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, ferroelectric materials, non-linear optical materials, and colossal magnetoresistive thin films. Many of these applications require that the material be fabricated in the form of a thin film. 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. 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.

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. We find that the reaction of MBr₂ (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.

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

We have determined the crystal structure of Th(BH\textsubscript{4})\textsubscript{4} and confirmed that it is
isomorphous with the tetragonal form of its uranium analogue. Of the four BH\textsubscript{4} groups per
formula unit, two are terminal and are bound to thorium in a tridentate $\kappa^3$ fashion, and the other
two BH\textsubscript{4} groups bridge between neighboring Th centers in a bis(bidentate) $\kappa^2,\kappa^2$ 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\textsuperscript{0} vs f\textsuperscript{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.\textsuperscript{15,16}

Treatment of ThCl\textsubscript{4} with lithium tetrahydroborate in various ether solvents affords the
complexes Th(BH\textsubscript{4})\textsubscript{4}(Et\textsubscript{2}O), Th(BH\textsubscript{4})\textsubscript{4}(thf), and Th(BH\textsubscript{4})\textsubscript{4}(dme). Crystal structures show that all
four BH\textsubscript{4} groups are tridentate, making the thorium atoms 14 coordinate. Addition of tertiary
phosphines to Th(BH\textsubscript{4})\textsubscript{4}(Et\textsubscript{2}O) yields the new Lewis base adducts, Th(BH\textsubscript{4})\textsubscript{4}(PMe\textsubscript{3})\textsubscript{2},
Th(BH\textsubscript{4})\textsubscript{4}(PET\textsubscript{3})\textsubscript{2}, and Th(BH\textsubscript{4})\textsubscript{4}(dmpe)\textsubscript{2}. The crystal structure of Th(BH\textsubscript{4})\textsubscript{4}(PET\textsubscript{3})\textsubscript{2} is similar to
that of Th(BH\textsubscript{4})\textsubscript{4}(Et\textsubscript{2}O). In Th(BH\textsubscript{4})\textsubscript{4}(dmpe)\textsubscript{2}, two of the BH\textsubscript{4} groups are $\kappa^2$ and two are $\kappa^3$. All
of the Lewis base adducts of Th(BH\textsubscript{4})\textsubscript{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 Th(BH\textsubscript{4})\textsubscript{4}(dmpe)\textsubscript{2} is the first thorium complex to
contain $\kappa^2$ BH\textsubscript{4} groups.

The reaction of ThCl\textsubscript{4} with six equiv. of LiBH\textsubscript{4} in diethyl ether produces the compound
[Li(Et\textsubscript{2}O)\textsubscript{2}][Th(BH\textsubscript{4})\textsubscript{5}]. The thorium center is surrounded by six borohydride ligands, four of
which are coordinated in a tridentate $\kappa^3$ fashion. The other two BH\textsubscript{4} groups bridge between
neighboring Th centers in a bis(bidentate) $\kappa^2,\kappa^2$ fashion, forming a polymeric structure. This is
the first structurally characterized 16 coordinate compound of any kind. [Li(Et\textsubscript{2}O)\textsubscript{2}][Th(BH\textsubscript{4})\textsubscript{5}]
reacts with thf to form [Li(thf)\textsubscript{4}][Th(BH\textsubscript{4})\textsubscript{5}(thf)], which contains a monomeric anion. The
thorium atom is coordinated by five $\kappa^3$ borohydride groups and one thf molecule, giving an
overall coordination number of 16. [Li(Et\textsubscript{2}O)\textsubscript{2}][Th(BH\textsubscript{4})\textsubscript{5}] can also be treated with 12-crown-4 to
produce the [Li(12-crown-4)\textsubscript{2}][Th(BH\textsubscript{4})\textsubscript{6}] salt. The environment about the thorium atom is
essentially the same as that in [Li(Et\textsubscript{2}O)\textsubscript{2}][Th(BH\textsubscript{4})\textsubscript{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 [Li(12-crown-4)\textsubscript{2}][Th(BH\textsubscript{4})\textsubscript{6}]-thf. Ellipsoids are drawn at the 30\% probability level.
References


