

Coordination Polymers

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New Twists and Turns for Actinide Chemistry: Organometallic Infinite Coordination Polymers of Thorium Diazide

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Abstract: Two organometallic 1D infinite coordination polymers and two organometallic monometallic complexes of thorium diazide have been synthesized and characterized. Steric control of these self-assembled arrays, which are dense in thorium and nitrogen, has also been demonstrated: infinite chains can be circumvented by using steric bulk either at the metallocene or with a donor ligand in the wedge.

Over the past two decades, significant effort has been devoted to the design and construction of new molecular organic frameworks and self-assembled coordination complexes, not only for their vast variety of intriguing structural topologies, but also because of their potential as microporous, magnetic, and optically interesting materials.^[1] These metal–organic materials routinely feature organometallic transition-metal complexes as nodes because of the well-defined coordination geometries that d-block transition-metal centers provide. In contrast, the use of organometallic actinide complexes as directional building blocks in these metal–organic materials is exceedingly rare; there are only a few bis(cyclopentadienyl)thorium and -uranium systems where the metallocene component provides sufficient directionality to make supramolecular ring aggregates.^[2] This is not surprising, considering that the increased nodality of f-orbitals enables actinide metal centers to participate in unconventional bonding interactions, and the more flexible nature of their coordination chemistry makes them less controllable and predictable.^[3]

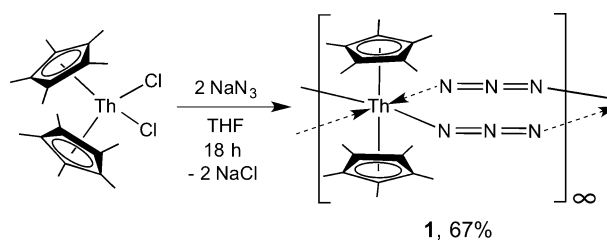
Recently, we have been investigating the chemistry of organoactinide azide complexes.^[4] Metal azides can be converted into nitrides through the loss of dinitrogen using photolysis or thermolysis. Both actinide azide and nitride species are of interest due to their proposed use in accident-tolerant fuel cycles, but very little is known about their chemical behavior. Experimental data on organometallic actinide azide complexes are limited, and dominated by uranium examples.^[2a,4,5]

An examination of the published organometallic multinuclear uranium azide complexes suggests the beginning of a trend: the metallocene examples tend to form ring

structures. However, there are only two such examples in the literature: an organometallic octanuclear ring with alternating azides and nitrides $[(C_5Me_4R)_2U(\mu-N)U(\mu-\eta^1:\eta^1-N_3)(C_5Me_4R)_2]_3$ ($R = Me, H$) and an organometallic uranium diazide trimer $[(C_5Me_5)_2U(\mu-\eta^1:\eta^1-N_3)(N_3)]_3$.^[2a,b]

We now report that metallocene thorium azide complexes do not follow the structural trend of organometallic uranium azides: instead of rings, multinuclear metallocene thorium azide complexes form open polymeric infinite chains, which are dense in thorium and nitrogen. We also demonstrate structural control in these systems: infinite chains can be circumvented by using steric bulk either at the metallocene or with a donor ligand in the wedge.

The reaction of $[(C_5Me_5)_2ThCl_2]$ ^[6] with two equivalents of sodium azide in tetrahydrofuran is complete in 18 h and affords the metallocene thorium diazide complex $[(C_5Me_5)_2Th(\mu-\eta^1:\eta^1-N_3)_2]_\infty$ (**1**) in 67% yield (Scheme 1). The solid-state structure of complex **1** consists of a one-dimensional (1D) infinite chain of thorium centers doubly bridged by end-to-end azides (Figure 1). The repeating unit of this coordination polymer is the thorium diazide $\{(C_5Me_5)_2Th-(N_3)_2\}$, and each thorium atom is coordinated by six ligands (two C_5Me_5 rings and four azides) with an approximate trigonal prismatic coordination geometry. The azide ligands bridge the thorium centers with alternating dative and anionic metal–ligand bonds. The chains of this coordination polymer have a zigzag motif, with a Th–Th–Th angle of 86.85° and an average Th–N–N angle of $138.9(5)^\circ$; the average N(1)–Th–N(3) angle is $77.79(18)^\circ$. The through-space Th...Th distance (bisecting the azide ligands) is $6.311 \text{ \AA}$.



Scheme 1. Synthesis of $[(C_5Me_5)_2Th(\mu-\eta^1:\eta^1-N_3)_2]_\infty$ (**1**).

Although there are several transition-metal compounds with the same structure as complex **1**,^[7] its 1D infinite chain of metal centers doubly bridged by end-to-end azides is a first for the actinides and is unique to thorium. As outlined in Scheme 2, uranium polynuclear azide compounds include the following: the previously mentioned octanuclear ring^[2a] and

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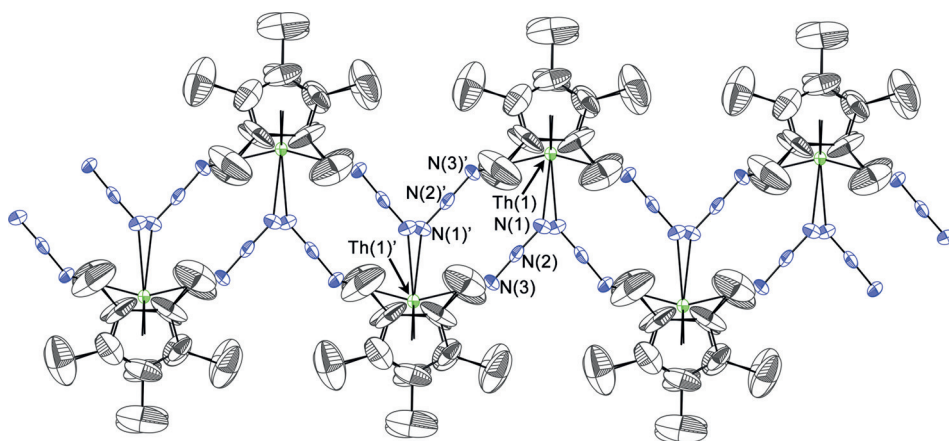


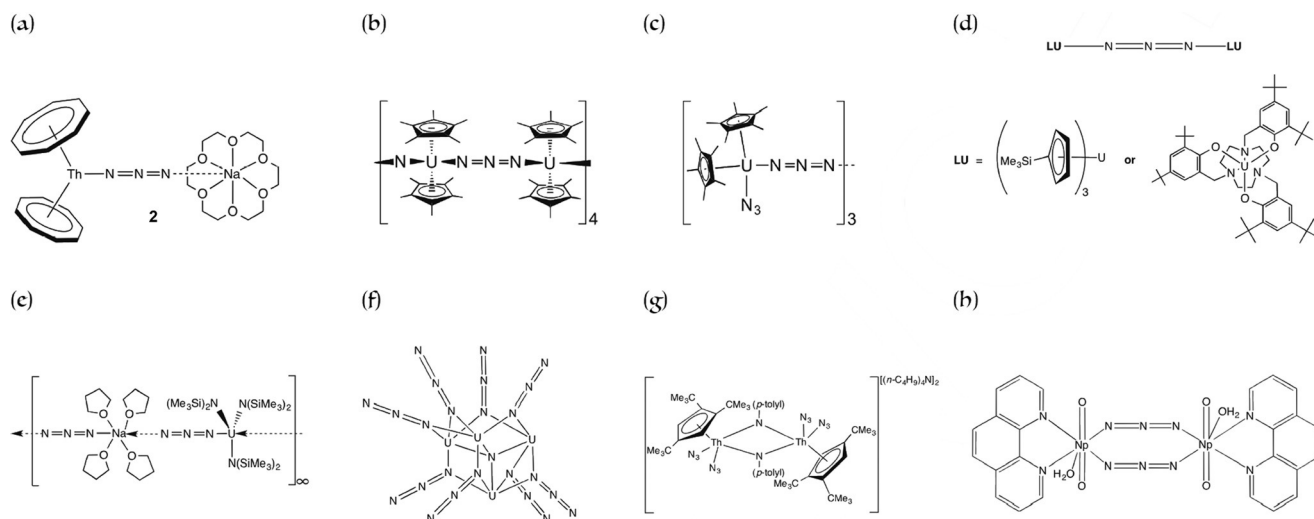
Figure 1. Molecular structure of $[(C_5Me_5)_2Th(\mu-\eta^1:\eta^1-N_3)_2]_\infty$ (**1**) (20% probability ellipsoids). Infinite chain truncated and hydrogen atoms omitted for clarity. Selected bond distances (Å): Th(1)–N(1) 2.612(6), Th(1)–N(3) 2.462(5), N(1)–N(2) 1.149(7), N(2)–N(3) 1.168(7), Th(1)–C_{cent} 2.603(7). Selected bond angles (°): Th(1)–N(1)–N(2) 133.4(5), Th(1)–N(3)–N(2) 144.4(4), N(1)–Th(1)–N(3) 73.42(18), N(1)–N(2)–N(3) 82.16(17), N(1)–N(2)–N(3) 177.1(7), C_{cent}–Th(1)–C_{cent} 121.4(3).

trimer;^[2b,8] dinuclear complexes with a single end-to-end azide;^[5f,h] 1D infinite chains of uranium and sodium singly bridged with end-to-end azides,^[9] and a tetranuclear azido/nitrido cluster^[10] (Scheme 2b–f). The only other polynuclear actinide azide complexes are an anionic dinuclear thorium complex^[11] (Scheme 2g) and a neptunium dimer doubly bridged with end-to-end azides^[12] (Scheme 2h).

Only three other structurally characterized thorium azide complexes exist in the literature.^[11,13] Complex **1** is quite different from these in several striking ways, most significantly in its infinite chain polymeric structure. Of the three, the anionic mononuclear bent thorocene with a single Na⁺-capped azide, $[Na^*][(C_8H_8)_2Th(\mu-\eta^1:\eta^1-N_3)]$ ($Na^* = Na(18\text{-crown-6})$; **2**; Scheme 2a)^[13a] is our choice for a structural

comparison to **1**, because it is the only one with two carbocyclic π -ligands and no ligands other than azides. In complex **1**, the Th–N bond lengths are Th–N(3) = 2.462(5) Å and Th–N(1) = 2.612(6) Å (anionic and dative metal–azide bonds, respectively); in the thorocene azide **2**, the Th–N₃ bond length falls right in between at 2.518(4) Å. The Th(1)–C_{cent} (C_{cent} = cyclopentadienyl centroid) bond length in complex **1** is 2.603(7) Å; this is significantly longer than in the thorocene azide **2** (2.10 Å), which can be attributed to the steric bulk of the extended chain and the larger number of ligands in the thorium coordination sphere (six in complex **1** versus three in complex **2**), as well as better overlap of the π^* -orbitals of C₈H₈ with the thorium f-orbitals.^[14] The difference is also due to the larger steric profile of the carbocyclic ligand (C₅Me₅ versus C₈H₈); the Th(1)–C_{cent} bond length in complex **1** is closer to that of the starting material $[(C_5Me_5)_2ThCl_2]$ (2.53(4) Å).^[15] The N–N bond lengths are nearly identical, with a Δd value of 0.019 Å (Δd = difference between the N_α – N_β and N_β – N_γ bond lengths in Th–N_α–N_β–N_γ); the N_β – N_γ bond is the shorter of the two in **1**.

Complex **1** was also characterized by vibrational spectroscopy. Consistent with the presence of two azides with different degrees of asymmetry,^[7] the IR spectrum displays two characteristic $\nu_{\text{asym}}(N_3)$ bands (toluene solution: 2147 and



Scheme 2. a) $[(C_8H_8)_2Th(\mu-\eta^1:\eta^1-N_3)][Na^*]$ ($Na^* = Na(18\text{-crown-6})$) (**2**);^[13a] b)–h) all the structurally characterized polynuclear actinide azide complexes reported in the literature: b) octanuclear uranium ring with alternating azides and nitrides;^[2a] c) uranium diazide trimer;^[2b] d) dinuclear complexes with a single end-to-end azide;^[5f,h] e) 1D infinite chain of uranium and sodium singly bridged with end-to-end azides^[9] (a second, similar complex was subsequently reported^[9b]); f) tetranuclear azido/nitrido cluster (only the core is shown for clarity);^[10] g) anionic dinuclear thorium complex;^[11] h) neptunium dimer doubly bridged with end-to-end azides.^[12]

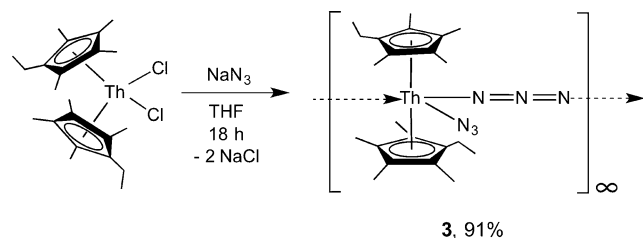
Table 1: Infrared and Raman spectroscopic data for the thorium diazide compounds.

Compound	IR solution, $\nu_{\text{asym}}(\text{N}_3)$	IR solid, $\nu_{\text{asym}}(\text{N}_3)$	Raman, $\nu_{\text{sym}}(\text{N}_3)$	Raman, $\nu_{\text{asym}}(\text{N}_3)$
$[(\text{C}_5\text{Me}_5)_2\text{Th}(\mu\text{-}\eta^1\text{-}\eta^1\text{-}\text{N}_3)_2]_\infty$ (1)	2147, 2083	2112, 2081	1390–1460	2070–2094
$[(\text{C}_5\text{Me}_4\text{Et})_2\text{Th}(\mu\text{-}\eta^1\text{-}\eta^1\text{-}\text{N}_3)(\text{N}_3)]_\infty$ (3)	2151, 2083	2116, 2079	1390–1450	2067–2103
$[(1,2,4\text{-iBu}_3\text{-C}_5\text{H}_2)_2\text{Th}(\text{N}_3)_2]$ (4)	2110, 2093	2106, 2087	1330–1475	2080–2120
$[(\text{C}_5\text{Me}_5)_2\text{Th}(\text{N}_3)_2(\text{TPPO})]$ (5)	2077	2071	1356–1440	2080–2160

2083 cm^{-1} ; neat solid: 2112 and 2081 cm^{-1} ; Table 1). These values are comparable to the previously reported thorium azides (2075 cm^{-1} , 2070 cm^{-1} , 2063 cm^{-1}),^[11,13] and are consistent with those reported for uranium azides (211–2105 cm^{-1}).^[2b,5h,9,16] In the Raman spectrum of complex **1**, a feature representing multiple azide species is observed in the ranges 1390–1460 cm^{-1} ($\nu_{\text{sym}}(\text{N}_3)$) and 2070–2094 cm^{-1} ($\nu_{\text{asym}}(\text{N}_3)$). To our knowledge, these are the first Raman data reported for a structurally characterized actinide azide complex. These ranges are comparable to shifts reported for transition-metal azide complexes ($\nu_{\text{sym}}(\text{N}_3) = 1278\text{--}1410 \text{ cm}^{-1}$,^[7g,i,17] $\nu_{\text{asym}}(\text{N}_3) = 2012\text{--}2177 \text{ cm}^{-1}$).^[17a,b,18]

With the goal of disrupting the bridged structure of complex **1**, we moved to a slightly more sterically demanding cyclopentadienyl ligand, $\text{C}_5\text{Me}_4\text{Et}$. The reaction of $[(\text{C}_5\text{Me}_4\text{Et})_2\text{ThCl}_2]$ with two equivalents of NaN_3 in THF is complete in 18 h and affords the thorium azide complex $[(\text{C}_5\text{Me}_4\text{Et})_2\text{Th}(\mu\text{-}\eta^1\text{-}\eta^1\text{-}\text{N}_3)(\text{N}_3)]_\infty$ (**3**) in 91 % yield (Scheme 3).

As illustrated in Figure 2, the molecular structure of complex **3** is also a 1D infinite chain coordination polymer,

**Scheme 3.** Synthesis of $[(\text{C}_5\text{Me}_4\text{Et})_2\text{Th}(\mu\text{-}\eta^1\text{-}\eta^1\text{-}\text{N}_3)(\text{N}_3)]_\infty$ (**3**).

but with the repeating unit $\{(\text{C}_5\text{Me}_4\text{Et})_2\text{Th}(\mu\text{-}\eta^1\text{-}\eta^1\text{-}\text{N}_3)(\text{N}_3)\}$. The chain is composed of thorium centers bridged by one end-to-end azide ligand, instead of two as in complex **1**. In addition, every thorium center in complex **3** is bound to one terminal azide ligand. Five ligands are coordinated to each thorium metal center in a distorted trigonal bipyramid, with the chain azide units as the axial ligands. Interestingly, the chains of complex **3**, which run parallel to the *c* axis, form 3_1 -helices, with an average $\text{N}_{\text{bridging}}\text{-Th-N}_{\text{bridging}}$ angle of 155.14° (Figure 2b).^[19] As with complex **1**,^[20] transition-metal compounds with this structural motif (1D infinite chain, with one bridging and one terminal azide per metal center) do exist,^[21] but this is the first of its kind for the actinides. Similar to **1**, the bridging azide ligands in **3** are bound to thorium with a dative interaction at one end and an anionic metal–ligand bond at the other end; however, unlike in complex **1**, the difference in the Th–N bond length between these two types of bonds is negligible, only 0.02 Å (avg). On the other hand, as expected, the average terminal azide Th–N₃ bond (2.377(4) Å) is approximately 0.1 Å shorter than in the bridging azide ligands (2.468(5) Å). This difference in the nature of the azide ligands is borne out in their Δd values: in complex **3**, the bridging azide ligands exhibit nearly identical $\text{N}_\alpha\text{-N}_\beta$ and $\text{N}_\beta\text{-N}_\gamma$ bond lengths, with an average $\Delta d_{\text{bridging}}$ value of only 0.005 Å, while the average $\Delta d_{\text{terminal}}$ value is 0.167 Å, with the $\text{N}_\alpha\text{-N}_\beta$ bond being shorter.

Complex **3** was also characterized by vibrational spectroscopy, with results similar to **1**. It has two $\nu_{\text{asym}}(\text{N}_3)$ absorbance bands in the IR spectrum (toluene solution: 2151 and 2083 cm^{-1} ; neat solid: 2116 and 2079 cm^{-1}); its Raman shift ranges are 1390–1450 ($\nu_{\text{sym}}(\text{N}_3)$) and 2067–2103 ($\nu_{\text{asym}}(\text{N}_3)$).

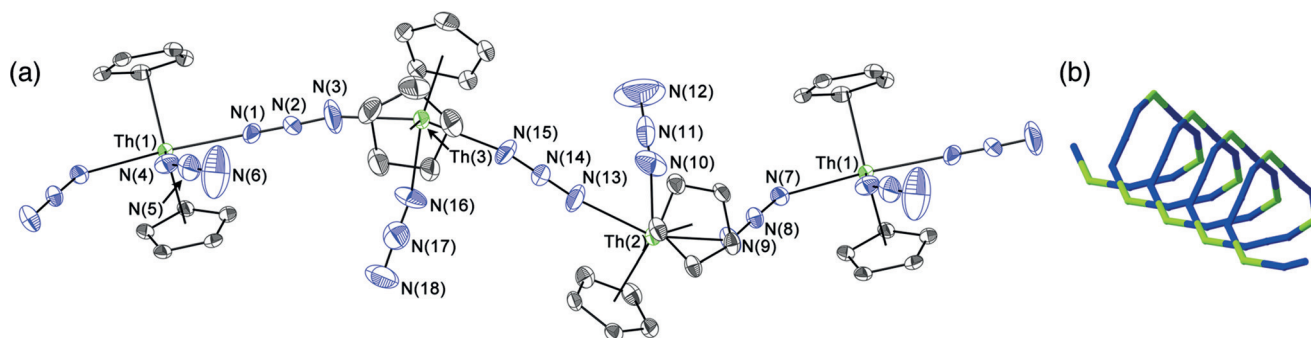
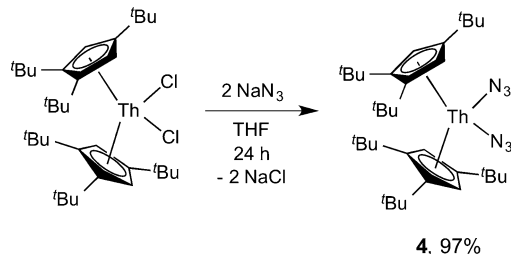


Figure 2. a) Molecular structure of $[(\text{C}_5\text{Me}_4\text{Et})_2\text{Th}(\mu\text{-}\eta^1\text{-}\eta^1\text{-}\text{N}_3)(\text{N}_3)]_\infty$ (**3**; 50 % probability ellipsoids). Infinite chain truncated and cyclopentadienyl methyl and ethyl groups are omitted for clarity. Selected bond distances (Å): Th(1)–N(1) 2.469(3), Th(1)–N(7) 2.481(3), Th(1)–N(4) 2.378(4), N(1)–N(2) 1.144(4), N(2)–N(3) 1.154(5), N(4)–N(5) 1.041(6), N(5)–N(6) 1.249(7) Th–C_{cent} (avg) 2.518(4). Selected bond angles (°): Th(1)–N(1)–N(2) 177.4(3), Th(1)–N(4)–N(5) 145.1(4), Th(1)–N(7)–N(8) 144.6(3), N(1)–N(2)–N(3) 178.6(5), N(4)–N(5)–N(6) 179.5(7), C_{cent}–Th(1)–C_{cent} (avg) 137.7(1). b) Stick model showing the 3_1 -helix of the backbone of complex **3**.

Finally, we determined that the formation of a polymeric organometallic thorium diazide compound is completely avoided by using the voluminous 1,2,4-*t*Bu₃-C₅H₂ ligand. Reaction of [(1,2,4-*t*Bu₃-C₅H₂)₂ThCl₂]^[6] with two equivalents of sodium azide in tetrahydrofuran is complete in 24 h and yields the thorium azide complex [(1,2,4-*t*Bu₃-C₅H₂)₂Th(N₃)₂] (**4**) in 97% yield (Scheme 4).



Scheme 4. Synthesis of [(1,2,4-*t*Bu₃-C₅H₂)₂Th(N₃)₂] (**4**).

A crystallographic study of **4** confirmed that both azide ligands are terminal and bound in an η^1 coordination mode (Figure 3). To date, there are only three structurally characterized mononuclear uranium diazide complexes in the literature,^[5e,9a] and **4** represents the first thorium example. Despite the considerable steric bulk of the 1,2,4-*t*Bu₃-C₅H₂ ligands, the average Th–N₃ bond in **4** (2.2938(18) Å) is about 0.08 Å shorter than the average Th–N₃ bond length of the terminal azide ligands in **3** (2.377(4) Å), a fact attributable to the mononuclear nature of **4** versus the steric bulk of the extended chain and the extra ligand in the thorium coordination sphere of **3**. Furthermore, the average Th–N₃ bond length in **4** is comparable to the average U–N₃ length of 2.219(6) Å in (1,2,4-*t*Bu₃-C₅H₂)₂U(N₃)₂,^[5e] considering that

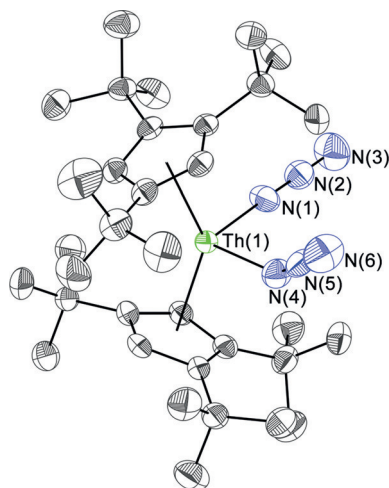
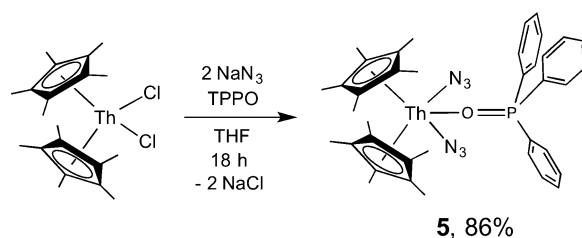


Figure 3. Molecular structure of (1,2,4-*t*Bu₃-C₅H₂)₂Th(N₃)₂ (**4**; 50% probability ellipsoids). Hydrogen atoms omitted for clarity. Selected bond distances (Å): Th(1)–N(1) 2.2758(18), Th(1)–N(4) 2.3117(17), N(1)–N(2) 1.202(2), N(2)–N(3) 1.143(2), N(4)–N(5) 1.206(2), N(5)–N(6) 1.149(2), Th(1)–C_{cent} 2.565(2), Th(1)–C_{cent'} 2.552(2). Selected bond angles (°): Th(1)–N(1)–N(2) 173.75(16), Th(1)–N(4)–N(5) 144.87(14), N(1)–Th(1)–N(4) 100.94(6), N(1)–N(2)–N(3) 179.4(2), N(4)–N(5)–N(6) 179.4(2), C_{cent}–Th(1)–C_{cent'} 140.84(6).

the effective ionic radius of Th^{IV} is 0.05 Å larger than that of U^{IV}.^[22] The average Th(1)–C_{cent} bond length in **4** (2.559(2) Å) falls in between those in complexes **1** and **3** (2.603(7) Å and 2.518(4) Å, respectively). The mononuclearity and lower coordination number of **4** also account for it possessing the widest C_{cent}–Th–C_{cent} angle of the series, 140.84(6)°; this value is consistent with the uranium analogue (143°).^[5e] Interestingly, complex **4** has one azide bound linearly to the thorium center (Th(1)–N(1)–N(2) = 173.75(16)°) while the other is bound at an angle (Th(1)–N(4)–N(5) = 144.87(14)°), and the same phenomenon was observed in the uranium analogue (176.3(5)° and 159.2(6)°).^[5e] The two N_α–N_β (1.202(2) and 1.206(2) Å) and two N_β–N_γ bonds (1.143(2) and 1.149(2) Å) in **4** are nearly identical. The average Δd value is 0.058 Å, with the N_β–N_γ bond being shorter.

Complex **4** was also characterized by vibrational spectroscopy; it has two $\nu_{\text{asym}}(\text{N}_3)$ bands in its IR spectrum (toluene solution: 2110 and 2093 cm^{−1}; neat solid: 2106 and 2087 cm^{−1}); its Raman shift ranges are 1330–1475 ($\nu_{\text{sym}}(\text{N}_3)$) and 2080–2120 cm^{−1} ($\nu_{\text{asym}}(\text{N}_3)$).

To demonstrate an alternative method of control over structure, we sought to circumvent the formation of the infinite chain in complex **1** by deploying a bulky donor ligand, triphenylphosphine oxide (TPPO), to coordinate within the metallocene wedge along with the azide ligands. Indeed, when one equivalent of TPPO is added to the reaction between [(C₅Me₅)₂ThCl₂] and two equivalents of sodium azide in tetrahydrofuran, the resulting complex is [(C₅Me₅)₂Th(N₃)₂(TPPO)] (**5**), which was isolated in 86% yield (Scheme 5).



Scheme 5. Synthesis of [(C₅Me₅)₂Th(N₃)₂(TPPO)] (**5**).

The molecular structure of compound **5** is shown in Figure 4. Both azide ligands are terminal, bound to the thorium center in the η^1 coordination mode. There are five ligands coordinated to the thorium center in a distorted trigonal bipyramidal geometry, with the azide moieties as the axial ligands. The average Th–N bond length in **5** is 2.3829(16) Å, similar to the average Th–N bond length of the terminal azides in coordination polymer **3** (2.377(4) Å) and longer by about 0.09 Å than the average Th–N₃ bond in mononuclear **4** (2.2938(18) Å). As in **4**, the two N_α–N_β bond lengths in **5** (1.189(2) and 1.198(2) Å) are similar in value, as are the two N_β–N_γ bond lengths (1.147(2) and 1.150(2) Å); the average Δd value for the azides in **5** is 0.045 Å, and similar to **1** and **3**, the N_β–N_γ bond is shorter.

Complex **5** was also characterized by vibrational spectroscopy and has values similar to **1**, **3**, and **4**: the $\nu_{\text{asym}}(\text{N}_3)$ absorbance band in its IR spectrum is at 2077 cm^{−1} (toluene

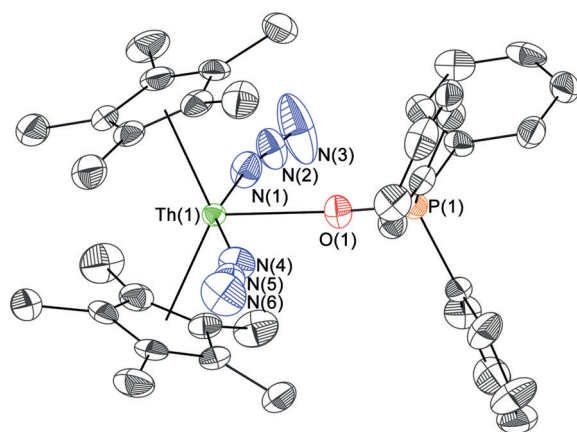


Figure 4. Molecular structure of $[(C_5Me_5)_2Th(N_3)_2(TPPO)]$ (**5**; 50% probability ellipsoids). Hydrogen atoms omitted for clarity. Selected bond distances (Å): Th(1)-N(1) 2.3863(16), Th(1)-N(4) 2.3795(16), N(1)-N(2) 1.189(2), N(2)-N(3) 1.147(2), N(4)-N(5) 1.198(2), N(5)-N(6) 1.150(2), Th(1)-O(1) 2.3660(13), Th(1)-C_{cent} 2.554(2), Th(1)-C_{cent'} 2.533(2). Selected bond angles (°): Th(1)-N(1)-N(2) 170.59(14), Th(1)-N(4)-N(5) 160.76(14), N(1)-Th(1)-N(4) 154.63(6), N(1)-N(2)-N(3) 179.3(2), N(4)-N(5)-N(6) 179.0(2), Th(1)-O(1)-P(1) 166.84(8), C_{cent}-Th(1)-C_{cent'} 133.54(6).

solution; 2071 cm^{-1} , neat solid); its Raman shift ranges are 1356–1440 ($\nu_{sym}(N_3)$) and 2080–2160 cm^{-1} ($\nu_{asym}(N_3)$).

Given the 1D infinite polymer structures of coordination polymers **1** and **3** in the solid-state and the fair-to-good solubility of both compounds in toluene and benzene, we wanted to determine if their extended structures are maintained in solution. The data from 1H NMR, IR, and Raman spectroscopic analysis did not provide convincing evidence for one scenario over the other, so we turned to diffusion ordered spectroscopy (DOSY) experiments to probe the solution structures.^[23] Diffusion coefficients were obtained for compounds **1** and **3–5** by using 1H NMR diffusion experiments ($[D_6]$ benzene, 298 K) with a stimulated echo pulse sequence. The hydrodynamic radius of each compound was subsequently derived from its diffusion coefficient. The radii of **1** and **3** were found to be of the same order of magnitude as the radii of mononuclear **4** and **5**, with an average size corresponding to a dimer and trimer for compounds **1** and **3**, respectively. This evidence suggests that the extended structures of **1** and **3** are not maintained and break up in solution, but they do not form monomeric species.

To conclude, this study presents the synthesis and characterization of the first family of metallocene thorium diazide complexes, including the first organometallic infinite coordination polymers of actinides. These compounds were characterized using X-ray crystallography, IR and multinuclear NMR spectroscopy, and, for the first time for any structurally characterized actinide azide complex, Raman spectroscopy. Although comparable to bonding motifs observed for several transition-metal systems, it is unclear why the thorium azides $[(C_5Me_5)_2Th(\mu-\eta^1-\eta^1-N_3)_2]_\infty$ (**1**) and $[(C_5Me_4Et)_2Th(\mu-\eta^1-\eta^1-N_3)(N_3)]_\infty$ (**3**) crystallize in open polymeric forms in contrast to the closed oligomeric ring structures observed for the uranium systems. Although there is a measurable (0.05 Å) difference in the metal ionic

radii of Th^{IV} and U^{IV} , it is difficult to attribute such a significant structural difference to this property alone. Nevertheless, both the open polymeric (thorium) and closed oligomeric (uranium) diazide forms provide arrays dense in actinide and nitrogen, as well as opportunities for developing actinide nitride chemistry. Further exploration into tuning the structure of organoactinide azides, with an eye towards the number and nature of the azide ligands, as well as the conversion of these new organometallic thorium azide complexes into nitrides is currently underway.

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