

# Synthesis and Properties of a Fifteen-Coordinate Complex: The Thorium Aminodiboranate $[\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4]^*$

Scott R. Daly, Paula M. B. Piccoli, Arthur J. Schultz,\* Tanya K. Todorova, Laura Gagliardi,\* and Gregory S. Girolami\*

The concept of coordination number is extremely useful and is widely employed to describe the local chemical environments of atoms. Originally defined by Alfred Werner in 1893,<sup>[1]</sup> the coordination number is closely related to many other important properties such as atomic radius,<sup>[2]</sup> molecular and electronic structure,<sup>[3]</sup> and chemical reactivity.<sup>[4,5]</sup> An important modification of Werner's original concept was the recognition that, for certain ligands such as ethylene, two linked atoms jointly occupy a single coordination site.<sup>[6]</sup> This modified definition is widely used to describe both transition-metal (d-block) and inner-transition-metal (f-block) complexes.<sup>[7]</sup>

An interesting question is: what is the largest possible coordination number?<sup>[8]</sup> This question has recently been considered theoretically, and the 15-coordinate ion  $\text{PbHe}_{15}^{2+}$  has been predicted to be a bound species.<sup>[9]</sup> The complexes tetrakis(cyclopentadienyl)uranium  $[\text{UCp}_4]$  and its thorium analogue  $[\text{ThCp}_4]$  are each connected to 20 atoms,<sup>[10]</sup> but the Werner coordination number of 12 (counting  $\pi$  bonds as occupying one site) is widely acknowledged to be more appropriate to describe the metal–ligand bonding in these compounds.<sup>[11]</sup>

Very high Werner coordination numbers are seen for metal complexes of the borohydride anion  $\text{BH}_4^-$ ,<sup>[12,13]</sup> which can coordinate to a single metal through as many as three

hydrogen atoms. From an electronic perspective, each B–H–M interaction involves a separate electron pair,<sup>[4,14]</sup> and each B–H–M interaction can be considered as a separate bond. Accordingly,  $[\text{Zr}(\text{BH}_4)_4]$ ,<sup>[15–17]</sup>  $[\text{Hf}(\text{BH}_4)_4]$ ,<sup>[15,16,18]</sup>  $[\text{Np}(\text{BH}_4)_4]$ ,<sup>[19]</sup> and  $[\text{Pu}(\text{BH}_4)_4]$ ,<sup>[19]</sup> all have coordination numbers of 12, and  $[\text{Th}(\text{BH}_4)_4]$ ,<sup>[15,16]</sup>  $[\text{Pa}(\text{BH}_4)_4]$ ,<sup>[19]</sup> and  $[\text{U}(\text{BH}_4)_4]$ ,<sup>[20]</sup> all of which are polymers in the solid state, have coordination numbers of 14. Some derivatives of these compounds also have high coordination numbers, such as the 14-coordinate tetrahydrofuran complex  $[\text{U}(\text{BH}_4)_4(\text{thf})_2]$ .<sup>[21]</sup> No complex of any kind, however, has been definitively shown to adopt a Werner coordination number higher than 14.<sup>[16,22]</sup>

Herein, we report the synthesis, single-crystal X-ray and neutron diffraction studies, and DFT investigations of the first 15-coordinate complex. DFT calculations suggest that this complex may adopt a 16-coordinate structure in the gas phase. This compound extends our recent studies of a new class of chelating borohydride ligands, that is, the aminodiborates,<sup>[23–26]</sup> some of which form highly volatile complexes that are useful as precursors for the chemical vapor deposition of thin films.<sup>[25,26]</sup>

Reaction of  $\text{ThCl}_4$  with four equivalents of sodium *N,N*-dimethylaminodiboranate,  $\text{Na}(\text{H}_3\text{BNMe}_2\text{BH}_3)$ , in tetrahydrofuran produced  $[\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4]$  (**1**), which could be isolated as colorless prisms by crystallization from diethyl ether. The IR spectrum of **1** contains strong bands at  $2420\text{ cm}^{-1}$  that arise from terminal B–H stretches, and at  $2264$  and  $2208\text{ cm}^{-1}$  that arise from bridging B–H–Th stretches. For comparison,  $[\text{Th}(\text{BH}_4)_4]$  contains a strong terminal B–H band at  $2530\text{ cm}^{-1}$  and bridging B–H–M bands at  $2270$ ,  $2200$ , and  $2100\text{ cm}^{-1}$ .<sup>[16]</sup> The  $^1\text{H}$  NMR spectrum of **1** ( $\text{C}_6\text{D}_6$  at  $20^\circ\text{C}$ ) contains peaks at  $\delta = 2.11\text{ ppm}$  (s,  $\text{NMe}_2$ ) and  $\delta = 4.23\text{ ppm}$  (br 1:1:1:1 q,  $J_{\text{BH}} = 90\text{ Hz}$ ,  $\text{BH}_3$ ); the terminal and bridging B–H units thus exchange rapidly on the NMR time scale. The  $^{11}\text{B}$  NMR spectrum consists of a binomial quartet at  $\delta = -2.75\text{ ppm}$ , which arises from coupling of the  $^{11}\text{B}$  nuclei with the three rapidly exchanging  $^1\text{H}$  nuclei ( $J_{\text{HB}} = 90\text{ Hz}$ ). For comparison, the  $^{11}\text{B}$  spectrum of  $[\text{Th}(\text{BH}_4)_4]$  consists of a quintet at  $\delta = -8.0\text{ ppm}$  ( $J_{\text{BH}} = 86.5\text{ Hz}$ ).<sup>[16]</sup>

Single-crystal X-ray and neutron diffraction studies of **1** reveal that it is monomeric with four chelating aminodiboranate ligands. The eight boron atoms describe a distorted  $D_{2d}$  dodecahedral structure, in which boron atoms B1, B2, B2A, and B1A describe one planar trapezoidal array, and atoms B3, B4, B5, and B6 describe the other (Figure 1). The B2–Th1–B2A and B4–Th1–B6 angles between wingtip boron atoms are almost linear at  $172.61(12)^\circ$  and  $171.85(13)^\circ$ , respectively. Interestingly, seven of the eight Th–B distances (those for boron atoms B1–B5) range from  $2.882(3)$  to  $2.949(3)\text{ \AA}$ , but

[\*] S. R. Daly, Prof. G. S. Girolami  
School of Chemical Sciences  
University of Illinois at Urbana-Champaign  
600 South Matthews Avenue, Urbana, IL 61801 (USA)  
Fax: (+1) 217-244-3186  
E-mail: girolami@scs.illinois.edu

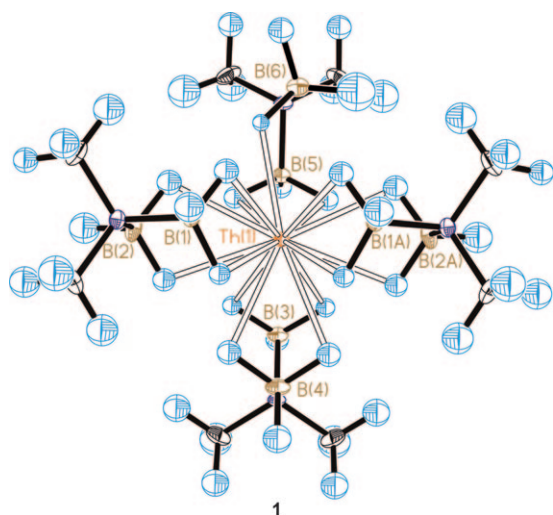
Dr. P. M. B. Piccoli, Dr. A. J. Schultz  
Intense Pulsed Neutron Source, Argonne National Laboratory  
Argonne, IL 60439 (USA)  
E-mail: ajschultz2@gmail.com

Prof. L. Gagliardi  
University of Minnesota, Department of Chemistry  
207 Pleasant St. SE, Minneapolis, MN 55455-0431 (USA)  
E-mail: gagliard@umn.edu

Dr. T. K. Todorova  
Department of Physical Chemistry, Sciences II, University of Geneva  
30, Quai Ernest Ansermet, 1211 Geneva 4 (Switzerland)

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**Figure 1.** Molecular structure of  $[\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4]$  (**1**) from neutron diffraction data. Ellipsoids are drawn at the 20% probability level. Th orange, B tan, N purple, C black, H blue.

the eighth distance ( $\text{Th1}\cdots\text{B6}$ ) is significantly longer at 3.193(5) Å.

Both the X-ray and neutron diffraction results clearly show that two hydrogen atoms on each boron atom bridge each of the seven short  $\text{Th}\cdots\text{B}$  contacts, but only one hydrogen atom bridges the long  $\text{Th}\cdots\text{B}$  contact. The thorium center therefore forms bonds with fifteen hydrogen atoms; accordingly, this is the first crystallographically characterized complex with a Werner coordination number of 15. The  $\text{Th}\cdots\text{H}$  distances calculated from the neutron diffraction study range from 2.37(2) to 2.539(18) Å, which are longer than the bridging thorium hydride distance calculated from the neutron diffraction study of  $[(\text{Cp}^*\text{ThH})_2(\mu\text{-H})]$  ( $\text{Th}\cdots\text{H} = 2.29(3)$  Å;  $\text{Cp}^* = \text{pentamethylcyclopentadienyl}$ ),<sup>[27]</sup> and those observed from the single-crystal XRD study of  $[\text{Cp}^*\text{ThH}]$  and the  $\mu_2$ -bridging hydrides in  $[\text{Th}_3(\mu_3\text{-H})_2(\mu_2\text{-H})_4(\text{O}-2,6\text{-}t\text{Bu}_2\text{C}_6\text{H}_3)_6]$  at 2.33(13) and 2.0(1)–2.3(1) Å, respectively.<sup>[28]</sup> Structurally characterized complexes such as  $[\text{Th}(\text{H}_3\text{BCH}_3)_4(\text{Et}_2\text{O})]$  and  $[\text{Th}(\text{H}_3\text{BCH}_3)_4(\text{thf})_2]$ , which contain bridging  $\text{Th}\cdots\text{H}\cdots\text{B}$  units, have  $\text{Th}\cdots\text{H}$  distances that range between 2.27(6) and 2.72(1) Å, which are similar to those observed in **1**.<sup>[29]</sup>

Although the aminodiborane ligands in **1** are chelating ligands, the coordination mode of **1** is not the only mode possible for this anion. For example, the analogous reaction of  $\text{UCl}_4$  with  $\text{Na}(\text{H}_3\text{BNMe}_2\text{BH}_3)$  results in reduction to form the related  $\text{U}^{\text{III}}$  compound  $[\text{U}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3]$ , which crystallizes in two different forms.<sup>[24]</sup> In one of the two forms, some of the aminodiborane ligands bridge between metal centers in a  $[\text{U}(\kappa^3\text{-H}_3\text{BNMe}_2\text{BH}_3\text{-}\kappa^3)\text{U}]$  fashion. We have also seen bridging modes in aminodiborane compounds of the lanthanides.<sup>[25]</sup>

Quantum chemical calculations using DFT<sup>[30]</sup> show that isolated molecules of **1** adopt fully symmetric structures with  $D_{2d}$  symmetry; interestingly, the lengthening of one  $\text{Th}\cdots\text{B}$  distance as seen in the crystal structure is not reproduced in the modeling studies. In order to determine whether inter-

molecular forces are responsible for this structural feature, optimizations were carried out on finite cluster ensembles containing one, two, three, four, and six  $[\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4]$  units cut out of the experimental crystal structure of **1**. In all cases, the complex maintains the nearly ideal  $D_{2d}$  structure seen for the isolated molecule, in which the  $\text{Th}\cdots\text{B}$  distances (for the inner and outer sites of the dodecahedron)<sup>[31]</sup> are 2.88 and 2.95 Å, respectively. Remarkably, however, a geometry for **1** that is in a very good agreement with that determined from the X-ray and neutron diffraction experiments results from the imposition of periodic boundary conditions on the arrays. Specifically, exactly one  $\text{Th}\cdots\text{B}$  interaction is long (3.08 Å) whereas the others lie between 2.85 and 2.93 Å; the elongated  $\text{Th}\cdots\text{B}$  vector in every molecule in the array lies in the crystallographic  $ac$  plane. We attribute the distortion to steric crowding, which occurs between the bulky aminodiborane ligands attached to the “overcoordinated” Th center, and is relieved by lengthening one bond because of the nonsymmetric environment surrounding each molecule in the crystal.

We have gathered evidence that the steric crowding in **1** leads to special reactivity that results in lowering the coordination number. Heating **1** to 100°C produced quantitative yields of the mixed aminodiborane/borohydride complex  $[\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_2(\text{BH}_4)_2]$  (**2**), in which the coordination number is reduced from 15 to 14. This transformation involves the quantitative loss of one equivalent of  $(\text{NMe}_2\text{BH}_2)_2$ , as shown by an in situ  $^{11}\text{B}$  NMR study. The X-ray crystal structure of **2** (Figure S2 in the Supporting Information) shows that the six boron atoms are arranged around the metal center in a distorted octahedron, as indicated by the presence of three large B–Th–B angles:  $\text{B1-Th1-B4}$ ,  $\text{B2-Th1-B5}$ , and  $\text{B3-Th1-B6}$  are 143.5(2)°, 141.0(3)°, and 140.1(3)°, respectively. The distances of  $\text{Th}\cdots\text{B}$  to the  $\text{BH}_4^-$  ligands are 2.583(10) and 2.608(9) Å, which are typical of Th complexes of tridentate borohydride ligands.<sup>[13]</sup> The distances of  $\text{Th}\cdots\text{B}$  to the aminodiborane ligands range from 2.848(9) to 2.882(9) Å, and are slightly shorter than those observed in **1**. The Th center forms bonds with fourteen hydrogen atoms; the chemically equivalent  $\text{Th}\cdots\text{H}$  distances, constrained to be equal within an estimated standard deviation of 0.01 Å, are 2.43(2) and 2.35(3)–2.36(3) Å for the aminodiborane and borohydride ligands, respectively.

The present results set a new record of fifteen for the highest Werner coordination number reported to date for any compound. This high coordination number is made possible by combining a very large metal atom with very small ligands. DFT calculations suggest that the isolated molecule has full  $D_{2d}$  symmetry with a coordination number of 16, but that the crowded nature of the inner coordination sphere is sufficiently destabilizing that molecule distorts and becomes 15-coordinate in the solid state. This finding suggests that the discovery of metal complexes with Werner coordination numbers equal to 16 should be possible with the correct combination of metal and ligands.

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