

Part I. Synthesis and Characterization of Calcium and Strontium Compounds of *N,N*-Dimethylaminodiboranate

Part II. High Coordination Number Compounds of Thorium Borohydride

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The heavier alkaline earth metals in group 2 of the periodic table (Ca, Sr, and Ba) are key components of high temperature superconductors,¹ ferroelectric materials,² non-linear optical materials,³ and colossal magnetoresistive thin films.⁴ Many of these applications require that the material be fabricated in the form of a thin film.⁵ Of the various ways to deposit thin films, particularly attractive are metal organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD), because they offer the potential for large area growth and the advantages of good composition control, high film uniformity, and excellent conformal step coverage on non-planar device geometries.⁶ But both MOCVD and ALD depend on the availability of volatile metal-containing precursors. Owing to the relatively large radii and relatively small charges of the heavier group 2 ions suitably volatile precursors are scarce.^{7,8}

Our group has recently been investigating the chemistry of the *N,N*-dimethylaminodiboranate (DMADB) ligand and have found that it makes volatile compounds of many metals in the periodic table.^{9,10} We find that the reaction of MBr_2 ($M = Ca$ or Sr) with two equiv of $Na(DMADB)$ in thf yields $M(DMADB)_2(thf)_x$, ($x = 2$ for Ca and 3 for Sr). Treating the thf adducts with dme, diglyme, or tmeda in thf affords the new compounds $M(DMADB)_2(dme)_x$, ($x = 1$ for Ca and 2 for Sr), $M(DMADB)_2(diglyme)$, and $M(DMADB)_2(tmeda)$, respectively.

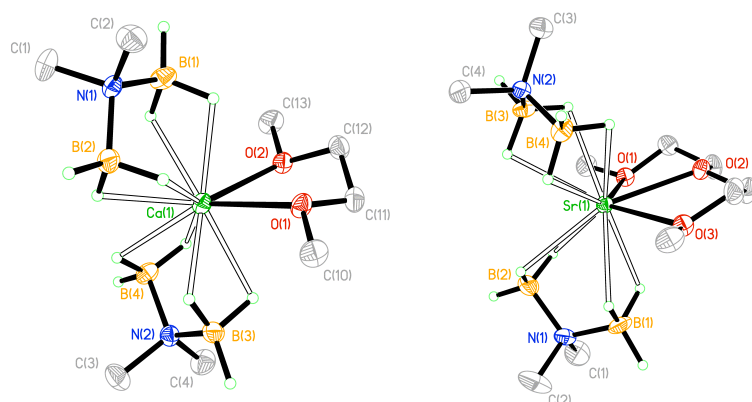


Figure 1: Molecular structure of $Ca(DMADB)_2(dme)$ and $Sr(DMADB)_2(diglyme)$. Ellipsoids are drawn at the 30% probability level. Hydrogens attached to carbon have been removed for clarity

When heated, the dme, diglyme, and tmeda compounds of Ca melt without decomposition, and can be sublimed readily under reduced pressure (1 Torr) at 90 °C for dme, and 120 °C for diglyme and tmeda. The diglyme and tmeda compounds of Sr also melt without decomposition, and can be sublimed readily under reduced pressure (1 Torr) at 120 °C. These compounds are some of the most volatile calcium and strontium compounds known, and are promising candidates as CVD precursors for the growth of thin films.

Thorium is another element that forms few volatile compounds, and so we have investigated the chemistry of thorium borohydrides. Metal tetrahydroborates are a fascinating class of compounds with several potential technological uses.¹¹ For example, the volatility of

metal tetrahydroborates makes these compounds of interest as precursors for the chemical vapor deposition of metal diboride phases,^{12,13} which have some very attractive properties, including high hardnesses, high melting points, moderate strength, resistance to wear and corrosion, and good electrical conductivities.¹⁴

We have determined the crystal structure of $\text{Th}(\text{BH}_4)_4$ and confirmed that it is isomorphous with the tetragonal form of its uranium analogue. Of the four BH_4^- groups per formula unit, two are terminal and are bound to thorium in a tridentate κ^3 fashion, and the other two BH_4^- groups bridge between neighboring Th centers in a bis(bidentate) κ^2, κ^2 fashion. The metal centers are linked into a three-dimensional polymer that consists of interconnected helical chains wound about fourfold screw axes. The most interesting result is that the Th and U complexes show some systematic differences in bond distances and angles, which are tentatively attributed either to the different f-electron configurations of these two ions (f^0 vs f^2) or to the lower energies of the f-orbitals on uranium. Few other examples of such electronic effects in actinide chemistry have been postulated.^{15,16}

Treatment of ThCl_4 with lithium tetrahydroborate in various ether solvents affords the complexes $\text{Th}(\text{BH}_4)_4(\text{Et}_2\text{O})_2$, $\text{Th}(\text{BH}_4)_4(\text{thf})_2$, and $\text{Th}(\text{BH}_4)_4(\text{dme})$. Crystal structures show that all four BH_4 groups are tridentate, making the thorium atoms 14 coordinate. Addition of tertiary phosphines to $\text{Th}(\text{BH}_4)_4(\text{Et}_2\text{O})_2$ yields the new Lewis base adducts, $\text{Th}(\text{BH}_4)_4(\text{PMe}_3)_2$, $\text{Th}(\text{BH}_4)_4(\text{PEt}_3)_2$, and $\text{Th}(\text{BH}_4)_4(\text{dmpe})_2$. The crystal structure of $\text{Th}(\text{BH}_4)_4(\text{PEt}_3)_2$ is similar to that of $\text{Th}(\text{BH}_4)_4(\text{Et}_2\text{O})_2$. In $\text{Th}(\text{BH}_4)_4(\text{dmpe})_2$, two of the BH_4^- groups are κ^2 and two are κ^3 . All of the Lewis base adducts of $\text{Th}(\text{BH}_4)_4$ are volatile and may be sublimed in vacuum. The results show that thorium complexes of unidentate phosphines can be made and are stable enough to isolate and characterize. The compound $\text{Th}(\text{BH}_4)_4(\text{dmpe})_2$ is the first thorium complex to contain $\kappa^2 \text{BH}_4^-$ groups.

The reaction of ThCl_4 with six equiv. of LiBH_4 in diethyl ether produces the compound $[\text{Li}(\text{Et}_2\text{O})_2][\text{Th}(\text{BH}_4)_5]$. The thorium center is surrounded by six borohydride ligands, four of which are coordinated in a tridentate κ^3 fashion. The other two BH_4^- groups bridge between neighboring Th centers in a bis(bidentate) κ^2, κ^2 fashion, forming a polymeric structure. This is the first structurally characterized 16 coordinate compound of any kind. $[\text{Li}(\text{Et}_2\text{O})_2][\text{Th}(\text{BH}_4)_5]$ reacts with thf to form $[\text{Li}(\text{thf})_4][\text{Th}(\text{BH}_4)_5(\text{thf})]$, which contains a monomeric anion. The thorium atom is coordinated by five κ^3 borohydride groups and one thf molecule, giving an overall coordination number of 16. $[\text{Li}(\text{Et}_2\text{O})_2][\text{Th}(\text{BH}_4)_5]$ can also be treated with 12-crown-4 to produce the $[\text{Li}(12\text{-crown-4})_2]_2[\text{Th}(\text{BH}_4)_6]$ salt. The environment about the thorium atom is essentially the same as that in $[\text{Li}(\text{Et}_2\text{O})_2][\text{Th}(\text{BH}_4)_5]$ except the bidentate borohydride groups are not bridging. This is the first homoleptic monomer with a coordination number of 16.

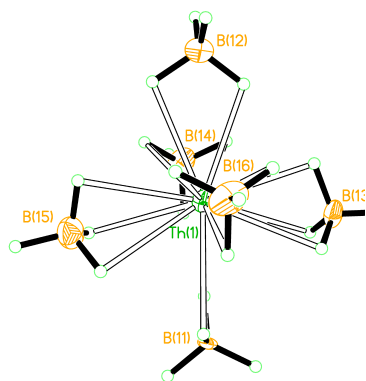


Figure 2: Molecular structure of the anion in $[\text{Li}(12\text{-crown-4})_2][\text{Th}(\text{BH}_4)_6] \cdot \text{thf}$. Ellipsoids are drawn at the 30% probability level.

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