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Oligomerization of Metal—Oxygen Bonds in Thorium Alkoxide Chemistry: X-ray Crystal Structures of $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ and $Th_2(OCHEt_2)_8(py)_2$

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Reaction of the thorium(IV) metallacycle $[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3)$ with 4 equiv of 2-propanol in toluene generates a homoleptic thorium isopropoxide $[Th(O\text{-}i\text{-}Pr_4]_x$ (**1**) in good yield. In contrast, the reaction of the thorium metallacycle with 4 equivalents of 2-propanol in toluene, followed by the addition of excess pyridine and crystallization from hexane, yields the tetrameric complex $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ (**2**). However, if compound **1** is allowed to "age" for 2 days, no reaction with pyridine and the aged material is observed. Compound **2** may also be prepared by the metathesis reaction of $ThBr_4(THF)_4$ with 4 equiv of potassium isopropoxide in THF followed by the addition of excess pyridine. An X-ray crystal structure of **2** revealed a zigzag chain of four thorium atoms comprised of a dimer of edge-shared bioctahedra joined by one axial and one equatorial bridging alkoxide ligand. The local coordination geometry about each thorium atom is that of a distorted octahedron, and the thorium atoms at each end of the zigzag chain are capped with a pyridine ligand. Average terminal and bridging Th—O distances are 2.172 and 2.420 Å. The Th—N distance is 2.740 Å, and nonbonding Th--Th distances average 4.031 Å. A similar reaction between $[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3)$ and 4 equiv of pentan-3-ol in toluene followed by addition of excess pyridine and crystallization from hexane yields the dimeric complex $Th_2(OCHEt_2)_8(py)_2$ (**3**). An X-ray crystal structure of **3** revealed a centrosymmetric edge-sharing bioctahedron with average Th—O, Th—μ—O, Th—N, and Th--Th distances of 2.170, 2.427, 2.730, and 4.055 Å, respectively. Crystal data for **2** (at –170 °C): Triclinic space group $P\bar{1}$, $a = 11.211(2)$ Å, $b = 18.689(4)$ Å, $c = 9.984(2)$ Å, $\alpha = 101.65(1)°$, $\beta = 108.57(1)°$, $\gamma = 75.60(1)°$, $V = 1903.52$ Å^3, $Z = 1$, $d_{calc} = 1.772$ g cm^{-3}, $R(F) = 0.0441$, $R_w(F) = 0.0453$. Crystal data for **3** (at –70 °C): Triclinic space group $P\bar{1}$, $a = 11.302(3)$ Å, $b = 11.458(3)$ Å, $c = 14.191(3)$ Å, $\alpha = 113.02(2)°$, $\beta = 92.50(2)°$, $\gamma = 115.82(2)°$, $V = 1470.9$ Å^3, $Z = 1$, $d_{calc} = 1.345$ g cm^{-3}, $R(F) = 0.0448$, $R_w(F) = 0.0498$.

Introduction

Alkoxide and aryloxide ligands of general formula OR^- have found an extensive use in transition metal inorganic and organometallic chemistry due in part to their adjustable steric requirements, ability to bridge more than one metal center, and their ability to stabilize mid to high oxidation states through variable π-electron donation.[2-5] More recently, the use of alkoxide ligation in lanthanide and actinide chemistry has begun to attract considerable interest.[6-8] While a great deal of thorium and uranium alkoxide chemistry was reported by Bradley and Gilman during the 1950's and 1960's, it is only recently that new structural data and reaction chemistry has begun to emerge.[8] A great deal of this recent work has focused on the determination of which ligand systems yield crystalline compounds and provide useful starting materials for further development of actinide alkoxide chemistry.

The key starting material in Bradley's early 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 $NaO\text{-}i\text{-}Pr$ in 2-propanol solvent as outlined in eq 1.[9] Other thorium alkoxides were then conveniently

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

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

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

$$[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3) + 4HOCH\text{-}i\text{-}Pr_2 \rightarrow {}^1/_2Th_2(OCH\text{-}i\text{-}Pr_2)_8 + 3HN(SiMe_3)_2 \quad (3)$$

$$ThBr_4(THF)_4 + 4KO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3 \rightarrow Th(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4 + 4KBr \quad (4)$$

prepared by alcohol interchange as outlined in eq 2.[10-16] More recently, we and others have found that alcoholysis of the thorium metallacycle $[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3)$ or metathesis

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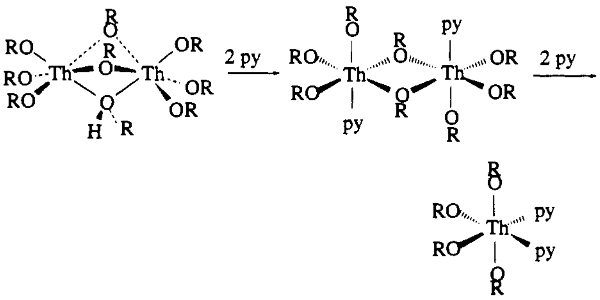
of $\mathrm{ThBr_4(THF)_4}$ gives high yields of halide- and alkali metal-free thorium alkoxides as outlined in eqs 3 and 4.[17–19]

During our studies of thorium *tert*-butoxide complexes,[20] we were unable to isolate a homoleptic $\mathrm{Th(O\text{-}\mathit{t}\text{-}Bu)_4}$ complex, consistent with the observations of Sattelberger *et al.* on the uranium *tert*-butoxide system.[21] Instead, we discovered that, in the absence of a Lewis base, the confacial bioctahedral alcoholate dimer $\mathrm{Th_2(O\text{-}\mathit{t}\text{-}Bu)_8(HO\text{-}\mathit{t}\text{-}Bu)}$ is formed, while, in the presence of a stoichiometric amount of pyridine, this alcoholate dimer is cleaved to produce monomeric $\mathrm{Th(O\text{-}\mathit{t}\text{-}Bu)_4(py)_2}$ as illustrated in eq 5.[20] ^{1}H NMR monitoring of the reaction shown in eq 5 was consistent with the presence of an intermediate complex of formula $\mathrm{Th_2(O\text{-}\mathit{t}\text{-}Bu)_8(py)_2}$, but this species was not isolated. We also found that $\mathrm{Th_2(O\text{-}\mathit{t}\text{-}Bu)_8(HO\text{-}\mathit{t}\text{-}Bu)}$ is susceptible to hydrolysis to give trimetallic $\mathrm{Th_3O(O\text{-}\mathit{t}\text{-}Bu)_{10}}$, suggesting that this trimer was the solution species (in boiling benzene) which gave a molecular complexity of 3.4 in Bradley's original studies. In Bradley's seminal studies of secondary alkoxides of thorium,[12] ebullioscopic molecular weight determinations in boiling benzene indicated a molecular complexity of 3.8 for isopropoxide, and 4.1 for isopentoxide ligands. Since we found that the *tert*-butoxide complexes were quite hydrolytically sensitive, it seemed possible that the higher order oligomers for isopropoxide and isopentoxide ligands observed by Bradley could also have been a result of hydrolysis and subsequent formation of oxo–alkoxide clusters. In the present work, we describe the synthesis and structural characterization of thorium isopropoxide and isopentoxide complexes and the relationship of these complexes to those reported by Bradley.



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Results and Discussion

Synthesis and Reactivity. The room-temperature reaction between the thorium metallacycle of formula $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\overline{\mathrm{Th}(\mathrm{CH_2SiMe_2N}}\mathrm{SiMe_3})$ and 4 equiv of 2-propanol in toluene, followed by low-temperature crystallization from hexane, yields a white amorphous powder of empirical formula $\mathrm{Th(O\text{-}\mathit{i}\text{-}Pr)_4}$ (**1**) as outlined in eq 6. ^{1}H NMR spectra of this solid show a single isopropoxide resonance, but all attempts to obtain crystalline material for X-ray diffraction studies were unsuccessful. If, however, the same reaction is carried out in the presence of an excess (12 equiv per Th) of pyridine, a white crystalline product of formula $\mathrm{Th_4(O\text{-}\mathit{i}\text{-}Pr)_{16}(py)_2}$ (**2**) is obtained in 20% crystallized yield based on eq 7. ^{1}H NMR spectra of the crystalline product showed the presence of coordinated pyridine, in a ratio of *ca.* 8 isopropoxide ligands to each pyridine ligand consistent with the formulation of $\mathrm{Th_4(O\text{-}\mathit{i}\text{-}Pr)_{16}(py)_2}$. However, if the original $[\mathrm{Th(O\text{-}\mathit{i}\text{-}Pr)_4}]_x$ product (**1**) is allowed to stand for 2 days prior to the addition of excess pyridine, only the white solid of empirical formula $[\mathrm{Th(O\text{-}\mathit{i}\text{-}Pr)_4}]_x$ can be recovered. This observation is suggestive that the $[\mathrm{Th(O\text{-}\mathit{i}\text{-}Pr)_4}]_x$ solid has undergone a further transformation, in analogy with aluminum isopropoxides,[22,23] where the occurrence of several different oligomers has been demonstrated.[24]

$$[(\mathrm{Me_3Si})_2\mathrm{N}]_2\overline{\mathrm{Th}(\mathrm{CH_2SiMe_2N}}\mathrm{SiMe_3}) + 4\mathrm{HO\text{-}\mathit{i}\text{-}Pr} \rightarrow [\mathrm{Th(O\text{-}\mathit{i}\text{-}Pr)_4}]_x + 3\mathrm{HN(SiMe_3)_2} \quad (6)$$

$$[(\mathrm{Me_3Si})_2\mathrm{N}]_2\overline{\mathrm{Th}(\mathrm{CH_2SiMe_2N}}\mathrm{SiMe_3}) + 4\mathrm{HO\text{-}\mathit{i}\text{-}Pr} \xrightarrow{\mathrm{py}} {}^1/_4\mathrm{Th_4(O\text{-}\mathit{i}\text{-}Pr)_{16}(py)_2} + 3\mathrm{HN(SiMe_3)_2} \quad (7)$$

$$\mathrm{ThBr_4(THF)_4} + 4\mathrm{NaO\text{-}\mathit{i}\text{-}Pr} \xrightarrow[(2)\ \mathrm{py}]{(1)\ \mathrm{THF}} {}^1/_4\mathrm{Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2} + 4\mathrm{NaBr} \quad (8)$$

At this point it was not clear if pyridine in the reaction mixture of eq 7 served to stabilize a tetrameric $[\mathrm{Th(O\text{-}\mathit{i}\text{-}Pr)_4}]_4$ complex or to break up polymeric $[\mathrm{Th(O\text{-}\mathit{i}\text{-}Pr)_4}]_x$ with the fortuitous isolation of a tetrameric product. Recall that previous studies on *tert*-butoxide complexes indicated that a stoichiometric amount of pyridine would cleave dimeric complexes to form monomeric $\mathrm{Th(O\text{-}\mathit{t}\text{-}Bu)_4(py)_2}$.[20] To provide additional insight into this question, we examined the metathesis of $\mathrm{ThBr_4(THF)_4}$ to see whether monomeric or tetrameric products were formed. The reaction of $\mathrm{ThBr_4(THF)_4}$ with 4 equiv of potassium isopropoxide in THF solution followed by the addition of a stoichiometric amount of pyridine also produces the tetrameric bis(pyridine) adduct $\mathrm{Th_4(O\text{-}\mathit{i}\text{-}Pr)_{16}(py)_2}$ (**2**), as outlined in eq 8. The reaction proceeds smoothly at room temperature and appears to be complete within several hours. Recrystallization from a *ca.* 50:1 hexane/pyridine mixture gives the white, crystalline product in 80% yield based on eq 8. The addition of further equivalents of pyridine only produces compound **2**. Compound **2** is readily soluble in hexane, benzene, and toluene.

In order to investigate the effect of a slight increase in steric bulk upon the product nuclearity, a toluene solution of the thorium metallacycle $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\overline{\mathrm{Th}(\mathrm{CH_2SiMe_2N}}\mathrm{SiMe_3})$ was treated with 4 equivalents of isopentanol (pentan-3-ol) at room temperature. Removal of solvent left a colorless oil which was extremely soluble in hexane and resisted all efforts at crystallization. However, in analogy with the isopropoxide system, addition of excess pyridine (12 equiv per Th) to a hexane solution of this oil, followed by cooling to −40 °C, yielded colorless crystals of $\mathrm{Th_2(OCHEt_2)_8(py)_2}$ (**3**) in 60% yield according to eq 9. ^{1}H NMR spectra of the crystalline product exhibited a 4:1 ratio of isopentoxide to pyridine ligands consistent with the formulation of $\mathrm{Th_2(OCHEt_2)_8(py)_2}$.

$$[(\mathrm{Me_3Si})_2\mathrm{N}]_2\overline{\mathrm{Th}(\mathrm{CH_2SiMe_2N}}\mathrm{SiMe_3}) + 4\mathrm{HOCHEt_2} \xrightarrow{\mathrm{py}} {}^1/_2\mathrm{Th_2(OCHEt_2)_8(py)_2} + 3\mathrm{HN(SiMe_3)_2} \quad (9)$$

Solid-State and Molecular Structures. Both $\mathrm{Th_4(O\text{-}\mathit{i}\text{-}Pr)_{16}(py)_2}$ (**2**) and $\mathrm{Th_2(OCHEt_2)_8(py)_2}$ (**3**) have been examined by single-crystal X-ray diffraction studies during this work. In both cases, the unit cell revealed discrete molecules. A summary of data collected and crystallographic parameters is given in Table 1. Atomic positional parameters are given in Tables 2 and 3.

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Table 1. Summary of Crystallographic Data[a]

compd	**2**	**3**
empirical formula	$C_{58}H_{122}N_2O_{16}Th_4$	$C_{50}H_{98}N_2O_8Th_2$
color; habit	colorless	colorless
crystal dimens, mm	0.10 × 0.12 × 0.12	0.20 × 0.20 × 0.32
space group	$P\bar{1}$	$P\bar{1}$
cell dimens		
a, Å	11.211(2)	11.302(3)
b, Å	18.689(4)	11.458(3)
c, Å	9.984(2)	14.191(3)
α, deg	101.65(1)	113.02(2)
β, deg	108.57(1)	92.50(2)
γ, deg	75.60(1)	115.82(2)
V, Å^3	1903.52	1470.9
Z (molecules/cell)	1	1
fw	2031.77	1319.4
D_{calc}, g cm^{-3}	1.772	1.345
abs coeff, cm^{-1}	60.026	52.69
λ(Mo Kα)	0.710 69	0.710 73
temp., °C	−170	−70
2θ range, deg	6.0–45.0	2.0–50.0
measd reflcns	5046	7074
unique intensities	4965	6734
obsd reflcns	3651 ($F > 2.33\sigma(F)$)	5166 ($F > 4.0\sigma(F)$)
$R(F)$[b]	0.0441	0.0448
$R_w(F)$[c]	0.0453	0.0498
goodness-of-fit	1.706	1.20

[a] **2** = $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$; **3** = $Th_2(OCHEt_2)_8(py)_2$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F) = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

$Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ (2). Single crystals of **2** suitable for an X-ray diffraction study were grown from a hexane/pyridine solution by slow cooling to −40 °C. The structure was determined from diffraction data collected at −170 °C. A ball-and-stick view of the solid-state structure giving the atom-numbering scheme used in the tables is shown in Figure 1. Selected bond distances and bond angles are given in Table 4. Compound **2** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$, with the center of the molecule residing upon an inversion center generating a zigzag chain of four thorium atoms. The molecule consists of two edge-shared bioctahedra of $[Th_2(O\text{-}i\text{-}Pr)_8py]$ units, joined by one axial and one equatorial bridging alkoxide ligand. The bridging alkoxides that join the halves of the molecule make up a third edge-shared bioctahedral unit. Thorium atoms at each end of the zigzag chain are capped with a pyridine ligand. Terminal Th—O bond distances average 2.172 Å and are similar to the average terminal Th—O distances of 2.154, 2.155, 2.182, and 2.154 Å seen in aliphatic alkoxide complexes $Th_2(OCH\text{-}i\text{-}Pr_2)_8$,[17] $Th(O\text{-}t\text{-}Bu)_4(py)_2$,[20] $NaTh_2(O\text{-}t\text{-}Bu)_9$,[20] and $\{[(\eta^5\text{-}C_5Me_5)_2Th(\mu\text{-}O_2C_2Me_2)]_2\}$.[25] As expected, the bridging Th—O distances are considerably longer and average 2.420 Å. These distances can be compared to the average bridging Th—O distances of 2.436 and 2.464 Å seen in $Th_2(OCH\text{-}i\text{-}Pr_2)_8$[17] and $NaTh_2(O\text{-}t\text{-}Bu)_9$,[20] respectively. The pyridine ligand exhibits a Th—N distance of 2.740(14) Å and can be compared to the Th—N distance of 2.61(1) Å found in the chelating 2-(6-methylpyridyl)methyl ligand of $Th(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2(CH_2\text{-}py\text{-}6\text{-}Me)_2$,[26] 2.696 Å in $Th(O\text{-}2,6\text{-}Me_2C_6H_3)_4(py)_2$,[18] 2.754 Å (av) found for the quinolinato ligands in $Th(C_3H_7NO)(C_9H_6NO)_4$,[27] and 2.752(7) Å in $Th(O\text{-}t\text{-}Bu)_4(py)_2$.[20] Nonbonding Th ··· Th distances are 4.029(3) Å within the $[Th_2(O\text{-}i\text{-}Pr)_8py]$ unit [*i.e.* Th(1) ··· Th(2)] and 4.034(3) Å from Th(1) to its symmetry-generated neighbor Th(1a). Bond angles about the thorium metal centers are considerably distorted from ideal octahedral values, especially those involving the bridging ligands. For example the O(21)—Th(2)—O(25) angle is 67.5(3)° and the O(33)—Th(1)—O(33a) angle is 66.1(4)°. Terminal alkoxide ligands exhibit very obtuse Th—O—C angles averaging 167.2° and are comparable to those angles seen in other aliphatic thorium alkoxide structures.[17,20]

Table 2. Selected Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$[a]

	10^4x	10^4y	10^4z	$10B_{iso}$
Th(1)	620(1)	971.9(3)	634(1)	14
Th(2)	−1878(1)	2927.9(3)	852(1)	17
N(3)	−31(13)	3447(8)	3129(14)	27
C(4)	645(19)	3900(11)	2980(18)	36
C(5)	1435(20)	4272(10)	4144(21)	40
C(6)	1570(19)	4153(14)	5466(20)	46
C(7)	854(24)	3729(16)	5683(20)	62
C(8)	89(23)	3366(13)	4479(23)	55
O(9)	−3429(10)	2684(6)	−1040(10)	21
C(10)	−4425(15)	2729(9)	−2288(17)	24
C(11)	−4644(17)	3436(10)	−2881(17)	31
C(12)	−5630(16)	2593(10)	−2070(19)	30
O(13)	−1749(10)	3985(6)	312(11)	21
C(14)	−1917(17)	4727(10)	298(18)	29
C(15)	−1801(18)	4861(10)	−1110(21)	36
C(16)	−3189(19)	5123(10)	496(20)	37
O(17)	−2946(10)	3328(6)	2421(11)	24
C(18)	−3684(18)	3550(10)	3389(19)	34
C(19)	−5082(20)	3566(13)	2610(25)	52
C(20)	−3428(26)	4273(13)	4259(25)	62
O(21)	−1088(10)	1703(6)	1621(10)	18
C(22)	−1427(18)	1293(11)	2463(20)	34
C(23)	−535(19)	1346(11)	3969(21)	40
C(24)	−2795(18)	1492(10)	2385(19)	33
O(25)	−165(10)	2184(6)	−160(11)	23
C(26)	247(18)	2364(10)	−1254(18)	29
C(27)	−895(20)	2675(11)	−2431(18)	38
C(28)	1161(19)	2906(12)	−590(20)	38
O(29)	2055(10)	1263(6)	2572(11)	25
C(30)	2955(16)	1561(9)	3792(16)	27
C(31)	4134(18)	990(10)	4269(18)	33
C(32)	3295(20)	2210(1)	3391(21)	42
O(33)	−917(9)	281(6)	−1066(10)	18
C(34)	−1948(15)	749(8)	−1969(15)	19
C(35)	−1854(17)	528(11)	−3488(17)	32
C(36)	−3212(13)	702(9)	−1822(16)	21
O(37)	1868(10)	693(6)	−722(11)	22
C(38)	2954(15)	529(9)	−1239(17)	25
C(39)	3934(17)	964(12)	−280(22)	40
C(40)	2556(19)	657(11)	−2783(20)	41

[a] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959,** *12*, 609.

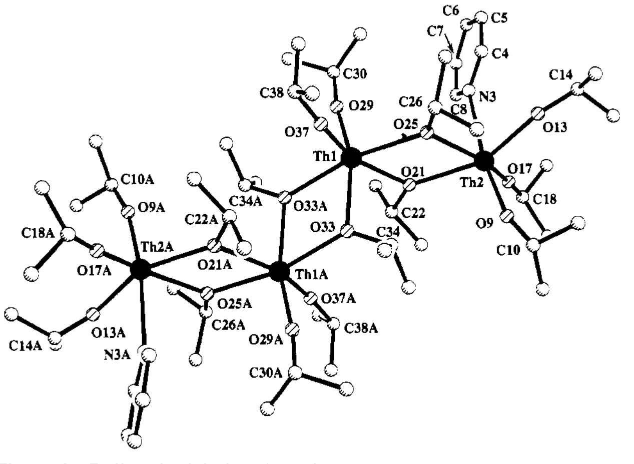

Figure 1. Ball and stick drawing of the molecular structure of $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ showing the zigzag arrangement of edge-shared bioctahedra and giving the atom-numbering scheme used in the tables.

$Th_2(OCHEt_2)_8(py)_2$ (3). Single crystals of **3** suitable for an X-ray diffraction study were grown from a hexane/pyridine solution by slow cooling to −40 °C. The structure was determined from diffraction data collected at −70 °C. A ball-and-stick view of the solid-state structure giving the atom-numbering scheme

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Table 3. Selected Fractional Coordinates and Equivalent Isotropic Displacement Coefficients[a] (Å^2) for $Th_2(OCHEt_2)_8(py)_2$

	10^5x	10^5y	10^5z	U(eq)
Th(1)	1 139(3)	8 077(3)	15 730(2)	386(1)
O(1)	10 033(41)	−2 703(45)	1 690(32)	418(8)
O(2)	15 030(52)	30 850(48)	20 030(39)	664(9)
O(3)	12 268(46)	7 541(51)	28 381(35)	581(8)
O(4)	−14 698(49)	10 352(54)	22 702(39)	658(9)
N(1)	−15 419(53)	−19 883(56)	12 181(44)	566(9)
C(1N)	−22 995(59)	−31 158(60)	2 892(52)	545(9)
C(2N)	−32 113(68)	−44 637(68)	1 885(59)	780(9)
C(3N)	−33 353(70)	−46 663(67)	10 975(60)	855(9)
C(4N)	−25 385(72)	−34 943(71)	20 548(58)	914(9)
C(5N)	−16 766(68)	−22 310(69)	20 808(56)	778(9)
C(1)	18 798(62)	−9 185(68)	1 735(56)	678(9)
C(2)	32 457(81)	2 300(81)	9 250(75)	946(9)
C(3)	11 361(80)	−23 260(78)	2 870(76)	912(9)
C(4)	40 564(82)	13 925(80)	6 280(75)	981(9)
C(5)	17 876(80)	−32 693(80)	419(76)	989(9)
C(6)	23 363(74)	46 098(72)	26 393(71)	1059(9)
C(7)	16 538(84)	52 958(85)	23 587(80)	1244(9)
C(8)	37 112(83)	50 559(85)	28 698(80)	1212(9)
C(9)	41 627(84)	46 376(85)	34 211(79)	1188(9)
C(10)	14 785(86)	65 099(85)	30 207(81)	1368(9)
C(11)	18 676(72)	8 439(74)	37 520(63)	966(9)
C(12)	28 818(82)	5 535(83)	37 022(77)	1063(9)
C(13)	19 415(83)	20 364(84)	47 461(77)	1103(9)
C(14)	7 193(82)	20 937(83)	48 915(77)	1088(9)
C(15)	34 327(82)	1 503(82)	44 564(75)	1076(9)
C(16)	−23 282(82)	13 266(82)	29 351(78)	1033(9)
C(17)	−18 571(83)	28 343(84)	35 069(81)	1208(9)
C(18)	−37 829(86)	−678(86)	26 738(80)	1281(9)
C(19)	−42 726(82)	−13 152(81)	21 798(75)	1098(9)
C(20)	−30 727(83)	32 642(84)	35 430(79)	1275(9)

Table 4. Selected Bond Distances (Å) and Angles (deg) for $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$

Th(1)—Th(1A)	4.034(3)	Th(1)—Th(2)	4.029(3)
Th(1)—O(21)	2.422(10)	Th(1)—O(25)	2.413(10)
Th(1)—O(29)	2.158(10)	Th(1)—O(33A)	2.389(10)
Th(1)—O(33)	2.424(10)	Th(1)—O(37)	2.150(10)
Th(2)—O(9)	2.181(10)	Th(2)—O(13)	2.199(10)
Th(2)—O(17)	2.173(9)	Th(2)—O(21)	2.425(10)
Th(2)—O(25)	2.446(10)	Th(2)—N(3)	2.740(14)

O(21)—Th(1)—O(25)	68.1(3)	O(21)—Th(1)—O(29)	91.2(4)
O(21)—Th(1)—O(33)	88.8(3)	O(21)—Th(1)—O(33A)	106.9(3)
O(21)—Th(1)—O(37)	157.0(4)	O(25)—Th(1)—O(29)	98.6(4)
O(25)—Th(1)—O(33)	100.8(3)	O(25)—Th(1)—O(33A)	166.5(3)
O(25)—Th(1)—O(37)	89.2(4)	O(29)—Th(1)—O(33)	159.1(4)
O(29)—Th(1)—O(33A)	94.0(4)	O(29)—Th(1)—O(37)	96.1(4)
O(33)—Th(1)—O(33A)	66.1(4)	O(33)—Th(1)—O(37)	92.0(4)
O(33a)—Th(1)—O(37)	94.5(4)	O(9)—Th(2)—O(13)	96.1(4)
O(9)—Th(2)—O(17)	100.1(4)	O(9)—Th(2)—O(21)	99.8(4)
O(9)—Th(2)—O(25)	94.7(4)	O(9)—Th(2)—N(3)	171.4(4)
O(13)—Th(2)—O(17)	101.1(4)	O(13)—Th(2)—O(21)	156.6(4)
O(13)—Th(2)—O(25)	94.3(4)	O(13)—Th(2)—N(3)	75.6(4)
O(17)—Th(2)—O(21)	92.9(4)	O(17)—Th(2)—O(25)	157.2(4)
O(17)—Th(2)—N(3)	79.5(4)	O(21)—Th(2)—O(25)	67.5(3)
O(21)—Th(2)—N(3)	88.7(4)	O(25)—Th(2)—N(3)	88.4(4)
Th(2)—O(9)—C(10)	164.1(10)	Th(2)—O(13)—C(14)	160.1(10)
Th(2)—O(17)—C(18)	176.2(11)	Th(1)—O(21)—Th(2)	112.5(4)
Th(1)—O(25)—Th(2)	112.0(4)	Th(1)—O(29)—C(30)	171.7(10)
Th(1)—O(33)—Th(1)	113.9(4)	Th(1)—O(37)—C(38)	163.8(10)

used in the tables is shown in Figure 2. Selected bond distances and bond angles are given in Table 5. Compound **3** crystallizes in the triclinic space group $P\bar{1}$, with the center of the dimeric molecule residing on an inversion center. The overall molecular geometry is that of an edge-sharing bioctahedron, with a pyridine ligand occupying one axial position on each thorium atom. All of the terminal alkoxide ligands have very similar Th—O bond distances, with no significant difference observed between those alkoxides *trans* to a bridging alkoxide and those *trans* to pyridine. These terminal and bridging Th—O distances average 2.170 and 2.427 Å (respectively) and are very similar to those observed in **2**. The Th—N distance of the pyridine ligand is 2.730(6) Å, again very similar to that seen in **2**. The nonbonding Th · · · Th distance is 4.055(2) Å. The O—Th—O angles between the terminal alkoxide ligands are in the range 95.4(2) to 99.4(2)°, while the O(1)—Th(1)—O(1a) angle for the bridging alkoxide ligands is considerably more acute at 66.7(2)°. This relatively acute angle is presumably a result of the large (>4 Å) nonbonding metal–metal separation. Terminal alkoxide ligands exhibit obtuse Th—O—C angles averaging 166.5°.

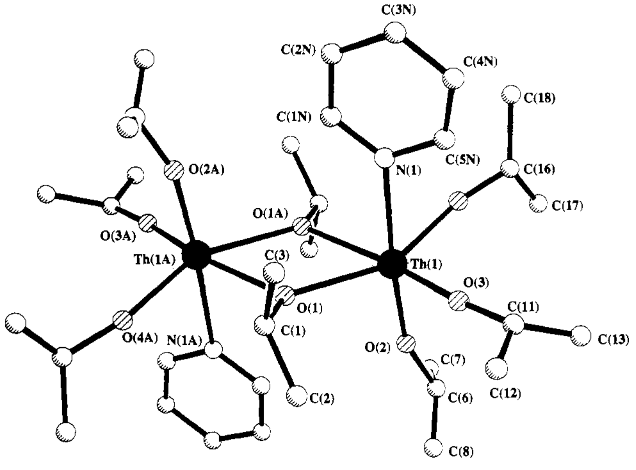

Figure 2. Ball and stick drawing of the molecular structure of $Th_2(OCHEt_2)_8(py)_2$ emphasizing the edge-shared bioctahedron and giving the atom-numbering scheme used in the tables. Methyl carbon atoms have been omitted for clarity.

Table 5. Selected bond Distances (Å) and Angles (deg) for $Th_2(OCHEt_2)_8(py)_2$

Th(1)—O(1)	2.416(5)	Th(1)—O(2)	2.179(5)
Th(1)—O(3)	2.183(6)	Th(1)—O(4)	2.147(6)
Th(1)—N(1)	2.730(6)	Th(1)—Th(1A)	4.055(2)
Th(1)—O(1A)	2.438(5)		

O(1)—Th(1)—O(2)	97.9(2)	O(1)—Th(1)—O(3)	97.4(2)
O(2)—Th(1)—O(3)	95.4(2)	O(1)—Th(1)—O(4)	154.6(1)
O(2)—Th(1)—O(4)	99.4(2)	O(3)—Th(1)—O(4)	99.3(2)
O(1)—Th(1)—N(1)	84.8(2)	O(2)—Th(1)—N(1)	174.8(2)
O(3)—Th(1)—N(1)	79.8(2)	O(4)—Th(1)—N(1)	79.5(2)
O(1)—Th(1)—O(1A)	66.7(2)	O(2)—Th(1)—O(1A)	94.0(2)
O(3)—Th(1)—O(1A)	162.5(2)	O(4)—Th(1)—O(1A)	93.6(2)
N(1)—Th(1)—O(1A)	91.1(2)	Th(1)—O(1)—C(1)	129.5(4)
Th(1)—O(1)—Th(1A)	113.3(2)	Th(1)—O(2)—C(6)	159.6(6)
Th(1)—O(3)—C(11)	171.5(5)	Th(1)—O(4)—C(16)	168.4(5)

Spectroscopic Characterization. NMR spectra were somewhat uninformative with regard to the solution structures of **1**–**3**. In the case of $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ (**2**), room-temperature ^1H NMR spectra in C_6D_6 showed only one type of isopropoxide resonance and the presence of coordinated pyridine, in a ratio of *ca.* 8 isopropoxide ligands to each pyridine consistent with the formulation of $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$. Cooling a toluene-$d_8$ solution of **2** results in broadening of the isopropoxide resonances, but a static structure could not be observed even at −90 °C. For the dimeric species $Th_2(OCHEt_2)_8(py)_2$ (**3**), ambient-temperature ^1H NMR spectra show only one type of alkoxide and one type of coordinated pyridine in a 4:1 ratio, again indicating the presence of a fluxional process which equivalences terminal and bridging isopentoxide ligands. ^1H NMR spectra of **1** and **2** in the presence of excess pyridine show a single resonance for coalesced pyridine.

Infrared spectra in the region between 4000 and 400 cm^{-1} show only absorption bands characteristic of the coordinated ligands.[28] Upon complex formation, pyridine vibrations in the high frequency region are not appreciably shifted, whereas the in-plane ring deformation mode is generally shifted from 604 cm^{-1} to higher energy.[29] The observed shift of this vibrational

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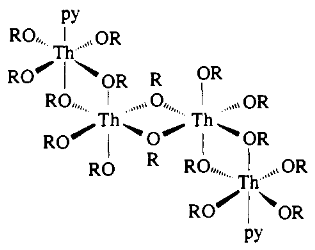
(28) For a general review of IR spectra of metal alkoxides, see: Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978. Malhotra, K. C.; Martin, R. C. *J. Organomet. Chem.* **1982**, *239*, 1159. Chisholm, M. H.; Clark, D. L.; Huffman, J. C. *Polyhedron* **1985**, *4*, 1203.

mode to 622 cm^{-1} in $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ and 621 cm^{-1} in $Th_2(OCHEt_2)_8(py)_2$ is consistent with coordinated pyridine.[29] Solid-state (Nujol) IR spectra of **2** and **3** exhibit strong absorptions in the region 900–1150 cm^{-1} as expected for the presence of alkoxide ligands. In addition, solid-state (Nujol) IR spectra of **1** and **2** exhibit a medium-intensity band at 2620 cm^{-1}, which is in a region characteristic of the presence of agostic M—H—C interactions.[30] However, a close examination of the interatomic distances in the crystal structure of **2** reveals no unusually close M—C contacts with any of the isopropoxide ligands.

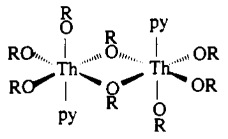
Concluding Remarks

In previous work on the alkoxide chemistry of thorium, we have shown that dimeric alkoxide complexes such as $Th_2(OCH\text{-}i\text{-}Pr_2)_8$ and $Th_2(O\text{-}t\text{-}Bu)_8(HO\text{-}t\text{-}Bu)$ will react with a stoichiometric amount (2 equiv per Th) of pyridine to produce mononuclear bis(pyridine) adducts $Th(OR)_4(py)_2$ in which the pyridine ligands occupy *cis* positions in a pseudo-octahedral molecular geometry.[17,20] In the two examples discussed in this work, however, even an excess (12 equiv per Th) of pyridine fails to break up the dimeric unit in $Th_2(OCHEt_2)_8(py)_2$ (**3**) or the tetrameric unit in $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ (**2**). These two complexes appear to behave in a manner more analogous to that of the neodymium species $Nd_2(OCH\text{-}i\text{-}Pr_2)_6L_2$ (L = THF, py, $^1/_2$DME), which we have found to retain their dimeric structure even after reaction with an excess of neat dimethoxyethane.[31]

The solid-state structures of these new pyridine adducts are both based on edge-shared bioctahedra, and the structures of **2** and **3** are illustrated schematically in **I** and **II**.

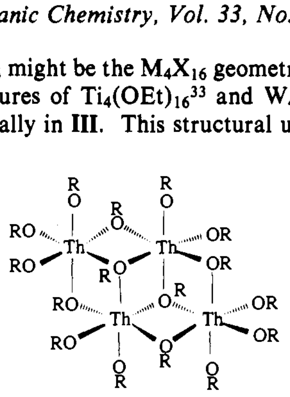


I



II

The fact that the tetrameric complex $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ (**2**) was formed *via* both alcoholysis and metathesis reactions from monomeric starting materials suggests the formation of a common intermediate which reacts with pyridine to form **2**. In addition, we know that, in the absence of a Lewis base, there appears to be more than one oligomeric form of $[Th(O\text{-}i\text{-}Pr)_4]_x$ (**1**). When $[Th(O\text{-}i\text{-}Pr)_4]_x$ is initially formed, it will react with excess (12 equiv per Th) pyridine to generate tetrameric **2**, but the aged material no longer shows a propensity to react with pyridine. The identity of the initially-formed pyridine-free solid has not been definitively established other than the empirical formula of $[Th(O\text{-}i\text{-}Pr)_4]_x$. In Bradley's seminal studies on secondary alkoxides of thorium,[12] ebullioscopic molecular weight determinations indicated a molecular complexity of 3.8 for isopropoxide, and 4.1 for isopentoxide ligands. We speculate that the initial product of both alcoholysis and metathesis reactions may be $[Th(O\text{-}i\text{-}Pr)_4]_4$, which is capable of coordinating 2 equiv of pyridine to produce $Th_4(O\text{-}i\text{-}Pr)_{16}(py)_2$ (**2**). We presume that, on standing, an initially-formed $[Th(O\text{-}i\text{-}Pr)_4]_4$ can undergo further solid-state oligomerization through Th—O bonds form $[Th(O\text{-}i\text{-}Pr)_4]_n$ ($n > 4$) or a further transformation to an oxo species in analogy to $Th_3O(O\text{-}t\text{-}Bu)_{10}$[20] or $Y_5O(O\text{-}i\text{-}Pr)_{13}$.[32] A reasonable structure for $Th_4(O\text{-}i\text{-}Pr)_{16}$ might be the M_4X_{16} geometry observed in the solid-state structures of $Ti_4(OEt)_{16}$[33] and $W_4(OEt)_{16}$[34] and is shown schematically in **III**. This structural unit has historical significance in the field of metal alkoxide chemistry since, in 1958, Bradley proposed a structural theory for metal alkoxides based on the metal atoms ability to achieve its preferred coordination environment through the minimum degree of oligomerization possible.[35] The structure of $Ti_4(OEt)_{16}$ represented the first structural verification of Bradley's proposal and demonstrated that each Ti atom in $Ti_4(OEt)_{16}$ could achieve octahedral coordination through four μ_3-OR and two μ_2-OR bridges. The addition of 2 equiv of pyridine to this structural unit could lead, with minimal skeletal rearrangement, to the tetrameric structure shown in **I**.



III

In summary, our work on the alkoxide chemistry of thorium has shown that not only does the degree of oligomerization of the metal alkoxide show a strong dependence upon the steric requirements of the alkoxide ligand but also the propensity of the resulting compound to undergo cleavage in the presence of a Lewis base is strongly influenced by the nature of the alkoxide ligand.

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. Thorium-232 metal was obtained from Los Alamos National Laboratory stock and machined into turnings. $ThBr_4(THF)_4$ was prepared by dissolution of thorium metal turnings into a THF solution of elemental bromine as described previously.[36] $[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3)$[18] and $NaN(SiMe_3)_2$[37] were prepared as described previously. 2-Propanol was distilled from sodium and stored in the drybox. 3-Pentanol was purchased from Aldrich and degassed prior to use. Potassium isopropoxide was prepared by the reaction of potassium hydride with 2-propanol in THF. Solvents, except for pyridine, were degassed and distilled from Na/K alloy under nitrogen. Pyridine was distilled from CaH_2 under argon. 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 Brüker AF 250 or WM 300 spectrometers in benzene-d_6 or toluene-d_8. All ^{1}H NMR chemical shifts are reported in ppm relative to the ^{1}H 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, as Nujol mulls between KBr plates. Element 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.

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Synthesis. [Th(O-*i*-Pr)$_4$]$_x$ (1). To a solution of 0.95 g (1.34 mmol) of thorium metallacycle $[\text{Me}_3\text{Si})_2\text{N}]_2\overline{\text{Th}(\text{CH}_2\text{SiMe}_2\text{N}}\text{SiMe}_3)$ in 60 mL of toluene was added 0.32 g (5.32 mmol) of HO-*i*-Pr. The mixture was allowed to stir overnight, after which time the solvent was removed *in vacuo* to produce a feathery white solid. This solid was redissolved in hexanes and filtered through a Celite pad (with washing of pad, total volume of solvent used was approximately 75 mL). The volatiles were removed *in vacuo* to give a white solid. Yield: 370 mg. ^{1}H NMR (250 MHz, toluene-d_8): δ 4.67 (m, J = 5 Hz, 4H, C*H*Me$_2$), 1.48 (d, J = 5 Hz, 24H, CH*Me$_2$*). IR (Nujol mull, KBr plates): 2621 (m), 1368 (s), 1335 (m), 1304 (w), 1250 (w), 1160 (s), 1144 (s), 1131 (s), 1002 (s), 987 (s), 952 (m), 932 (m), 837 (m), 825 (m), 806 (m), 527 (m), 480 (m), 453 (m), 446 (m), 412 cm^{-1} (m).

Th$_4$(O-*i*-Pr)$_{16}$(py)$_2$ (2). Method A. To a solution of 1.90 g (2.67 mmol of thorium metallacycle $[(\text{Me}_3\text{Si})_2\text{N}]_2\overline{\text{Th}(\text{CH}_2\text{SiMe}_2\text{N}}\text{SiMe}_3)$ in 100 mL of toluene was added 1.90 g of an 2-propanol/benzene azeotrope (34 wt % *i*-PrOH, 10.75 mmol). This solution was stirred at room temperature for 24 h. All solvent was removed *in vacuo* to leave a white solid; this was dissolved in 75 mL of hexane, and the mixture was filtered through Celite to give a clear, colorless filtrate. To the filtrate was added 2 mL of pyridine and the solution stirred for 10 min. The volume of the solution was reduced to *ca.* 5 mL and placed at −40 °C. Over several days, colorless crystals were deposited. These were collected by decantation and allowed to dry. Yield: ca. 250 mg (18%).

Method B. A 6.00-g amount (7.14 mmol) of ThBr$_4$(THF)$_4$ was dissolved in 150 mL of THF in a 250-mL Erlenmeyer flask. To this solution was added 2.81 g (28.62 mmol) of solid potassium isopropoxide over a period of 10 min, to produce a white precipitate. This suspension was stirred at room temperature for 24 h and then filtered through Celite to give a clear, pale yellow filtrate. All solvent was removed *in vacuo* to leave an off-white solid; this was dissolved in 100 mL of hexane, and the mixture was filtered again through Celite. The volume of the filtrate was reduced to 15 mL, and then 0.25 mL of pyridine added. This solution was placed at −40 °C, producing a white crystalline mass overnight. The solid was collected on a frit and allowed to dry. Yield: 2.92 g (80%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.65 (d, 2 H, *ortho* py), 6.95 (t, 1 H, *para* py), 6.69 (m, 2 H, *meta* py), 4.67 (br m, 8 H, C*H*Me$_2$), 1.49 (d, J = 6 Hz, 48 H, CH*Me$_2$*). IR (Nujol mull, KBR plates): 2620 (m), 1598 (w), 1576 (vw), 1358 (m), 1331 (m), 1248 (w), 1163 (s), 1143 (s), 1128 (s), 1001 (s), 986 (s), 951 (s), 931 (m), 837 (m), 824 (m), 805 (m), 750 (w), 741 (w), 725 (w), 719 (w), 699 (w), 622 (w), 525 (m), 515 (m), 481 (m), 478 (m), 448 cm^{-1} (m). Anal. Calcd for $\text{C}_{58}\text{H}_{122}\text{N}_2\text{O}_{16}\text{Th}_4$: C, 34.29; H, 6.05; N, 1.38. Found: C, 33.60; H, 5.90; H, 1.13.

Th$_2$(OCHEt$_2$)$_8$(py)$_2$ (3). To a solution of 1.50 g (2.11 mmol) of $[(\text{Me}_3\text{Si})_2\text{N}]_2\overline{\text{Th}(\text{CH}_2\text{SiMe}_2\text{N}}\text{SiMe}_3)$ in 100 mL of toluene was added dropwise a solution of 0.78 g (8.85 mmol) of pentan-3-ol 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 colorless oil. This oil was redissolved in 20 mL of toluene and 2 mL of pyridine added. After being stirred for 1 h, the solution was stripped to dryness and the solid residue dissolved in 15 mL of hexane. This solution was placed at −40 °C. Overnight, large colorless crystals were deposited. These were collected by decantation and allowed to dry. Yield: 0.81 g (58%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 8.76 (d, J = 5 Hz, 2 H, *ortho* py), 6.92 (t, J = 7 Hz, 1 H, *para* py), 6.70 (m, 2 H, *meta* py), 4.15 (quintet, J = 6 Hz, 4 H, C*H*Et$_2$), 1.81 (quintet, J = 7 Hz, 16 H, C*H$_2$*CH$_3$), 1.10 (t, J = 7 Hz, 24 H, CH$_2$C*H$_3$*). IR (Nujol mull, cm^{-1}): 1597 (m), 1492 (w), 1443 (s), 1350 (m), 1327 (w), 1307 (w), 1270 (w), 1221 (w), 1128 (s), 1049 (s), 1019 (sh, m), 991 (s), 954 (m), 919 (m), 856 (m), 835 (w), 787 (m), 760 (w), 752 (m), 702 (m), 621 (m), 569 (m), 533 (m), 478 (m), 442 (m). Anal. Calcd for $\text{C}_{50}\text{H}_{98}\text{N}_2\text{O}_8\text{Th}_2$: C, 45.52; H, 7.49; N, 2.12. Found: C, 45.55; H, 7.58; N, 2.70.

Crystallographic Studies. Th$_4$(O-*i*-Pr)$_{16}$(py)$_2$ (2). Crystal data, collection, and processing parameters are given in Table 1. A small crystal measuring 0.10 × 0.12 × 0.12 mm was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat using standard inert-atmosphere handling techniques employed by the IUMSC,[38] where it was cooled to −170 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement confirmed the correct choice to be $P\bar{1}$. Data were collected using a standard moving crystal-moving detector technique with fixed background counts at each extreme of the scan. Equivalent data were averaged after correction for Lorentz and polarization terms to yield a set of unique intensities.

The structure was solved by location of the metal atom in a Patterson synthesis, followed by standard Fourier techniques. All hydrogen atoms were placed in fixed, idealized positions for the full-matrix refinement. Final refinement using 3651 unique observed $[F > 2.33\sigma(F)]$ reflections converged at R = 0.0441 and R_w = 0.0453. A final difference Fourier was featureless, with several peaks of intensity up to 1.5 e/Å^3 in the vicinity of the metals.

Th$_2$(OCHEt$_2$)$_8$(py)$_2$ (3). A small colorless crystal measuring 0.20 × 0.20 × 0.32 mm was selected under the microscope using an argon purge. It was affixed to the end of a glass fiber using silicone grease and transferred to the goniometer head of a Siemens R3m/V diffractometer with traphite monochromated Mo Kα radiation, where it was cooled to −70 °C for characterization and data collection. Unit cell parameters were determined from the least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 50 accurately centered reflections in a 2θ range of 27–32°. Two reflections were chosen as intensity standards and were measured every 7200 s of X-ray exposure time, and two orientation controls were measured every 250 reflections.

The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans was applied. The structure was readily solved by Patterson methods and subsequent difference Fourier maps. There was a great deal of disorder on the alkoxide carbon atoms, and this was modeled by using two conformations of the ethyl groups in a 70:30 occupancy ratio. 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 (except for the carbon atoms with 30% occupancy, which were refined without hydrogen atoms attached), final refinement using 5166 unique observed $[F > 4.0\sigma(F)]$ reflections converged at R = 0.0448 and R_w = 0.0498 {where $w = [\sigma^2(F) + 0.0007(F)^2]^{-1}$}. All calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc., 1990). A final difference Fourier contained some residual electron density around the thorium metal atom, the largest peak being of magnitude 1.28 e/Å^3.

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Supplementary Material Available: Tables of data collection parameters, fractional coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters for **2** and **3** (12 pages). Ordering information is given on any current masthead page.

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