

Aminodiboranates: Syntheses, Structures, and Applications for Chemical Vapor Deposition

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Thin film deposition is an important process used in the manufacturing of microelectronics and hard coatings.¹ Although thin films can be deposited by physical vapor deposition (PVD) methods such as evaporation or sputtering, one of the major limitations of PVD is its line-of-sight nature, which makes it impossible to grow uniformly-thick (i.e., conformal) films on non-flat substrates, especially those that contain recesses with high aspect ratios.² In contrast to PVD, chemical vapor deposition (CVD)³ can afford conformal films on non-flat substrates if the CVD precursor used has sufficient vapor pressure to access the conformal growth zone.⁴

Borohydrides, such as BH_4^- and B_3H_8^- , have been used to prepare highly volatile metal complexes with group 4 metals and chromium, and these are outstanding CVD precursors for the deposition of metal diboride thin films.⁵ However, the small size and instability of these borohydrides precludes their use with a wide variety of metals. Recently, we discovered a new class of metal complexes known as the aminodiboranates (Figure 1). The aminodiboranate ligands typically chelate to metals through four B-H-M bridges, making them larger than BH_4^- and B_3H_8^- . Highly volatile *N,N*-dimethylaminodiboranate (DMADB) complexes of $\text{M}(\text{H}_3\text{BNMe}_2\text{BH}_3)_2$, where M = Mg, Ti, Cr, Mn, and Mo, have been prepared and used as precursors for the deposition of thin films by CVD.⁶

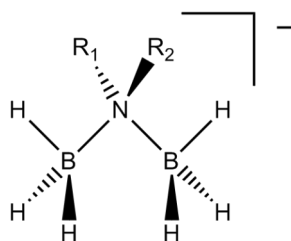


Figure 1. General structure of aminodiboranate ligands.

The large size of the DMADB ligand makes it well suited for the preparation of volatile lanthanide precursors. For instance, $\text{Ln}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$ and $\text{Ln}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3(\text{thf})$ complexes have been prepared for all lanthanides except Pm.⁷ The tetrahydrofuran complexes are monomeric, and most of them adopt 13-coordinate structures in which each DMADB group chelates to the metal center by means of four B-H \cdots Ln bridges (each BH_3 group is $\kappa^2\text{H}$; i.e., forms two B-H \cdots Ln interactions). For the smallest three lanthanides, Tm, Yb, and Lu, the metal center is 12 coordinate because one of the DMADB groups chelates to the metal center by means of only three B-H \cdots Ln bridges. The structures of the base-free $\text{Ln}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$ complexes are highly dependent on the size of the lanthanide ions: as the ionic radius decreases, the coordination number decreases from 14 (Pr) to 13 (Sm) to 12 (Dy, Y, Er). The $\text{Ln}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$ compounds, which are highly volatile and sublime at temperatures as low as

65 °C in vacuum, are suitable for the deposition of lanthanide oxide and lanthanide boride thin films by CVD.

The reaction of ThCl_4 with four equivalents of $\text{Na}(\text{H}_3\text{BNMe}_2\text{BH}_3)$ in tetrahydrofuran produces the new complex $\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4$.⁸ The thorium center forms bonds with fifteen hydrogen atoms; accordingly, *this is the first example of a fifteen-coordinate atom of any kind*. As determined by both single crystal X-ray and single crystal neutron diffraction studies, the eight boron atoms describe an approximate D_{2d} dodecahedral structure in which seven of the $\text{Th}\cdots\text{B}$ distances lie between 2.88 and 2.95 Å, but the eighth is significantly longer at 3.19 Å (Figure 2). Two hydrogen atoms on each boron atom bridge each of the short $\text{Th}\cdots\text{B}$ contacts, but only one bridges the long $\text{Th}\cdots\text{B}$ contact. Compound **1** reacts at elevated temperatures to produce $(\text{NMe}_2\text{BH}_2)_2$ and the mixed aminodiboranate/tetrahydroborate complex $\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_2(\text{BH}_4)_2$. The reaction of UCl_4 with $\text{Na}(\text{H}_3\text{BNMe}_2\text{BH}_3)$ in diethyl ether affords the uranium(III) product $\text{U}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$, which has been crystallized as two different structural isomers from pentane and toluene, respectively.⁹

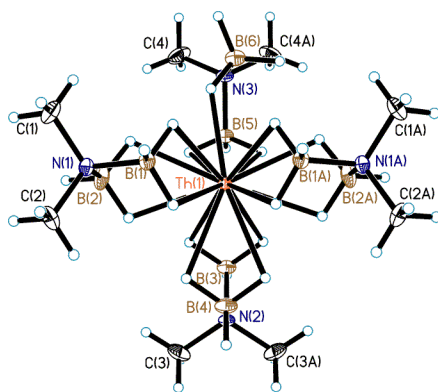


Figure 2. Structure of $\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4$ from single crystal X-ray diffraction data.

New aminodiboranate ligands can be prepared using the same synthetic method used for $\text{Na}(\text{H}_3\text{BNMe}_2\text{BH}_3)$. For instance, reduction of ammonia borane, $\text{NH}_3\cdot\text{BH}_3$, with Na in refluxing tetrahydrofuran affords the unsubstituted aminodiboranate $\text{Na}(\text{H}_3\text{BNH}_2\text{BH}_3)$. Reduction of other amine boranes with Na, where amine = NH_2Me , NH_2Et , $\text{HN}(\text{C}_4\text{H}_8)$, affords the new aminodiboranate salts $\text{Na}(\text{H}_3\text{BNHMeBH}_3)$, $\text{Na}(\text{H}_3\text{BNHEtBH}_3)$, and $\text{Na}[\text{H}_3\text{BN}(\text{C}_4\text{H}_8)\text{BH}_3]$. Grinding MgBr_2 with two equivalents of $\text{Na}(\text{H}_3\text{BNHEtBH}_3)$ yields the highly volatile $\text{Mg}(\text{H}_3\text{BNHEtBH}_3)_2$, which condenses as a viscous oil during sublimation attempts. The collected oil slowly crystallizes to yield long needles suggesting that it is “crystallographically frustrated” due to the asymmetry of the $\text{H}_3\text{BNHEtBH}_3$ ligand. Treatment of ErCl_3 with three equivalents of $\text{Na}(\text{H}_3\text{BNH}_2\text{BH}_3)$ in tetrahydrofuran affords the new erbium complex $\text{Er}(\text{H}_3\text{BNH}_2\text{BH}_3)\text{Cl}_2(\text{thf})_3$, where only one chlorine atom has been replaced. The structure obtained by XRD reveals strong $\text{N-H}\cdots\text{Cl}$ contacts.

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