BIG METALS, SMALL LIGANDS: CHARACTERIZATION OF THE 15-COORDINATE COMPLEX THORIUM AMINODIBORANATE [Th(H₃BN(CH₃)₂BH₃)₄] BY SINGLE CRYSTAL NEUTRON DIFFRACTION

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1. ABSTRACT

The anionic borohydride ligand, [BH₄]⁻, is known to bind to metals by means of unidentate, bidentate, and tridentate binding modes, making it a useful ligand for the achievement of high coordination numbers in inorganic and organometallic complexes. Combinations of borohydride ligands with metal centers having large atomic radii often leads to complexes with coordination numbers higher than 12. Although 14-coordinate actinide complexes such as [U(BH₄)₄(thf)₂] have been previously reported, no complex with a coordination numbers higher than 14 has been unambiguously characterized. Due to the low sensitivity of X-rays for the detection of hydrogen atoms and the domination of the heavy metal in the scattered X-ray data, neutron diffraction data is invaluable for accurately characterizing such complexes.

Reaction of ThCl₄ with Na(H₃BNMe₂BH₃) in tetrahydrofuran produces the monomeric complex [Th(H₃BNMe₂BH₃)₄] (1), a molecule for which DFT calculations predict a theoretical maximum coordination number of 16 in the gas phase. Neutron diffraction data collected at the IPNS at low temperature reveal that fifteen of the hydrogen atoms on the chelating aminodiboranate ligands coordinate to the thorium center. The Werner coordination number of 15 in the solid state is the highest for any structurally characterized complex to date. Upon heating, complex 1 undergoes a thermal reaction to produce the sterically less crowded 14-coordinate [Th(H₃BNMe₂BH₃)₂(BH₄)₂] (2).

Herein we describe the structural characterization of 1, an analysis of its structure by DFT methods, and comparisons to analogous high coordination actinide complexes containing hydride or borohydride ligands.
2. BACKGROUND

In 1913, Alfred Werner became the first inorganic chemist to receive the Nobel Prize in Chemistry for his important work on coordination compounds and stereochemistry in inorganic complexes. His first paper on coordination chemistry, published in 1893 [1], built the foundation for modern inorganic chemistry as we know it. It defined a property that he called primary valence, but which is now known as coordination number. In all classical Werner coordination complexes, each coordination site involves a two-electron bond between the metal and a single atom of a ligand; the total number of such two-electron bonds formed by the metal is its coordination number. Later studies of organometallic complexes led to a revision of the coordination number concept: for ligands such as ethylene two atoms jointly occupy a single coordination site [2]. As an extension of this concept, the cyclopentadienyl ligand, \( \text{C}_5\text{H}_5^- \), is generally not regarded as occupying five coordination sites, but instead it is considered to be a 6-electron donor that occupies three coordination sites. Figure 1 illustrates two complexes, a classical Werner complex and an organometallic complex; even though different numbers of atoms are directly linked to the metal center, both complexes are classified as 6-coordinate.

![Figure 1: Two 6-coordinate, 18-electron complexes.](image)

As coordination numbers increase, geometries beyond common tetrahedral and octahedral shapes can be achieved. The 1977 review of high coordination number complexes by Drew is a superb analysis of the regular polyhedral shapes as they apply to inorganic and organometallic complexes [3]. At the time of the publication, only a scant number of very high coordinate complexes (coordination number > 10) had been reported. Most of these examples are complexes of lanthanides and actinides, as well as zirconium; these metals all have some of the largest radii in the periodic table. Several factors may influence the overall coordination number of a complex, among them being the atomic or ionic radius of the central atom, the electronic structure as alluded to above, and the sizes of the ligands. Shannon and Prewitt have illustrated,
for example, that the effective ionic radii of common cations increases with coordination number but decreases with increasing oxidation state, two important factors to consider when building high coordinate complexes [4]. A recent paper on proposed covalent atomic radii* reconfirm the long-known trend that the radii across a period of elements decrease with atomic number [5]. Figure 2, created from the data in Cordero et al., illustrates this trend well over the periodic table. To maximize the number of ligands about a metal center, therefore, we look for the largest possible metal with the smallest possible ligands, as shown by Hermann and coworkers in a theoretical investigation of the gas phase [Pb(He)₁₅]²⁺ [6].

![Graph of proposed atomic radii](image)

*Figure 2. A graph of the proposed atomic radii in Angstroms (Å) as a function of atomic number through Z = 96, reconstructed from data compiled from Cordero et al. [5]. The red data points are for each transition metal series, green points are for the lanthanide series, and blue points indicate the actinides.

One of the smallest ligands per coordination site is the chelating borohydride anion, [BH₄]⁻. This versatile ligand can bind to a single metal center through up to three of its own hydrides in a monodentate, bidentate or tridentate fashion (see Figure 3). Additionally the [BH₄]⁻ anion can bridge two or more metal centers in a polymeric or three-dimensional fashion in order to utilize all four of its hydrogen atoms. Electronically, like most agostic [7] or σ complexes [8], each B-H-M interaction can be counted as a separate three-center, two-electron bond [9,10]. In this way the borohydride anion has produced complexes possessing some of the highest Werner coordination numbers to date. Borohydride complexes with a Werner coordination number of 12 include [Zr(BH₄)₄] [11-13], [Hf(BH₄)₄] [11,12,14], [Np(BH₄)₄] [15] and [Pu(BH₄)₄] [15]. Even more impressively, the polymeric complexes [Th(BH₄)₄] [11,12], [Pa(BH₄)₄] [15] and

* Author’s note: Such data are often determined from a survey of the crystallographic literature and databases using bond distances to common atoms such as H, N, C and O. For these reasons it may still be wise, even though many journals no longer require it, to deposit published crystallographic structures of small molecules and extended solids to databases such as the Cambridge Structural Database or the Inorganic Crystal Structure Database.
[U(BH₄)₄] [16,17] and the monomeric compound [U(BH₄)₄(thf)₂] [18-20], have coordination numbers of 14. To date, however, no structurally characterized molecular complex has a Werner coordination number higher than 14.

Figure 3. Binding modes of the [BH₄]⁻ anion, from left to right: monodentate, bidentate and tridentate. The figure at bottom illustrates how the [BH₄]⁻ anion can act as a bridging ligand in order to create a polymeric structure.

Recently, we published a preliminary communication giving details of the first 15-coordinate complex to be structurally characterized, [Th(H₃BNMe₂BH₃)₄] (1) [21]. An analog of the borohydride anion, the chelating N,N-dimethylaminodiboranate ligand [22,23] was used to achieve this high coordination number. This manuscript describes the characterization of the complex, with particular emphasis on the structural determination using X-ray and neutron diffraction, as well as a comparison to similar lanthanide and actinide complexes that utilize this class of ligands. DFT calculations suggest that, in the gas phase, compound 1 adopts a coordination number of 16.

3. RESULTS

3.1 EXPERIMENTAL [21]

[Th(H₃BNMe₂BH₃)₄] (1) was produced from the reaction of ThCl₄ with four equivalents of Na(H₃BNMe₂BH₃) [23] in tetrahydrofuran (thf) at -78 °C and crystallized from toluene as described elsewhere [21]. Single crystal X-ray and neutron diffraction studies were carried out at -80 °C (193 K) in order to achieve the joint refinement of the neutron structure in the space group Pnma (no. 62, see below).

DFT quantum mechanical calculations on the geometry optimized molecules of 1 were carried out using the TURBOMOLE 5.9.1 package [24]. Periodic DFT calculations were carried out using the Vienna ab initio Simulation Package (VASP) [25,26]. A plane-wave basis set with a kinetic energy cutoff of 400 eV was used along with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The interaction between the ionic cores and the valence electrons was described by the projector augmented wave (PAW) method [27]. The integrations in the Brillouin zone employed a (2x3x4) Monkhorst-Pack grid [28]. All atoms were allowed to relax while keeping the lattice parameters fixed at the experimentally determined values (a = 18.8309, b = 13.4269, c = 9.6636 Å, α = β = γ = 90°).
3.2 NEUTRON DIFFRACTION

Neutron diffraction data were collected using the Single Crystal Diffractometer (SCD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (decommissioned, 2008; the SCD is currently installed at the Lujan Neutron Scattering Center at Los Alamos National Laboratory [29]). Because of the high atom percentage of boron in the molecule and boron’s large cross section for neutron absorption (767 barns for natural abundance boron; 1 barn = 10^{-24} cm^2), the crystals for the neutron diffraction experiment were limited in size. Owing to the low number of resultant neutron data, the data were collected at the same temperature as the X-ray diffraction experiment to enable a joint refinement of X-ray and neutron data using GSAS [30]. In the joint refinement, the unit cell metrics and positions of the heavy (non-hydrogen) atoms were determined first from the X-ray structure, and their positions and thermal parameters were fixed at those values. Hydrogen atom locations were first approximated from the X-ray structure and subsequently also located in the neutron Fourier maps; any differences were corrected according to the neutron-determined data. To increase the number of observations and improve the quality of the neutron refinement, soft restraints were included to restrain all terminal B-H bond distances to be equal and all B-H bond distances for B-H units bridging to Th to be equal. C-H bond distances were also restrained to be equal.

The crystallographic structure of [Th(H$_3$BNMe$_2$BH$_3$)$_4$] (1) as determined by X-rays and neutrons is shown in Figure 4. All four aminodiboranate ligands are chelating in a bidentate fashion to the metal center. Compound 1 is monomeric with the boron atoms distributed about the Th center in a distorted $D_{2d}$ dodecahedral arrangement. The Th–B distances (for B1 through B5) range from 2.882(3) to 2.949(3) Å, however the Th–B6 distance is appreciably longer and falls outside of this range at 3.193(5) Å. The molecule lies on the mirror plane at (x, $\frac{1}{4}$, z), and atom B6 was shown by neutron Fourier mapping to be disordered; it lies just off the mirror plane. One of its hydrogen atoms, H62, was shown to lie on the mirror plane so that the pendant –B6H$_3$ portion of the B5-N3-B6 chelating ligand is disordered. No other disorder of the molecule was found.

For the seven short Th–B contacts (B1-B5), two hydrogen atoms bridge between B and Th (as in the bidentate mode for BH$_4^-$). However for the long contact between Th and B6, only one H atom is bridging, bringing the total coordination number of the Th center to 15. The bridging Th-H distances range from 2.37(2) to 2.539(18) Å for 1.
3.3 SPECTROSCOPIC CHARACTERIZATION

The various covalent (Figure 3) and ionic metal-tetrahydroborate bonding modes each has a distinctive vibrational signature [31]. The infrared spectrum of [Th(H_3BNMe_2BH_3)_4] features a terminal B-H stretch as a strong band at 2420 cm\(^{-1}\) and bridging B-H stretches at 2264 and 2208 cm\(^{-1}\) [21]. These values compare well with those seen for [Th(BH_4)_4], which exhibits a terminal B-H stretch at 2530 cm\(^{-1}\) and bridging stretches at 2270, 2200, and 2100 cm\(^{-1}\) [12]. The [Th(BH_4)_5]^- anion is proposed to have tridentate BH_4 groups as judged from its IR spectrum, but this compound has not yet been investigated crystallographically.

As with many tetrahydroborate complexes, the terminal and bridging hydrogens exchange rapidly on the NMR time scale [31] and results in a broad quartet at \(\delta\ 4.23\) (\(^1\)H, 1:1:1:1 q, \(J_{BH} = 90\) Hz, BH_3) [21]. These hydrogen atoms couple with the natural abundance \(^{11}\)B to give rise to a binomial quartet at \(\delta -2.75\) in the \(^{11}\)B NMR spectrum [21]. By contrast, the \(^{11}\)B spectrum of [Th(BH_4)_4] shows a quintet at \(\delta -8.0\) but with a similar \(J_{BH}\) coupling constant of 86.5 Hz [12].

3.3 DFT CALCULATIONS

The DFT calculations, undertaken by the Gagliardi group at the University of Minnesota, show that isolated molecules of [Th(H_3BNMe_2BH_3)_4] adopt a completely symmetric structure with \(D_{2d}\) symmetry that
lacks the lengthened Th-B6 bond seen in the solid state structure. This result suggests that in the gas phase 1 possesses an unprecedented coordination number of 16. To investigate if crystal structure packing forces result in the disruption of the totally symmetric structure and disorder of the -B6H₃ group, geometry optimizations were carried out on larger clusters cut out of the experimental crystal structure. In these clusters, which consisted of two, three, four, and six [Th(H₃BNMe₂BH₃)₄] units, molecules of 1 still possess the fully symmetric $D_{2d}$ structure seen for the isolated molecule. However, when periodic boundary conditions are imposed on the molecular array, the molecules distort and one of the Th–B bonds lengthens significantly from a previous value of 2.85 – 2.93 Å to 3.08 Å, in relatively good agreement with the diffraction results. This elongated distance lies in the crystallographic ac plane, which is also consistent with the experimental result.

4. DISCUSSION

4.1 OTHER THORIUM COMPLEXES CONTAINING BRIDGING HYDRIDE LIGANDS OR Th-H-B INTERACTIONS

A search of the Cambridge Structural Database [32] returns 32 X-ray diffraction structures in which an actinide element is bound to a hydrogen atom. Of these, 28 have a B-H-An linkage, 5 of which are pyrazolylborate derivatives, and only 4 of the 32 contain thorium (there are two neptunium structures and the remaining complexes are uranium based). Only one of these 32 structures, (Cp*₂ThH)₂(μ-H)₂, has been characterized by neutron diffraction although some of the actinide tetrahydroborate compounds in the Inorganic Crystal Structure Database (ICSD) have been characterized in this way. The Th-H distances found for 1 are slightly longer than those to hydrides that bridge between Th centers, but are comparable to Th complexes in which the hydrides bridging between B and Th. Table 1 compares the Th-H distances in 1 with those in other molecules containing Th-H-Th or B-H-Th linkages.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Th-H distance, Å</th>
<th>Diff. method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Th(H₃BNMe₂BH₃)₄]</td>
<td>2.37(2) - 2.539(18)</td>
<td>Neutron</td>
<td>[21]</td>
</tr>
<tr>
<td>[(Cp*₂ThH)₂(μ-H)]</td>
<td>2.29(3)</td>
<td>Neutron</td>
<td>[33]</td>
</tr>
<tr>
<td>[Cp*₃ThH]</td>
<td>2.33(13)</td>
<td>X-ray</td>
<td>[34]</td>
</tr>
<tr>
<td>[Th₃(μ₃-H)₂(μ₂-H)₄(O-2,6-tBu₂C₆H₃)₆]</td>
<td>2.0(1) - 2.3(1)</td>
<td>X-ray</td>
<td>[34]</td>
</tr>
<tr>
<td>[Th(H₃BCH₃)₄(Et₂O)]</td>
<td>2.27(6) - 2.72(1)</td>
<td>X-ray</td>
<td>[35]</td>
</tr>
<tr>
<td>[Th(H₃BCH₃)₄(thf)]₂</td>
<td>2.27(6) - 2.72(1)</td>
<td>X-ray</td>
<td>[35]</td>
</tr>
<tr>
<td>(Ind*)₂Th(BH₄)₂ (Ind* = C₉Me₇)</td>
<td>2.466 – 2.531</td>
<td>X-ray</td>
<td>[36]</td>
</tr>
</tbody>
</table>

### 4.2 OTHER AMINODIBORANATE COMPLEXES OF LARGE METALS

The aminodiboranate ligand has been recently employed to synthesize a large number of complexes of the lanthanides [37] and uranium [38]. For example, the reaction of LnCl₃ (Ln = Pr, Sm, Er) with three equivalents of Na(H₃BNMe₂BH₃) in tetrahydrofuran (thf) affords complexes of stoichiometry Ln(H₃BNMe₂BH₃)₃(thf), which loses thf upon sublimation [37]. The size of the Ln atom has a significant effect on the resulting chemical structure of the base-free Ln(H₃BNMe₂BH₃)₃ complexes; none of the structures is monomeric and the aminodiboranate ligands exhibit a variety of different binding modes (Figure 5). In the Pr complex, each 14-coordinate Pr atom is bound to 2 chelating ligands and 2 ligands that bridge between metal centers to form a polymeric structure; each boron atom in the chelating ligands forms two B-H-Pr bonds and each boron atom in the bridging ligands forms three B-H-Pr bonds. For Sm, all three of its ligands are chelating to the metal center but it is also coordinated datively to one hydrogen atom from a neighboring molecule in the polymeric chain for a coordination number of 13. Er(H₃BNMe₂BH₃)₃ is a dimer in which each 12-coordinate Er atom is bound to two chelating ligands and two bridging ligands each bound in an Er(κ²H-H₃BNMe₂BH₃-κ²H)Er manner. The sizes of these atoms are progressively smaller, and the effect on the structures is marked.

The reaction of UCl₄ with four equivalents of Na(H₃BNMe₂BH₃) in an Et₂O suspension results in the evolution of gas and the formation of the trivalent compound U(H₃BNMe₂BH₃)₄ [38]. A similar reduction of U⁴⁺ to U³⁺ is observed in the decomposition of U(BH₄)₄, which when heated changes color from green to brown and evolves B₂H₆ and H₂, likely resulting in the formation of
U(BH₄)₃ [16]. Depending on the solvent used for crystallization, U(H₃BNMe₂BH₃)₃ crystallizes in two structural isomers having different coordination numbers and ligand binding modes.

Table 2 outlines the binding modes of the three complexes in the lanthanide study and compares them to the uranium and thorium complexes. Figure 5 offers an illustration of the complex arrangements of the chelating aminodiboranate ligands around the respective metal centers as described above.

**TABLE 2**

Comparison of structures and ionic or covalent radii (r, Å) for lanthanide and actinide diaminoboranate complexes [37,38]. Ionic radii from Shannon [4] are for a coordination number (CN) of six.

<table>
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<tbody>
<tr>
<td>Er(H₃BNMe₂BH₃)₃</td>
<td>0.89</td>
<td>1.89</td>
<td>2 ( \kappa^2,\kappa^2 ) chelating, 1 ( \kappa^2,\kappa^2 ) bridging</td>
<td>dinuclear</td>
<td>12</td>
</tr>
<tr>
<td>α-U(H₃BNMe₂BH₃)₃</td>
<td>1.025</td>
<td>1.96</td>
<td>3 ( \kappa^2,\kappa^2 ) chelating + 1 ( \kappa^1H ) dative</td>
<td>polymeric</td>
<td>13</td>
</tr>
<tr>
<td>β-U(H₃BNMe₂BH₃)₃</td>
<td>1.025</td>
<td>1.96</td>
<td>2 ( \kappa^2,\kappa^2 ) chelating, 1 ( \kappa^3,\kappa^3 ) bridging</td>
<td>polymeric</td>
<td>14</td>
</tr>
<tr>
<td>Sm(H₃BNMe₂BH₃)₃</td>
<td>0.96</td>
<td>1.98</td>
<td>3 ( \kappa^2,\kappa^2 ) chelating + 1 ( \kappa^1H ) dative</td>
<td>polymeric</td>
<td>13</td>
</tr>
<tr>
<td>Pr(H₃BNMe₂BH₃)₃</td>
<td>0.99</td>
<td>2.03</td>
<td>2 ( \kappa^2,\kappa^2 ) chelating, 1 ( \kappa^3,\kappa^3 ) bridging</td>
<td>polymeric</td>
<td>14</td>
</tr>
<tr>
<td>Th(H₃BNMe₂BH₃)₄</td>
<td>0.94*</td>
<td>2.06</td>
<td>3 ( \kappa^2,\kappa^2 ) chelating, 2 ( \kappa^2,\kappa^1 ) chelating</td>
<td>monomeric</td>
<td>15</td>
</tr>
</tbody>
</table>

*calculated for Th⁴⁺ with CN = 6; for CN = 7, \( r = 1.05 \) from radii-unit cell volume plots and for CN = 12, \( r = 1.21 \) (calculated)

The increase in the coordination number of the metal center with increasing atomic radius is well precedent in f-metal chemistry; Shannon makes this observation in his review of effective ionic radii [4], and a 1980 study of cyclopentadienyl compounds of the lanthanides and actinides [39] also supports the trend seen in the aminodiboranate complexes highlighted here. Surprisingly, Shannon found that \( r_{\text{ionic}} \) for Th is far smaller than that of any of the other listed lanthanides or actinides in the table, which is the opposite result expected from periodic trends.

In Shannon and Prewitt’s review, the only coordination number for which radii are given for all the elements in Table 2 is coordination number 6. It should be noted that, because of the lack of structural data for six-coordinate Th⁴⁺ complexes, the radius for six-coordinate Th in Shannon and Prewitt’s table is calculated and not derived from radii-unit cell volume plots [4]. For higher coordination numbers, Shannon and Prewitt do not include radii for all the elements, so comparisons become more difficult to make, but even so the effective ionic radius for Th still appears to be smaller than those of the other ions in this discussion (for example: for CN = 9, \( r_{\text{ionic}} = 1.179 \; \text{for Pr}^{III}, \; 1.132 \; \text{for Sm}^{III}, \; 1.062 \; \text{for Er}^{III} \; \text{and 1.09 for Th}^{IV}, \; \text{all radii in Å} \).
In contrast to Shannon and Prewitt’s results, data for covalent radii compiled by Cordero et al. in 2006 from structures in the CSD and ICSD databases show a clear trend in which Th has the largest covalent radius of the elements in question, followed closely by Pr which achieves a high coordination number of 14 (see Figure 2 and Table 2). Over the years there has been much discussion about the relative contributions of ionic and covalent bonding in actinide complexes (see, for example, Raymond’s discussion in [39]). The small number of lanthanide and actinide compounds in the CSD makes it difficult to compare bond distances, and the extremely small number of such compounds that have been characterized by neutron diffraction (essential in the case of hydrogen atoms bound to a large metal center), makes a definitive comparison even more problematic.

Spectroscopic rather than structural studies are currently affording the most informative evidence about the bonding in actinide complexes. A fine feature article, published in 2007 by Denning [40], illustrates the use of optical spectroscopy, X-Ray absorption and emission spectroscopies, NMR spectroscopy as well as supporting computational methods to explore the degree of covalency in actinyl ions and their analogs. X-ray absorption spectroscopy (XAS), a technique useful in determining the percentage of orbital mixing between metal and ligand through analysis of the pre-edge absorption features, has more recently been employed by Kozimor et al. in the study of a series of analogous transition metal and actinide $\text{Cp}^*\text{MCl}_2$ molecules ($\text{Cp}^* = \text{C}_5\text{Me}_5$; $\text{M} = \text{Ti, Zr, Hf, Th and U}$) [41]. In this study, analysis of the clear pre-edge absorption features arising from excitation of a Cl 1s electron to the 3d, 4d or 5d antibonding orbitals of the group 4 transition metals, respectively, leads to a covalent character of 25%, 23% and 22%, respectively. Analysis of similar pre-edge features in the U spectrum yields a result of 9% Cl 3p covalent character for the U-Cl bond. Although the degree of covalency for U is less than that found for the group 4 metals, it is still a significant finding for the actinides in which such covalency has been highly debated, and the result lends support for the presence of some covalency in complexes such as $\text{I}$. Pre-edge XAS features for $\text{Cp}^*\text{ThCl}_2$ unfortunately could not be resolved to enable an evaluation of Cl 3p orbital mixing and determination of Th-Cl covalency. Such further spectroscopic studies, as they become available, will prove more illuminative than simple structural studies of the true extent of covalency in actinide complexes.

* Of 203 total structures in the CSD that contain a Ln-H linkage, 120 of these are characterized by a B-H-Ln bond. Of those 120, a total of 57 of these are borohydrides or borohydride analogs. Only one of these 203 structures has been characterized by neutron diffraction, and it does not contain a B-H-Ln bond. See the discussion under section 4.1 of this manuscript for similar statistics of the actinides.
Figure 5. Complexes of lanthanides and actinides illustrating the various binding modes of the aminodiboranate ligand, also listed in Table 2 and described in the text: (a) 14-coordinate Pr(H₃BNMe₂BH₃)₃, (b) 13-coordinate Sm(H₃BNMe₂BH₃)₃, (c) 12-coordinate Er(H₃BNMe₂BH₃)₃, (d) the 13-coordinate “α” phase of U(H₃BNMe₂BH₃)₃. Figures (a-c) reprinted with permission from S. R. Daly, D. Y. Kim, Y. Yang, J. R. Abelson, and G. S. Girolami, J. Am. Chem. Soc. 132, 2106-2107 (2010), copyright 2010 American Chemical Society. Figure (d) S. R. Daly and G. S. Girolami, Chem. Commun. 46, 407 (2010) – Reproduced by permission of The Royal Society of Chemistry.
4.2 STERIC OVERCROWDING

As described above, the DFT results indicate that the aminodiboranate ligands must be crowded about the Th center, because weak intermolecular packing forces can cause a distortion from the idealized 16-coordinate “gas-phase” structure to a less sterically demanding 15-coordinate structure. In the latter structure, one of the Th–B contacts is elongated, and only one hydrogen atom (instead of two) bridges between the B and Th centers. In fact, reactivity studies suggest that even the 15-coordinate structure is also somewhat crowded, as evidenced by the chemical change that takes place when 1 is heated to 100°C. One equivalent of (NMe₂BH₂)₂ is evolved, and the new thorium complex [Th(H₂BNMe₂BH₃)₂(BH₄)₂] (2) is generated. This monomeric complex, which has been structurally characterized by X-ray diffraction (see Figure 6), possesses two chelating κ²,κ²H aminodiboranate ligands and two tetrahydroborate ligands bound in a κ³H mode. The boron atoms are distributed about Th in a distorted octahedral fashion. The Th–B distances to the aminodiboranate ligand of 2.848(9) to 2.882(9) Å are slightly shorter than observed for the parent molecule 1, probably because 2 is less sterically crowded. Accordingly, the Th-H distances are also shorter at 2.43(2) and 2.35(3)–2.36(3) Å for the aminodiboranate and borohydride ligands, respectively.

5.0 CONCLUSIONS

The first complex possessing a Werner coordination number of 15, [Th(H₂BNMe₂BH₃)₄] (1), has been structurally characterized by both X-ray and neutron diffraction, which are essential tools in accurately characterizing metal hydride and borohydride complexes. Although DFT calculations predict a totally symmetric 16-coordinate geometry in the gas phase, the steric bulk of the chelating aminodiboranate ligand combined with intermolecular packing forces result in a change in the coordination geometry, breaking of one Th-H interaction, and a lessening of the coordination number to 15. Comparisons of the structures of a series of related lanthanide and actinide aminodiboranate complexes show that the atomic radius of the metal has a large...
influence on the metal-ligand bonding mode, resulting in complexes having a diverse array of both coordination number and number of chelating or bridging ligands. The thermal reactivity of 1, i.e., the loss of \((\text{NMe}_2\text{BH}_2)_2\) to yield the 14-coordinate \([\text{Th}(\text{H}_2\text{BNMe}_2\text{BH}_3)_2(\text{BH}_4)_2]\) (2), suggests that even the 15-coordinate structure of 1 seen in the solid state is still sufficiently crowded to promote conversion to a geometry with a lower coordination geometry. However, with a judicious choice of large metal and small ligands, complexes with stable 16-coordinate geometries do not seem implausible.

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