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Synthesis and Properties of a Fifteen-Coordinate Complex: The Thorium Aminodiboranate $[Th(H_3BNMe_2BH_3)_4]$**

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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,[1] the coordination number is closely related to many other important properties such as atomic radius,[2] molecular and electronic structure,[3] and chemical reactivity.[4,5] 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.[6] This modified definition is widely used to describe both transition-metal (d-block) and inner-transition-metal (f-block) complexes.[7]

An interesting question is: what is the largest possible coordination number?[8] This question has recently been considered theoretically, and the 15-coordinate ion $PbHe_{15}^{2+}$ has been predicted to be a bound species.[9] The complexes tetrakis(cyclopentadienyl)uranium $[UCp_4]$ and its thorium analogue $[ThCp_4]$ are each connected to 20 atoms,[10] but the Werner coordination number of 12 (counting π bonds as occupying one site) is widely acknowledged to be more appropriate to describe the metal–ligand bonding in these compounds.[11]

Very high Werner coordination numbers are seen for metal complexes of the borohydride anion BH_4^-,[12,13] 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,[4,14] and each B-H-M interaction can be considered as a separate bond. Accordingly, $[Zr(BH_4)_4]$,[15–17] $[Hf(BH_4)_4]$,[15,16,18] $[Np(BH_4)_4]$,[19] and $[Pu(BH_4)_4]$,[19] all have coordination numbers of 12, and $[Th(BH_4)_4]$,[15,16] $[Pa(BH_4)_4]$,[19] and $[U(BH_4)_4]$,[20] 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 $[U(BH_4)_4(thf)_2]$.[21] No complex of any kind, however, has been definitively shown to adopt a Werner coordination number higher than 14.[16,22]

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 aminodiboranates,[23–26] some of which form highly volatile complexes that are useful as precursors for the chemical vapor deposition of thin films.[25,26]

Reaction of $ThCl_4$ with four equivalents of sodium *N*,*N*-dimethylaminodiboranate, $Na(H_3BNMe_2BH_3)$, in tetrahydrofuran produced $[Th(H_3BNMe_2BH_3)_4]$ (**1**), which could be isolated as colorless prisms by crystallization from diethyl ether. The IR spectrum of **1** contains strong bands at 2420 cm^{-1} that arise from terminal B–H stretches, and at 2264 and 2208 cm^{-1} that arise from bridging B-H···Th stretches. For comparison, $[Th(BH_4)_4]$ contains a strong terminal B–H band at 2530 cm^{-1} and bridging B-H-M bands at 2270, 2200, and 2100 cm^{-1}.[16] The ^1H NMR spectrum of **1** (C_6D_6 at 20 °C) contains peaks at $\delta = 2.11$ ppm (s, NMe_2) and $\delta = 4.23$ ppm (br 1:1:1:1 q, $J_{BH} = 90$ Hz, BH_3); the terminal and bridging B–H units thus exchange rapidly on the NMR time scale. The ^{11}B NMR spectrum consists of a binomial quartet at $\delta = -2.75$ ppm, which arises from coupling of the ^{11}B nuclei with the three rapidly exchanging ^1H nuclei ($J_{HB} = 90$ Hz). For comparison, the ^{11}B spectrum of $[Th(BH_4)_4]$ consists of a quintet at $\delta = -8.0$ ppm ($J_{BH} = 86.5$ Hz).[16]

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)° and 171.85(13)°, respectively. Interestingly, seven of the eight Th···B distances (those for boron atoms B1–B5) range from 2.882(3) to 2.949(3) Å, but

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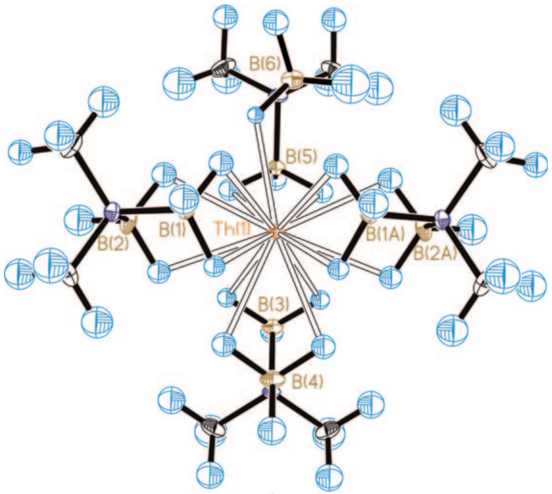

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Figure 1. Molecular structure of [Th($H_3BNMe_2BH_3$)$_4$] (**1**) from neutron diffraction data. Ellipsoids are drawn at the 20% probability level. Th orange, B tan, N purple, C black, H blue.

the eighth distance (Th1···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 Th···B contacts, but only one hydrogen atom bridges the long Th···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 Th–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 [(Cp^*_2ThH)$_2$(μ-H)] (Th–H = 2.29(3) Å; Cp* = pentamethylcyclopentadienyl),[27] and those observed from the single-crystal XRD study of [Cp^*_3ThH] and the μ_2-bridging hydrides in [$Th_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_4$(O-2,6-$tBu_2C_6H_3$)$_6$] at 2.33(13) and 2.0(1)–2.3(1) Å, respectively.[28] Structurally characterized complexes such as [Th(H_3BCH_3)$_4$]$_2$(Et_2O)] and [Th(H_3BCH_3)$_4$(thf)]$_2$, which contain bridging Th-H-B units, have Th–H distances that range between 2.27(6) and 2.72(1) Å, which are similar to those observed in **1**.[29]

Although the aminodiboranate 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 UCl_4 with Na($H_3BNMe_2BH_3$) results in reduction to form the related U^{III} compound [U($H_3BNMe_2BH_3$)$_3$], which crystallizes in two different forms.[24] In one of the two forms, some of the aminodiboranate ligands bridge between metal centers in a [U(κ^3-$H_3BNMe_2BH_3$-κ^3)U] fashion. We have also seen bridging modes in aminodiboranate compounds of the lanthanides.[25]

Quantum chemical calculations using DFT[30] show that isolated molecules of **1** adopt fully symmetric structures with D_{2d} symmetry; interestingly, the lengthening of one Th···B distance as seen in the crystal structure is not reproduced in the modeling studies. In order to determine whether intermolecular forces are responsible for this structural feature, optimizations were carried out on finite cluster ensembles containing one, two, three, four, and six [Th($BH_3NMe_2BH_3$)$_4$] 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 Th···B distances (for the inner and outer sites of the dodecahedron)[31] 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 Th···B interaction is long (3.08 Å) whereas the others lie between 2.85 and 2.93 Å; the elongated Th···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 aminodiboranate 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 aminodiboranate/borohydride complex [Th($H_3BNMe_2BH_3$)$_2$(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 (NMe_2BH_2)$_2$, as shown by an in situ ^{11}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: B1-Th1-B4, B2-Th1-B5, and B3-Th1-B6 are 143.5(2)°, 141.0(3)°, and 140.1(3)°, respectively. The distances of Th···B to the BH_4^- ligands are 2.583(10) and 2.608(9) Å, which are typical of Th complexes of tridentate borohydride ligands.[13] The distances of Th···B to the aminodiboranate 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 Th–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 aminodiboranate 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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