Th(1)–O(3)–C(7)	167.0(8)	O(6)–C(19)–C(20)	107.7(10)
O(3)–C(7)–C(8)	113.0(17)	O(2)–Na(1)–O(4)	78.6(4)
Th(1)–O(4)–Na(1)	87.3(4)	O(2)–Na(1)–O(6)	71.5(5)
Th(1)–O(4)–C(11)	158.2(10)	O(4)–Na(1)–O(4A)	151.7(7)
C(11)–O(4)–Na(1)	114.5(9)	Th(1)–O(6)–Na(1)	88.1(3)
O(4)–C(11)–C(13)	106.2(15)	O(6)–C(19)–C(21)	108.8(15)
O(4)–C(11)–C(14)	108.6(14)	O(4)–Na(1)–O(6)	78.5(4)
Th(1)–O(5)–C(15)	168.1(7)	O(5)–C(15)–C(18)	110.3(12)
O(5)–C(15)–C(17)	109.1(12)		

heterometallic $NaTh_2$ plane, the Th- -Th and Th- -Na distances are 3.731(1) and 3.380(11) Å, respectively. Each thorium atom is bound to six alkoxide oxygen atoms located at the vertices of a distorted octahedron. Terminal *tert*-butoxide ligands on thorium display average Th–O distances of 2.155(8) Å and are similar to the terminal distances found in **1** and $Th_2(OCH\text{-}i\text{-}Pr_2)_8$.[10] Doubly bridging *tert*-butoxide ligands display different Th–O bond distances depending on whether a Th–O–Th or Th–O–Na linkage is present. A Th–O distance of 2.280(10) Å is observed for the alkoxide bridging to Na, and 2.464(7) Å for those alkoxides bridging to another Th atom. Triply bridging alkoxide ligands that cap the $NaTh_2$ triangular unit display an average Th–O distance of 2.491(7) Å. The structurally related uranium and cerium analogs of **3**, of formulas $KU_2(O\text{-}t\text{-}Bu)_9$ and $NaCe_2(O\text{-}t\text{-}Bu)_9$, have been reported by Cotton[21] and Evans,[17] respectively, although the X-ray data collected for the cerium complex were of a quality which allowed only molecular connectivity to be established.[17]

By including the sodium atom in the metal count of **3**, one can see that the $NaTh_2$ triangular cluster unit is closely related to the well-known M_3X_{11} cluster unit observed (^1H NMR; vide infra) for compound **4**, $Th_3O(O\text{-}t\text{-}Bu)_{10}$, and these structural units are illustrated in **3** and **4**. Both **3** and **4** contain triply bridging ligands above and below the M_3 plane, with three doubly bridging alkoxide ligands within the M_3 plane. Hence $NaTh_2(O\text{-}t\text{-}Bu)_9$ may be viewed as a simple modification of the fundamental M_3X_{11} building block common in uranium,[22] yttrium,[23,24] lanthanum,[25] and group VI transition metal chemistry.[26] As noted by Cotton,[22] $U_3O(O\text{-}t\text{-}Bu)_{10}$ is structurally similar, in a qualitative sense, to the $M_3O(OR)_{10}$ cluster compounds (M = Mo, W) reported by Chisholm et al.[26] It is also apparent that the $M'M_2O_9$ structural unit seen in **3** is becoming more common as seen in the structures of $KU_2(O\text{-}t\text{-}Bu)_9$,[21] $NaCe_2(O\text{-}t\text{-}Bu)_9$,[17] $(DME)KZr_2(O\text{-}i\text{-}Pr)_9$,[27] $[ClCdZr_2(O\text{-}i\text{-}Pr)_9]_2$,[28] $KBa_2(OSiPh_3)_6(DME)_2$,[29] and $[(O\text{-}i\text{-}Pr)BaZr_2(O\text{-}i\text{-}Pr)_9]_2$.[30] Although there are no solid-state structural data for **2**, we propose a confacial bioctahedral geometry in analogy to the $MTh_2(OR)_9$ unit as illustrated in **2**. The proton attached to the bridging alcoholate is shown for accounting purposes only. ^1H NMR data reveal that the proton on the alcoholate ligand is scrambling rapidly between alkoxide ligand sites.



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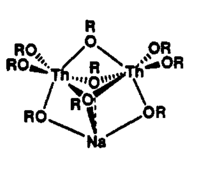
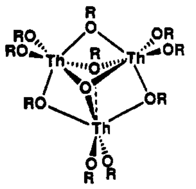


3



4

In the solid-state structure of **3** it is rather unusual that the $Na\text{-}\mu_2\text{-}O$ distances are longer than the $Na\text{-}\mu_3\text{-}O$ distances. One might expect these values to show the same behavior as the alkoxides bridging the thorium atoms: $\mu_3\text{-}OR > \mu_2\text{-}OR > OR$. Long μ_3-O bonds of an $[M_2(OR)_9]^-$ fragment bound to a heterometal center are a common feature seen in the chemistry of the $[Zr_2(O\text{-}i\text{-}Pr)_9]^-$ unit, and the long bonding interactions of

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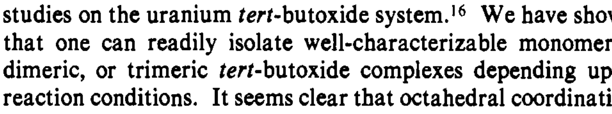
the μ_3 alkoxides are presumably due to a loss of electron density at oxygen with each successive bridge.[27,28,30] However, Cotton's structure of $KU_2(O\text{-}t\text{-}Bu)_9$ shows the same trend as $NaTh_2(O\text{-}t\text{-}Bu)_9$; the K–O distances are 2.94 and 2.75 Å for doubly and triply bridging alkoxides.[21] In the two actinide structures, there is no terminal ligand attached to the alkali metal atom, while in the zirconium complexes, such as $[BaZr_2(O\text{-}i\text{-}Pr)_{10}]_2$[30] and $(DME)KZr_2(O\text{-}i\text{-}Pr)_9$,[27] there are other ligands attached to the heterometal atom. These additional ligands may tend to pull the heterometal center away from the Zr_2 unit. To test this, we performed some simple trigonometric calculations on the $NaTh_2(O\text{-}t\text{-}Bu)_9$ structural unit. By leaving all atoms in place and simply pulling the sodium atom away from the Th–Th vector to make an equilateral triangle (Th–Th = Th–Na = 3.732 Å), one finds that the Na–μ_2O distance lengthens from 2.60 to 2.74 Å, while the Na–μ_3-O distance increases more dramatically from 2.40 to 2.75 Å. The fact that the triply bridging Na–O distances are shorter than the doubly bridging ligands appears to be simply geometrical. In the actinide structures with no other terminal ligand attached to the alkali metal atom, this atom is apparently tucked in tighter to the "basket" formed by the four oxygen atoms.

Terminal Th–O distances for both structures reported here are rather short, and the corresponding Th–O–C angles are large, ranging from 158.2 to 171.6°. Similar trends have been observed in early transition metal alkoxide compounds, where short M–O bonds and large M–O–C angles have been taken as structural evidence for oxygen-to-metal π-donation from alkoxide ligands.[31] Indeed, this is a commonly accepted phenomenon in early transition metal alkoxide and aryloxide chemistry.[31,32] However, a recent publication on four-coordinate aluminum alkoxides revealed that M–O bond length and M–O π bond order do not necessarily correlate.[33] A very short metal–oxygen bond may result from a high degree of ionic character or alternatively from multiple bonding, O pπ to M dπ. More electropositive metals in their highest oxidation states such as Al^{3+}, Zr^{4+}, or Th^{4+} might be expected to be more ionic in character than later, less electropositive d-block elements in the mid transition series. However, we note that in the case of transition elements, the short M–O bonds associated with π-bonding interactions are always accompanied by an obtuse M–O–C angle, while in four-coordinate aluminum alkoxides (no accessible d orbitals and little to no M–O π-bonding) short M–O distances are accompanied by more acute M–O–C angles ranging from 135 to 150°.[34] In addition, theoretical and spectroscopic studies have shown that empty thorium 6d orbitals are very low-lying[35] and therefore should be available for M–O π-bonding interactions. The trends in bond distances and angles seen in **1**, **3**, and $Th_2(OCH\text{-}i\text{-}Pr_2)_8$ may serve as structural evidence for *some* degree of oxygen-to-metal π-bonding in thorium alkoxides.

Spectroscopic Characterization. Room-temperature ^1H NMR spectra reveal only one type of alkoxide ligand for $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (**1**) presumably due to a fluxional process in solution. Low-temperature (−75 °C) spectra in toluene-d_8 failed to freeze out a limiting structure. The room-temperature ^1H NMR spectrum of $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ (**2**) in benzene-d_6 shows only one broad *t*-Bu signal (δ 1.54) and a broad resonance at δ 3.22, which we assign as the alcoholic O*H* proton. The intensity ratio of these two signals is *ca.* 80:1 consistent with these assignments. The exact position of the O*H* resonance changes as a function of solvent and concentration, consistent with our expectations of an alcoholic O*H* proton. We were unable to freeze out a static structure for **2** in toluene-d_8 in the temperature range +25 to −90 °C presumably due to rapid proton scrambling and/or alkoxide site exchange. Room-temperature ^1H NMR spectra of $NaTh_2(O\text{-}t\text{-}Bu)_9$ (**3**) displayed four types of alkoxide ligands in a static 4:2:2:1 ratio consistent with our expectations on the basis of the solid-state molecular structure. In the case of $Th_3O(O\text{-}t\text{-}Bu)_{10}$ (**4**), ^1H NMR spectroscopy revealed a static 3:3:3:1 pattern of *tert*-butoxide resonances indicative of the well-known $M_3O(OR)_{10}$ structural unit.[16,26]

During the course of our studies of thorium alkoxide complexes and their Lewis base adducts, we have found that the chemical shift of the ortho protons of a pyridine ligand bound to thorium are very sensitive to coordination environment. As a result, one can readily follow the course of the reaction between pyridine and the alcoholate dimer $Th_2(O\text{-}t\text{-}Bu)_9(HO\text{-}t\text{-}Bu)$ (**2**) by ^1H NMR spectroscopy at ambient temperatures. When less than 1 equiv of pyridine per thorium atom is added, a single ortho pyridine resonance at δ = 8.95 ppm is observed by ^1H NMR spectroscopy. When greater than 1 equiv of pyridine is added, a second ortho resonance is observed to grow in at δ = 8.53 ppm. As the pyridine titration continues, the original ortho resonance begins to disappear as the new resonance grows in until exactly 2 equiv of pyridine per thorium has been added. At this point, the ^1H NMR spectrum of the product is identical to that observed for $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (**1**). We take this as evidence for the displacement of coordinated $HO\text{-}t\text{-}Bu$ in **2** by pyridine to form a new dimer $Th_2(O\text{-}t\text{-}Bu)_8(py)_2$ (**5**), which can react with additional added pyridine to produce monomeric $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (**1**) as outlined in eq 8. The molecular geometry indicated for $Th_2(O\text{-}t\text{-}Bu)_8(py)_2$ (**5**) in eq 8 is based on the structure that we have observed in the solid state for $Th_2(OCHEt_2)_8(py)_2$.[36]



2 **5** **1** (8)

Concluding Remarks

During the course of our studies we have been unable to isolate and characterize a homoleptic $Th(O\text{-}t\text{-}Bu)_4$ complex, consistent with the observations of Sattelberger and co-workers in their studies on the uranium *tert*-butoxide system.[16] We have shown that one can readily isolate well-characterizable monomeric, dimeric, or trimeric *tert*-butoxide complexes depending upon reaction conditions. It seems clear that octahedral coordination is the preferred coordination environment for the *tert*-butoxide ligand around thorium, and octahedral coordination has been found exclusively in the actinide, lanthanide, and yttrium *tert*-butoxide structures reported to date.[1,22–25,37] In the absence of added base, the dimeric six-coordinate alcoholate $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ is formed, and this is consistent with uranium and lanthanum *tert*-butoxide chemistry where polymetallic alcoholates of formulas $U_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ and $La_3(O\text{-}t\text{-}$

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$Bu)_9(HO\text{-}t\text{-}Bu)_2$ are formed.[16,25] In the presence of a good donor ligand such as pyridine, the alcoholate dimer is cleaved to produce monomeric $Th(O\text{-}t\text{-}Bu)_4(py)_2$. This is in contrast to the chemistry of yttrium complexes in which the trimetallic structure of $Y_3(O\text{-}t\text{-}Bu)_7Cl_2(THF)_2$ is characteristically retained in reactions of yttrium *tert*-butoxide complexes.[23,24,38] In the solid-state structures of **1** and **3**, the relatively short Th–O bonds, obtuse Th–O–C angles, and cis-pyridine ligands may serve as structural evidence for *some* degree of oxygen-to-metal π-bonding in aliphatic thorium alkoxides where virtual 6d orbitals are expected to be low-lying and available for such interactions.

During Bradley's pioneering work on the thorium *tert*-butoxide system in 1954, *tert*-butoxide complexes were prepared via alcohol interchange employing *tert*-butyl alcohol as solvent.[2] On the basis of the results reported here, it seems likely that such reaction conditions would favor $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ as the major product. However, we have not tested Bradley's preparative route since the exact nature of the $Th(O\text{-}i\text{-}Pr)_4$ starting material is still somewhat uncertain. But we have shown that $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ is susceptible to hydrolysis to give trimetallic $Th_3O(O\text{-}t\text{-}Bu)_{10}$. Since ebulliometric molecular weight determinations can take some time to establish equilibrium, it is possible that $Th_3O(O\text{-}t\text{-}Bu)_{10}$ was the solution species which gave a molecular complexity of 3.4 in Bradley's original studies.[2] We plan to test this hypothesis when we have completed our characterization of $Th(O\text{-}i\text{-}Pr)_4$ compounds.

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres glovebox. $ThI_4(THF)_4$,[13] $[\{(Me_3Si)_2N\}_2\overline{Th(CH_2SiMe_2N}SiMe_3)]$,[39] and $NaN(SiMe_3)_2$[40] were prepared as described previously. Potassium *tert*-butoxide was prepared by the reaction of potassium hydride with *tert*-butyl alcohol in THF. Solvents, except for pyridine, were degassed and distilled from Na/K alloy under nitrogen. Pyridine was distilled from CaH_2 under argon. *tert*-butyl alcohol was distilled from sodium and stored in the drybox. Benzene-d_6 and toluene-d_8 were degassed, dried over Na/K alloy, and then trap-to-trap distilled before use. Solvents were taken into the glovebox, and a small amount was tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded at 22 °C on Bruker WM 300 or AF 250 spectrometers in benzene-d_6 or toluene-d_8. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in benzene-d_6 or toluene-d_8 set at δ 7.15 or 2.09, respectively. Infrared spectra were recorded on a Perkin-Elmer 1500 spectrophotometer interfaced with a 1502 central processor. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Syntheses. $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (1). In the drybox, 7.00 g (6.81 mmol) of $ThI_4(THF)_4$ was dissolved in 100 mL of THF in a 250-mL Erlenmeyer flask and 10 mL of pyridine added. Then a solution of 3.15 g (28.1 mmol) of potassium *tert*-butoxide in 20 mL of THF was added to the flask to produce a white precipitate. This suspension was allowed to stir at room temperature for 24 h before being filtered through a Celite pad to give a clear, pale yellow filtrate. All solvent was removed *in vacuo* to leave a pale yellow solid, which was dissolved in 80 mL of 15:1 hexane/pyridine and filtered again through a Celite pad. The volume of the filtrate was reduced to 20 mL and placed at –40 °C. Overnight, colorless crystals were deposited. These were filtered off and allowed to dry. Yield: 1.04 g (22%). ^1H NMR (300 MHz, C_6D_6): δ 8.53 (br, 2H, ortho py), 6.96 (br m, 1H, para py), 6.65 (m, 2H, meta py), 1.60 (s, 18H, *t*-Bu). IR (Nujol mull, KBr plates): 1600 (w), 1595 (w), 1445 (sh, m), 1365 (m), 1355 (s), 1225 (m), 1205 (s), 1190 (s), 1070 (w), 1035 (w), 1023 (w), 987 (s), 962 (s), 931 (w), 912 (s), 830 (w), 772 (m), 756 (w), 727 (w), 701 (m), 622 (w), 614 (w), 524 (w), 497 (s), 480 (m). Anal. Calcd for $C_{26}H_{28}N_2O_4Th$: C, 45.74; H, 6.79; N, 4.10. Found: C, 45.38; H, 6.61; N, 5.06.

$Th_2(O\text{-}t\text{-}Bu)_8(H\text{-}O\text{-}t\text{-}Bu)$ (2). In the drybox, 4.00 g (5.62 mmol) of thorium metallacycle $[\{(Me_3Si)_2N\}_2\overline{Th(CH_2SiMe_2N}SiMe_3)]$ was dissolved in 100 mL of toluene in a 250-mL Erlenmeyer flask. To the stirred thorium solution was then added dropwise a solution of 1.88 g (25.4 mmol) of *tert*-butyl alcohol in 10 mL of toluene. The mixture was stirred at room temperature for 24 h, and then all solvent was removed *in vacuo* to leave a white solid. This solid was taken into 100 mL of hexane, and the mixture was filtered through a Celite pad. The volume of the filtrate was reduced to 15 mL and cooled to –40 °C, producing a mass of white crystals overnight. The crystals were decanted free from solvent and allowed to dry. Yield: 2.20 g (70%). ^1H NMR (300 MHz, C_6D_6): δ 3.22 (br, 1H, O*H*), 1.54 (s, 81H, *t*-Bu). ^1H NMR (250 MHz, C_7D_8): δ 2.87 (br, 1H, O*H*), 1.53 (s, 81H, *t*-Bu). IR (KBr plates, Nujol mull): 3171 (w), 1465 (s), 1365 (m), 1354 (m), 1227 (s), 1203 (s), 1188 (s), 1047 (w), 985 (s), 960 (s), 910 (s), 771 (m), 758 (m), 727 (w), 523 (w), 495 (s), 479 (s). Anal. Calcd for $C_{36}H_{81}O_9NaTh_2$: C, 38.50; H, 7.36; N, 0.00. Found: C, 38.52; H, 7.70; N, 0.03.

$NaTh_2(O\text{-}t\text{-}Bu)_9$ (3). In the drybox, 0.79 g (0.70 mmol) of $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ was dissolved in 50 mL of toluene in a 125-mL Erlenmeyer flask. Then 0.128 g (0.70 mmol) of solid sodium bis(trimethylsilyl)amide was added to the stirring thorium solution, and stirring continued at room temperature for 16 h. All solvent was removed in vacuo to leave a white solid, which was dissolved in 50 mL of hexane and filtered through a Celite pad. The volume of the filtrate was reduced to 10 mL and placed at –40 °C, producing colorless cubic crystals overnight. The crystals were filtered off and allowed to dry. Yield: 0.59 g (73%). ^1H NMR (300 MHz, C_6D_6): δ 1.71 (s, 1H), 1.69 (s, 2H), 1.53 (s, 4H), 1.26 (s, 2H). IR (Nujol mull, KBr plates): 1364 (s), 1355 (s), 1223 (s), 1202 (s), 1188 (s), 1046 (m), 1019 (w), 983 (s), 958 (s), 910 (s), 769 (m), 756 (sh), 692 (w), 523 (m), 495 (s), 479 (m). Anal. Calcd for $C_{36}H_{81}NaO_9Th_2$: C, 37.76; H, 7.13; N, 0.00. Found: C, 37.20; H, 6.07; N, 0.12.

$Th_3O(O\text{-}t\text{-}Bu)_{10}$ (4). In the drybox, 3.00 g (4.21 mmol) of thorium metallacycle was dissolved in 75 mL of toluene in a Schlenk reaction vessel, and 1.41 g (19.02 mmol) of dry *tert*-butyl alcohol added. The flask was removed from the drybox and attached to a Schlenk line, and 50 μL (0.90 mmol) of water was added via a microliter syringe. The solution was then refluxed under argon for 48 h and returned to the drybox. All solvent was removed *in vacuo* to leave a white solid residue, which was extracted into 100 mL of hexane and filtered through a Celite pad. The volume of the filtrate was reduced to ca. 75 mL and placed at –40 °C, producing a fluffy crystalline mass over a several days. This solid was filtered off and dried in vacuo. Yield: 0.58 g (29%). ^1H NMR (250 MHz, C_6D_6): δ 1.80 (s, 9H), 1.74 (s, 27H), 1.46 (s, 27H), 1.45 (s, 27H). IR (Nujol mull, KBr plates): 1364 (s), 1356 (s), 1238 (m, sh), 1227 (m), 1196 (s), 991 (m), 964 (s), 913 (s), 771 (m), 761 (sh), 668 (w), 529 (m), 497 (s), 480 (m). Anal. Calcd for $C_{40}H_{90}O_{11}Th_3$: C, 33.29; H, 6.29; N, 0.00. Found: C, 33.27; H, 6.09; N, 0.01.

Crystallographic Studies. $Th(O\text{-}t\text{-}Bu)_4(py)_2$ (1). Crystal data, collection, and processing parameters are given in Table I. A crystal measuring 0.15 × 0.15 × 0.25 mm was mounted in a sealed quartz Lindemann tube and placed on the goniometer head of an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were determined from the least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 accurately centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. Data were collected by ω scans.

The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans was applied. Equivalent reflections were merged, and systematically absent reflections were rejected. The structure was solved by routine Patterson and Fourier methods. During the initial least-squares refinement it became evident that there was a disorder problem in the three methyl carbons attached to C(5). Least-squares refinement varying the occupancies of these carbons indicated two sets of three methyl carbons with 57% and 43% occupancy. The occupancy was then fixed, and the least-squares refinement was completed. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate

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carbon atoms, final refinement using 2570 unique observed [$F > 4\sigma(F)$] reflections converged at $R = 0.040$ and $R_w = 0.055$ {where $w = [\sigma(F) + 0.000625(F)^2]^{-1}$}. No hydrogen atoms were included on the disordered carbons C(6), C(7), or C(8). All calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc., 1990).

$NaTh_2$(O-*t*-Bu)$_9$ (3). Crystal data, collection, and processing parameters are given in Table I. A crystal measuring 0.35 × 0.25 × 0.65 mm was mounted in a sealed quartz Lindemann tube and placed on the goniometer head of an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were determined from the least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 accurately centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. Data were collected by ω scans.

The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans was applied. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 2448 unique observed [$F > 6\sigma(F)$] reflections converged at $R = 0.038$ and $R_w = 0.054$ {where $w = [\sigma^2(F) + 0.000625(F)^2]^{-1}$}. All calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc., 1990).

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom coordinates for Th(O-*t*-Bu)$_4$py$_2$ and $NaTh_2$(O-*t*-Bu)$_9$ (3 pages). Ordering information is given on any current masthead page. Structure factor tables are available from the authors upon request.