

The First Structurally Characterised Homoleptic Thorium Alkoxide: X-Ray Crystal Structure of $[\text{Th}(\text{OCHPr}^i)_4]_2$, and NMR Evidence For a Monomer–Dimer Equilibrium

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The synthesis and X-ray crystal structure of the dimeric five-coordinate homoleptic thorium alkoxide $[\text{Th}(\text{OCHPr}^i)_4]_2$, the first X-ray structural characterisation of a homoleptic thorium alkoxide complex, are reported: ¹H NMR findings evidence an equilibrium between the dimer $[\text{Th}(\text{OCHPr}^i)_4]_2$ and its monomer $[\text{Th}(\text{OCHPr}^i)_4]$.

Although the field of transition metal and main group alkoxide chemistry is one of considerable current interest,¹ the alkoxide chemistry of the actinide elements, and especially that of thorium, has not been extensively developed. Indeed, a recent review emphasised the total absence of structural data for thorium alkoxide complexes.² A number of homoleptic thorium alkoxide complexes of composition $[\text{Th}(\text{OR})_4]$ (R =

Me, Et, Prⁱ, Prⁿ, Buⁿ) have been previously reported,^{3,4} but their characterisation is limited to elemental analysis and solution molecular weight determination. No crystallographic data have been reported for homoleptic aliphatic thorium alkoxides.² As part of our current interest in the alkoxide and aryloxy chemistry of thorium, we have prepared and structurally characterised a dimeric five-coordinate thorium

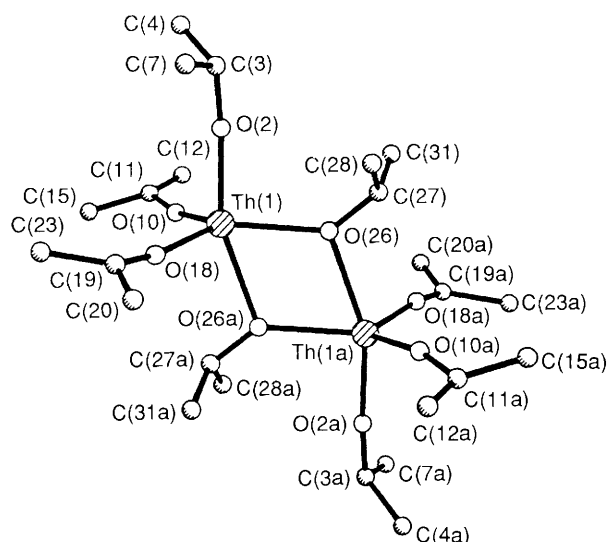


Fig. 1 A view of the molecular structure of **1**, showing the atom numbering scheme for pertinent atoms, and emphasising the fused trigonal bipyramidal coordination geometry. Methyl carbons of the $\text{OCH}(\text{CHMe}_2)_2$ ligands are omitted for clarity. Important bond lengths (Å) and angles ($^\circ$): Th(1)–O(2) 2.160(11), Th(1)–O(10) 2.141(11), Th(1)–O(18) 2.161(11), Th(1)–O(26) 2.408(10), Th(1)–O(26a) 2.463(11); O(2)–Th(1)–O(10) 98.2(4), O(2)–Th(1)–O(18) 94.8(5), O(2)–Th(1)–O(26) 93.9(4), O(2)–Th(1)–O(26a) 158.2(4), O(10)–Th(1)–O(18) 111.8(4), O(10)–Th(1)–O(26) 116.2(4), O(10)–Th(1)–O(26a) 98.7(4), O(18)–Th(1)–O(26) 129.2(4), O(18)–Th(1)–O(26a) 91.7(4), Th(1)–O(26)–Th(1a) 113.8(4), O(26)–Th(1)–O(26a) 66.2(4).

complex employing the sterically demanding 2,4-dimethyl-3-pentoxide ligand. This structural study provides the first example of a crystallographically characterised homoleptic aliphatic thorium alkoxide.

Treatment of the metallacycle $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Th}(\text{CH}_2\text{SiMe}_2\text{N-SiMe}_3)\}_2$ with four equivalents of 2,4-dimethylpentan-3-ol (di-*iso*-propylmethanol) in toluene at room temperature gave colourless crystals of $[\text{Th}(\text{OCHPr}_i)_4]_2$ **1**† in good yield upon cooling to -40 °C. The structure of **1** was determined from single crystal X-ray diffraction data collected at -171 °C,‡ and is shown in Fig. 1. The compound crystallises in the monoclinic space group $P2_1/n$ with two molecules per unit cell which reside on centres of inversion. Each thorium atom adopts a distorted trigonal bipyramidal geometry, and the Th_2O_8 core can be viewed as two ThO_5 trigonal bipyramids joined along a common axial-equatorial edge. The three equatorial bonds are distorted from the ideal (120°) trigonal angles, the actual values being 129.2(4), 111.8(4) and 116.2(4) $^\circ$; yet the trigonal ThO_3 unit is nearly planar. The axial O–Th–O unit is distorted (158.2°) from the idealized 180° , and may be due to steric demands in the bridge.

The fused trigonal bipyramidal geometry seen in **1** shows a striking similarity to the transition metal alkoxide structures of

† Satisfactory microanalytical results have been obtained for complexes **1**, **3** and **4**.

‡ *Crystal data* for **1**: $\text{C}_{56}\text{H}_{120}\text{O}_8\text{Th}_2$, $M = 1385.66$, monoclinic, space group $P2_1/n$, crystal size $0.12 \times 0.32 \times 0.32$ mm, $a = 12.115(2)$, $b = 20.820(3)$, $c = 13.002(2)$ Å, $\beta = 100.62(1)^\circ$, $V = 3223.38$ Å 3 , $Z = 2$, $D_c = 1.428$ g cm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 35.638$ cm $^{-1}$; 4212 unique reflections were collected. The limits of data collection were $6 \leq 2\theta \leq 45^\circ$. The structure was solved by a combination of Patterson and Fourier techniques and refined by full-matrix least-squares. Final discrepancy indices were $R_f = 0.0503$ and $R_{w_f} = 0.0484$ for those 2640 reflections with $F_o \geq 2.33 \sigma(F_o)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

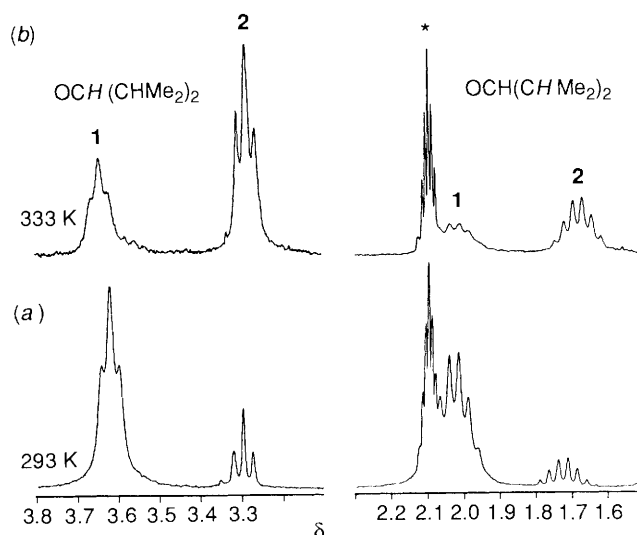
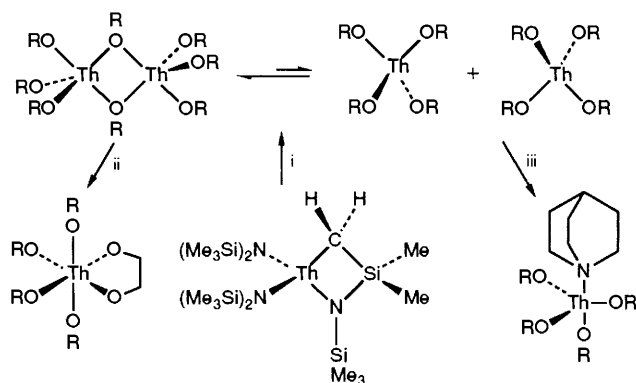


Fig. 2 ^1H NMR spectra of the methine region of a mixture of dimeric **1** and monomeric **2** at 293 K (a) and 333 K (b). Left and right spectra not to scale. The resonance marked with an asterisk denotes the ^1H impurity in $[\text{2H}_8]\text{toluene}$. Methine resonances assigned to **1** and **2** are labelled.

$[\text{Mo}(\text{OPr}^i)_4]_2$ ⁶ and $[\text{Mo}(\text{OPr}^i)_3(\text{NO})]_2$.⁷ Very few examples of five-coordination have been documented for the actinide metals, these being $[\text{Li}(\text{thf})_4][\text{M}(\text{O}-2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)_5]$ ($M = \text{U}, \text{Th}$; thf = tetrahydrofuran),⁸ $[\text{K}_2(\text{thf})_4][\text{U}(\text{NH}-2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)_5]_2$,⁹ $[\text{Li}][\text{UMe}(\text{OCHBu}^t)_4]$,¹⁰ and $[\text{U}(\text{NEt}_2)_4]$,¹¹ the last of which shows a fused axial-equatorial trigonal bipyramidal geometry similar to that found in **1**. Terminal Th–O distances are rather short at 2.154 Å (avg.), and virtually identical to the Th–O distance [2.154(8) Å] observed for the but-2-ene-2,3-diolate ligand in the X-ray structure of $\{[\text{Th}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-O}_2\text{C}_2\text{Me}_2)]_2\}$.¹² The corresponding Th–O–C angles are large, and range from 167.4 – 171.5° . 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.¹³ Theoretical and spectroscopic studies have shown that empty thorium 6d orbitals are very low-lying,¹⁴ and therefore should be available for M–O π -bonding interactions. The trends in bond distances and angles seen in **1** may serve as structural evidence for oxygen-to-metal π -bonding in thorium alkoxides. Similar indications arise from the near-planarity of the two bridging oxygen atoms; rehybridisation to an sp^2 planar arrangement makes the π -lone pairs available for π -bonding interactions in the bridge. Th–O distances for the bridging ligands (2.436 Å avg.) are, as expected, longer than those for terminal ligands. A Th–Th distance of 4.081(3) Å and the lack of valence electrons precludes any metal–metal bonding interaction.

Ambient temperature ^1H NMR spectra§ reveal resonances consistent with two species present in solution, and suggest an

§ *Selected NMR data* for **1** ^1H (250 MHz, C_7D_8) δ 3.72 (t, $J_{\text{H,H}}$ 5.5 Hz, 1 H, CHPr_i^2), 2.02 (octet, $J_{\text{H,H}}$ 5.8 Hz, 2 H, CHMe_2), 1.20 (d, $J_{\text{H,H}}$ 6.8 Hz, 6 H, CHMe_2) and 1.07 (d, $J_{\text{H,H}}$ 7 Hz, 6 H, CHMe_2); for **2**: ^1H (250 MHz, C_7D_8) δ 3.39 (t, $J_{\text{H,H}}$ 5.7 Hz, 1 H, CHPr_i^2), 1.72 (octet, $J_{\text{H,H}}$ 6.5 Hz, 2 H, CHMe_2), 1.10 (d, $J_{\text{H,H}}$ 6.5 Hz, 6 H, CHMe_2) and 0.99 (d, $J_{\text{H,H}}$ 6.7 Hz, 6 H, CHMe_2); for **3**: ^1H (300 MHz, C_6D_6) δ 3.44 (t, $J_{\text{H,H}}$ 5 Hz, 2 H, CHPr_i^2), 3.25 (s, 3 H, OMe), 3.06 (s, 2 H, $\text{OCH}_2\text{CH}_2\text{O}$), 1.84 (octet, $J_{\text{H,H}}$ 6 Hz, 4 H, CHMe_2), 1.20 (d, $J_{\text{H,H}}$ 6 Hz, 24 H, CHMe_2) and 1.10 (d, $J_{\text{H,H}}$ 6 Hz, 24 H, CHMe_2); for **4**: ^1H (300 MHz, C_6D_6) δ 3.47 (t, $J_{\text{H,H}}$ 6 Hz, 4 H, CHPr_i^2), 3.14 (m, 6 H, NCH_2), 1.80 (octet, $J_{\text{H,H}}$ 6 Hz, 8 H, CHMe_2), 1.35 (m, 7 H, CH_2CH and CH_2CH), 1.18 (d, $J_{\text{H,H}}$ 6 Hz, 24 H, CHMe_2) and 1.04 (d, $J_{\text{H,H}}$ 6 Hz, 24 H, CHMe_2).



Scheme 1 R = CHPr₂. Reagents and conditions: i, 4 equiv. HOCHPr₂, toluene, room temp., 24 h, 67%; ii, excess dme, toluene, room temp., 1 h, 73%; iii, 1 equiv. C₇H₁₃N, toluene, room temp., 1 h, 63%.

equilibrium between dimeric [Th(OCHPr₂)₄]₂ **1**, and its monomer [Th(OCHPr₂)₄] **2** as indicated in Scheme 1.¹⁵ The methine regions of the ¹H NMR spectra which support this assignment are shown in Fig. 2. There is one set of broadened methine resonances assigned to **1**, and a smaller, sharp set of resonances assigned to the monomer **2** [Fig. 2(a)]. Integrated intensities of ca. 9:1 for the ratio of **1**:**2** preclude any assignment of these resonances to [Th₂(OCHPr₂)₈] alone. Rather, the relative intensities together with the observation that the resonances of **1** are broad (presumably due to bridge-terminal exchange) and those of **2** are sharp is indicative of two separate species in solution at room temperature. Further evidence in support of this assignment is obtained from high temperature NMR experiments. Upon heating the sample, the resonances assigned to **1** decrease, whilst those assigned to **2** increase in intensity [Fig. 2(b)], consistent with an equilibrium between **1** and **2** in solution. At +60 °C the monomeric species **2** predominates in solution as seen in Fig. 2. Upon cooling to room temperature, the resonances of the dimer **1** grow back in rapidly, implying a low barrier to dimerisation (Scheme 1).

Addition of an excess of dme (dme = 1,2-dimethoxyethane) to toluene solutions of **1** results in the formation of the monomeric Lewis base adduct [Th(OCHPr₂)₄(dme)] **3** which may be isolated as colourless crystals in good yield (Scheme 1). Treatment of a toluene solution of **1** with one equivalent (per thorium atom) of the bulky Lewis base quinuclidine, allows the isolation of the five-coordinate complex [Th(OCHPr₂)₄(C₇H₁₃N)] **4**. Preliminary X-ray structural results confirm the trigonal bipyramidal geometry shown in Scheme 1.¹⁶ We presume that Lewis bases react with the monomer, **2**, thereby shifting the equilibrium until all of the dimer is consumed (Scheme 1). Room-temperature ¹H NMR spectra[§] reveal only one type of alkoxide ligand for both **3** and **4**, presumably due to dynamic exchange processes occurring in solution. We note the isolation by Bradley *et al.* of the complex [Th(OCMe₂-CCl₃)₄py₂],^{3c} (py = pyridine) although no mention was made of the stereochemistry of the molecule, and the preparation by Andersen and coworkers of the related uranium species [U{OCH(CF₃)₂}₄(thf)₂],¹⁷ [U{OC(CF₃)₃}₄(thf)₂]¹⁷ and [U(OCHBu^t)₄].¹⁰

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