

Metal Tetrahydridoborates and Tetrahydridoborato Metalates, 18^[1]Preparation and Molecular Structures of Tetrahydrofuran, Diethylene Diglycol Dimethyl Ether and 18-Crown-6 Complexes of Strontium and Barium Tetrahydridoborate[☆]

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Strontium bis(tetrahydridoborate)–bis(diglyme) / Barium bis(tetrahydridoborate)–bis(diglyme) /
Strontium bis(tetrahydridoborate)–1,4,7,13,16-hexaoxacyclooctadecane / Metal-hydrogen-boron bridges

The strontium and barium tetrahydridoborate complexes $M(\text{BH}_4)_2 \cdot 2$ diglyme and $M(\text{BH}_4)_2 \cdot 18$ -crown-6 ($M = \text{Sr}, \text{Ba}$) have been prepared from the solvates $M(\text{BH}_4)_2 \cdot 2$ THF by ligand displacement. ¹¹B-NMR and IR data reveal strongly polar bonding of the BH_4^- groups to the metal centers, and X-ray structural analyses of the diglyme and crown ether compounds show molecular units in which the BH_4^- group is

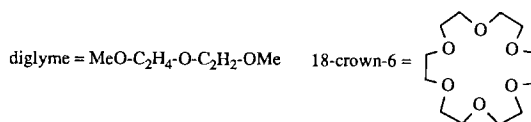
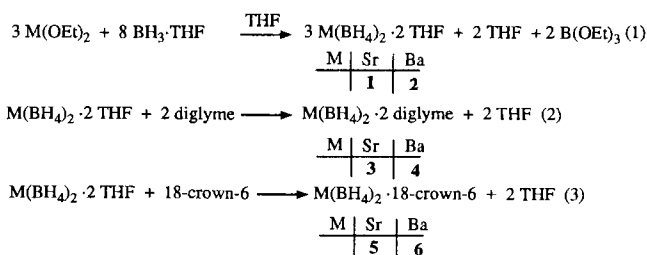
in contact via three H atoms with the metal center. In contrast, $M(\text{BH}_4)_2 \cdot 2$ THF compounds are chain polymers in the solid state, and each metal center is surrounded by 2 THF molecules in *trans* position and four BH_4^- groups each of which forms bridges with two metal centers. Estimations of the effective radius for the BH_4^- group indicate a high polarity for the M– BH_4 interaction.

The structures of metal tetrahydridoborates, both of the main group metals as well as of transition metals, show a large variety of bonding situations for the BH_4^- ion^[2,3]. Those of the transition metals seem to be dominated by their covalent character while the main-group metal tetrahydridoborates feature the full range between covalent [e.g. $\text{Al}(\text{BH}_4)_3$]^[4] and ionic bonding (e.g. CsBH_4)^[5]. The ionic character of the compounds increases within one group as the radius of the metal center increases as well as with decreasing electronegativity of the element in question^[6]. The tetrahydridoborate group may act as a bidentate ligand as observed for $\text{Al}(\text{BH}_4)_3$ ^[4] or $\text{Me}_2\text{-Ga}(\text{BH}_4)$ ^[7], or it can bind via three hydrogen atoms to the metal center as exemplified by $\text{Ca}(\text{BH}_4)_2 \cdot 2$ glyme^[8], or both kinds of binding may occur in the same molecule as shown for $\text{Ca}(\text{BH}_4)_2 \cdot 2$ diglyme^[9]. $\text{NaBH}_4 \cdot$ diglyme, on the other hand, features a polymeric structure^[10], and in the dimeric $(\text{LiBH}_4 \cdot \text{TMEDA})_2$ the BH_4^- group binds the Li centers in a unique way: one hydrogen atom forms a bridge with both Li atoms, and two more show a $\text{Li} \cdots \text{H} \cdots \text{B}$ interaction^[11]. As far as we are aware there are no structural data available for tetrahydridoborates of strontium and barium, and in order to get information on the effect of the increasing ionic radius of these elements on the bonding of the BH_4^- group to these centers we investigated the syntheses and structures of $M(\text{BH}_4)_2$ solvates ($M = \text{Sr}, \text{Ba}$) and report in this paper on solvates with THF, diglyme, and a crown ether.

Preparation of $M(\text{BH}_4)_2 \cdot 2$ diglyme and $M(\text{BH}_4)_2 \cdot 18$ -Crown-6

The most effective method for the preparation of strontium and barium tetrahydridoborate was developed by Wi-

berg and Hartwimmer^[12] by reaction of the metal ethoxides with diborane in THF according to eq. (1). This has the advantage that the byproducts $[\text{HB}(\text{OEt})_2$ and $\text{B}(\text{OEt})_3]$ can be readily removed in vacuo, but actually the alkaline earth metal tetrahydridoborates crystallize from the solutions as $M(\text{BH}_4)_2 \cdot 2$ THF (**1**, $M = \text{Sr}$; **2**, $M = \text{Ba}$). THF can be readily displaced from these by dissolving or suspending the THF adducts in diglyme or by adding 18-crown-6 to THF solutions of $M(\text{BH}_4)_2 \cdot n$ THF as shown in equations (2) and (3). The compounds $M(\text{BH}_4)_2 \cdot 18$ -crown-6 (**5**, $M = \text{Sr}$; **6**, $M = \text{Ba}$) precipitate from the THF solutions while compounds $M(\text{BH}_4)_2 \cdot 2$ diglyme (**3**, $M = \text{Sr}$; **4**, $M = \text{Ba}$) are soluble in diglyme although **4** only sparingly. However, all compounds dissolve readily in DMSO, and single crystals of **5** and **6** were obtained by slowly letting ether vapor diffuse into a DMSO solution of **5** or THF vapor in a DMSO solution of **6**. Single crystals of $\text{Sr}(\text{BH}_4)_2 \cdot 2$ diglyme



were obtained on cooling its saturated solution in diglyme to -25°C while the formation of single crystals of $\text{Ba}(\text{BH}_4)_2 \cdot 2$ diglyme is more difficult.

IR and NMR Spectra

It is well-known that ^{11}B -NMR spectra of tetrahydridoborates give an indication of the type of bonding both by their chemical shift, their $^1J(^{11}\text{B}^1\text{H})$ coupling constant, and the line shape of the resulting quintet^[13]. Thus, an aqueous solution of NaBH_4 shows a quintet consisting of five sharp lines with $\delta^{11}\text{B} = -41.2$ and $^1J(^{11}\text{B}^1\text{H}) = 80.7$ Hz^[14]. All six compounds under consideration exhibit the expected 1:4:6:4:1 quintet structure, and compared with the free BH_4^- ion the boron nuclei in the six compounds are noticeably deshielded [**1**: $\delta^{11}\text{B} = -36.4$ / $^1J(^{11}\text{B}^1\text{H}) = 80.5$ Hz; **2**: $-31.4/82$; **3**: $-35.2/82.4$, **4**: $-31.2/82.5$; **5**: $-34.9/82.1$; **6**: $-35.1/82.6$]. It should be noted that the boron atoms of the barium compound **4** are less shielded than those of the strontium compound **3** while the shielding is practically identical in both crown ether complexes. The largest difference in the shielding of the boron nuclei is found for the compound pair **1** and **2**.

Thus, the ^{11}B -NMR spectra of compounds **1–6** confirm the presence of BH_4^- ligands, and the δ values suggest that no free BH_4^- anions are present in the THF, diglyme, and DMSO solutions. However, because of the low-time resolution of NMR spectra no conclusion regarding the bonding of these groups to the metal centers is possible, and the fast rotation of the BH_4^- group to make all H atoms equivalent is a well-known and typical feature of almost all known tetrahydridoborates^[13,15].

The IR spectra offer a much better time resolution. Thus, the strontium compound **3** shows strong bands in the region for BH stretching vibrations at 2347 and 2247 cm^{-1} and a band of medium intensity at 2166 cm^{-1} . These data prohibit a definite conclusion as to the binding mode for the tetrahydridoborate group^[16]. However, the band at 2347 cm^{-1} is typical of a single terminal stretching mode and suggests a μ_3 -bonding of this ligand to the Sr center. The data definitely exclude the presence of free ionic BH_4^- which shows IR bands of different fine structure and intensities^[17,18].

The barium compound **4** exhibits five IR bands in the BH stretching region. This pattern is quite typical of μ_3 -bonded BH_4^- ligand as also observed for $\text{Ca}(\text{BH}_4)_2 \cdot 2$ glyme^[8]. Moreover, this pattern is also observed for the crown ether complexes **5** and **6**. The shift of 11 cm^{-1} to longer wavelength in **3** as compared with **4** would be compatible with an increase of the ionic character of the BH_4^- ligand in the barium crown ether complex. No definite conclusion as to the bonding of the BH_4^- unit can be drawn from the IR spectra of **1** and **2**. There are only three bands in the BH stretching region for **1** and six for **2**. This suggests that the structures of the two compounds might be different.

Group theory predicts three BH stretching vibrations of a μ_3 -bonded BH_4^- group with local C_{3v} symmetry. There should be one band of class A_1 for the terminal B–H bond

and two bands (class A_1 and E) for the BH_3 moiety. The latter should appear at lower wavenumber as a result of their bridging position which should give rise to weaker B–H bonding. However, this simple pattern is often not realized because of overlapping of the bands with those of the corresponding ^{10}B –H vibrations. These latter modes give less intense bands than those of the ^{11}B –H modes and may, therefore, often appear as shoulders only^[19]. In order to obtain better information on the bonding of the tetrahydridoborate group the crystal structures of the complexes reported here were determined.

Crystal and Molecular Structures

The THF complexes of $\text{Sr}(\text{BH}_4)_2$ and $\text{Ba}(\text{BH}_4)_2$ (**1** and **2**) crystallize in the monoclinic system. In spite of the fact that the β angles of the unit cells are very close to 90° suggesting the orthorhombic system, systematic extinctions were compatible only with the monoclinic space group $P2_1/n$. Both compounds are isomorphous, and there are only two formula units in the unit cell. Therefore, there is a crystallographically imposed symmetry for the molecule with the metal center coinciding with a crystallographic center of inversion. Figure 1 depicts a unit extending over three metal centers, and Figure 2 shows the arrangement of $\text{Sr}(\text{BH}_4)_2 \cdot 2$ THF in the unit cell. There are no separate $\text{M}(\text{BH}_4)_2 \cdot 2$ THF molecules in the crystal because this molecule is part of an infinite chain "polymer" with the chain oriented along the a axis of the unit cell. Figure 1 reveals the *trans* positions of the THF molecules (bond angle O–Sr–Oa = 180°). The Sr–B atom distance is 2.960 Å. More important are the contacts of the hydrogen atoms of the BH_4^- group with the metal center. As demonstrated by Figure 1 two of the four H atoms of each BH_4^- ligand are in contact with two adjacent metal centers while the remaining two form a bridge with one Sr atom only. The Sr–H atom distances lie in a rather narrow range [2.62 to $2.75(5)$ Å]. On the other hand, the B–H bond lengths range from $0.95(6)$ to $1.15(5)$ Å and appear to be rather short. The same holds for the barium compound **6** [1.03 – $1.13(5)$ Å]. However, in the case of $\text{Ba}(\text{BH}_4)_2 \cdot 2$ THF the boron-bonded H atom H4 is not

Figure 1. Combined space filling and ORTEP-type model of $\text{Sr}(\text{BH}_4)_2 \cdot 2$ THF (**1**); hydrogen atoms of the THF molecules are omitted

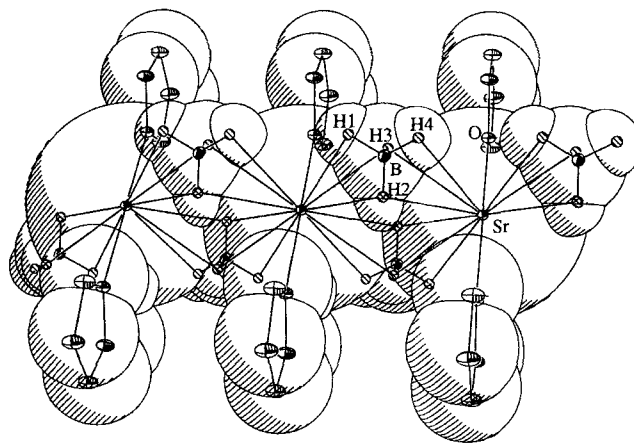
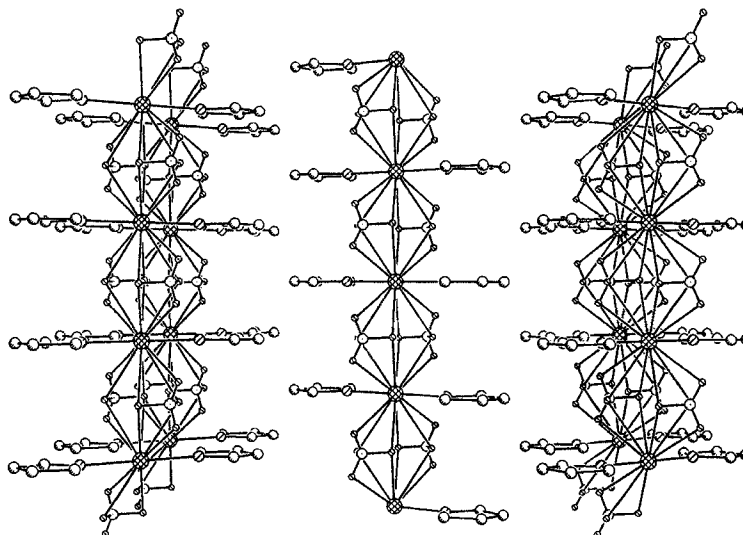


Figure 2. View along the *c* axis of compound **1** showing the arrangement of the chains in the unit cell

in close contact with the Ba center. These structural features suggest coordination number 14 or 12. But as the space filling model shows, this is simply due to the filling of the void between the neighboring Sr centers. This kind of M-BH₄ interaction is, as we surmise, a logical extension of the structural features observed for LiBH₄ · TMEDA^[11] and NaBH₄ · diglyme^[10].

The diglyme solvates **3** and **4** crystallize in the monoclinic space group *P*₂/*n* with *Z* = 2. Therefore, the molecules which build the unit cell must also possess a crystallographically imposed symmetry which is a center of inversion in which the metal atoms are placed. Figure 3 shows the molecular structure of one molecule of **3** (the barium compound **4** is isostructural and therefore needs not to be depicted). Structural parameters are given in Table 1. The most noticeable feature of the structure of **3** are the μ₃-bonded BH₄⁻ groups in the molecule. The positions of the

boron-bonded hydrogen atoms were revealed by difference Fourier synthesis even in the case of the barium compound **4**, and these were refined freely. However, because of the relatively large esd values no discussion as to bond lengths is justified except for the statement that there is practically no meaningful difference between the terminal and bridging B-H bonds.

The three Sr-O atom distances in **3** [2.728(3), 2.708(3), and 2.783(4) Å for atoms O1, O2, and O3, respectively] are not equal, the shortest bond is formed to the central atom O2. This pattern also holds for the barium compound **4** with Ba-O distances of 2.856(3), 2.853(3), and 2.895(4) Å, although the range is smaller than for **3**. The six oxygen atoms of the two diglyme molecules surrounding the Sr atom form a crown with distances to the best plane of -0.294, 0.331, and -0.288 Å. The Sr atom lies in this

Figure 3. ORTEP-type representation of the molecular structure of Sr(BH₄)₂ · 2 diglyme (**3**). Thermal ellipsoids represent a 25% probability; hydrogen atoms at the carbon atoms are omitted for clarity

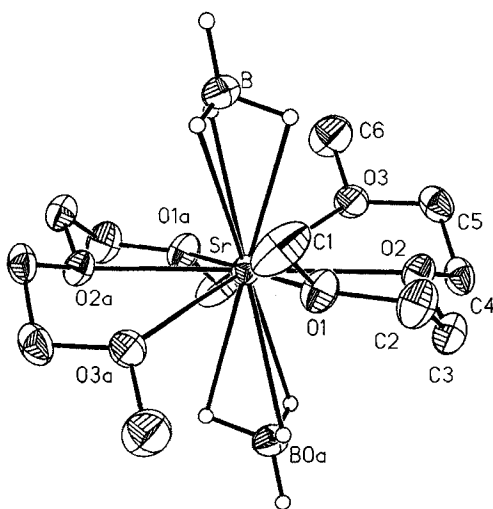


Table 1. Selected atom distances [Å], bond and torsional angles [°] for compounds **1**–**6**. Esd values are found in parentheses

	1	2	3	4	5	6
M-O1	2.544(3)	2.707(3)	2.728(3)	2.856(3)	2.714(3)	2.772(5)
M-O2			2.708(3)	2.853(3)		
M-O3			2.783(4)	2.895(4)		
M-B	2.960(6)	3.063(6)	2.916(7)	3.058(7)	2.833(6)	2.975(9)
M-H1		2.98(5)				
M-H2	2.71(5)	2.80(5)	2.64(4)	2.69(3)		2.66(4)
M-H3	2.75(5)	2.87(6)	2.77(4)	2.74(4)		
M-H4	2.91(5)		2.65(4)	2.95(5)	2.60(3)	
C1-O1	1.432(5)	1.430(6)	1.406(8)	1.430(8)	1.427(6)	1.443(5)
C2-O1			1.411(6)	1.414(8)	1.423(5)	1.415(7)
C3-O2			1.413(6)	1.422(7)		
C4-O2			1.419(7)	1.409(7)		
C5-O3			1.419(7)	1.413(6)		
C6-O3			1.411(9)	1.399(7)		
C2-C3	1.458(7)	1.436(9)	1.481(8)	1.486(9)	1.466(5)	1.478(11)
C4-C5			1.469(8)	1.477(7)		
O1-M-O2	180	180	58.6(1)	56.9(1)	60.2(1)	60.3(1)
O2-M-O3			58.6(1)	57.3(1)	60.2(1)	60.3(1)
O1-M-B			83.3(2)	84.6(1)	87.5(1)	86.8(1)
O1-M-B'			96.7(2)	95.4(1)	92.5(1)	93.2(1)
O2-M-B			96.0(2)	95.2(1)		
O3-M-B			83.3(2)	85.3(2)		
C-O1-C	106.8(4)	109.4(5)	112.0(4)	111.2(5)	108.2(4)	113.4(5)
C-O2-C			114.8(4)	114.4(4)		
C-O3-C			110.4(4)	111.6(4)		

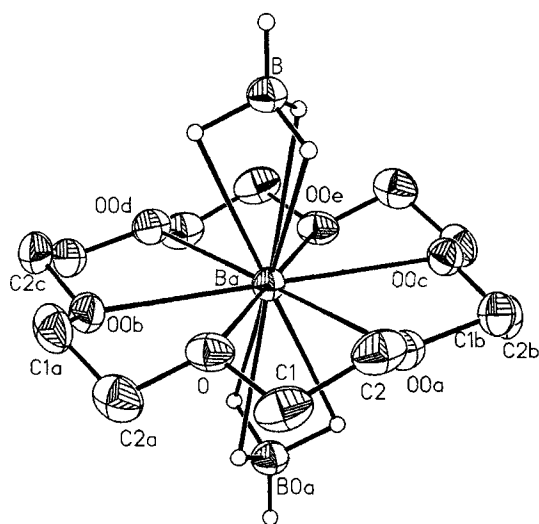
Torsion angles (°): **3**: C1-O1-C2-C3 -172.9, C4-O2-C3-C2 163.3, O1-C2-C3-O2 54.3, C3-O2-C4-C5 -166.6, C6-O3-C5-C4 179.2, O2-C4-C5-O3 -57.9.
4: C1-O1-C2-C3 -168.1, C4-O2-C3-C2 165.9, O1-C2-C3-O2 58.5, C3-O2-C4-C5 -170.4, C6-O3-C5-C4 177.5, O2-C4-C5-O3 -61.3.
5: C2a-O-C1-C2 178.3, O-C1-C2-O(a) 61.1, C1a-C2a-O-C1 -168.4.
6: C2a-O-C1-C2 179.3, O-C1-C2-O(a) -66.6, C1a-C2a-O-C1 170.7.

plane. Once again the oxygen atom O2 is exceptional since the sum of bond angles is 341.3° while those of O1 (353.6°) and O3 (352.1°) seem to approach sp^2 hybridization much closer than does that of O2. A similar situation is found for compound **4** with sums of bond angles of 336.8° for O2, 350.3° for O1, and 351.1° for O3. However, inspection of the C–O–C bond angles reveals angles close to tetrahedral at O2 both for **3** and **4**. We take this as evidence that the M–O interaction is highly polar and primarily indicates an ion-dipole interaction. On the other hand, the average Sr–O distances in **3** and the Ba–O distances in **4** are slightly shorter than the sum of their covalent radii (Sr–O: $2.15 + 0.66 = 2.81 \text{ \AA}$; Ba–O: $2.17 + 0.66 = 2.83 \text{ \AA}$). However, the sum of ionic radii for the alkaline earth metals and the covalent radius for oxygen (1.78 and 2.00 \AA) is much smaller than the observed distances. Consequently, these will not comply with Haaland's suggestion that bond lengths of metal center–ligand atom are larger by 0.1 to 0.3 \AA for a coordinative bond than for a normal covalent bond^[20].

Finally, one should note that the strontium-to-boron distance (2.918 \AA) is only 8.6% longer in **3** than the Sr–H atom distance and is shorter (2.978 \AA) than the sum of covalent radii for Sr and B atoms ($2.15 + 0.88 = 3.03 \text{ \AA}$), but in the case of **4** the observed Ba–B distance corresponds with the calculated value for the sum of the atomic radii ($2.17 + 0.88 = 3.05 \text{ \AA}$; found 3.05 \AA).

Like the compound pair **3** and **4**, the crown ether complexes **5** and **6** are also isomorphous and isostructural. They crystallize in the rhombohedral space group $R\bar{3}$ with $Z = 3$. Their metal atoms are fixed at a crystallographic inversion center and a threefold rotation axis. Figure 4 depicts the molecular structure of $\text{Ba}(\text{BH}_4)_2 \cdot 18\text{-crown-6}$ (**6**).

Figure 4. ORTEP-type representation of the molecular structure of $\text{Ba}(\text{BH}_4)_2 \cdot 18\text{-crown-6}$ (**6**) in the crystal. Thermal ellipsoids are drawn on a 25% probability level; hydrogen atoms at the carbon atoms are omitted for clarity



Once again, the μ_3 nature of the tetrahydridoborate group is readily noted. As is the case with **3** and **4** there is no significant difference in the B–H bond lengths between

terminal and bridging H atoms. The six oxygen atoms form a crown with the metal atom in its center and the oxygen atoms 0.417 \AA above and below the best plane for **5** (the value for **6** is 0.155 \AA). The sum of bond angles at the oxygen atoms is 342.4° in compound **5** and 346.2° in compound **6**. In addition, the M–O atom distances are slightly shorter than the sum of the covalent radii, while the M–B atom distances are definitively shorter than the sum of the covalent radii (3.03 \AA for **5**, 3.05 \AA for **6**).

Discussion

Tridentate tetrahydridoborate groups in mononuclear main-group metal tetrahydridoborates are still scarce. The few examples that are known are $\text{Ca}(\text{BH}_4)_2 \cdot 2 \text{ glyme}$ ^[18] and $\text{Ca}(\text{BH}_4)_2 \cdot 2 \text{ diglyme}$ ^[9]. The latter is not isostructural with **3** and **4** because the Ca center is coordinated by only five oxygen atoms. Moreover, there are two types of BH_4^- ligands, one is bonded in a μ_2 , the other in a μ_3 manner. If one considers the BH_4^- ligand as a pseudohalide, then the coordination number in all four compounds under consideration is 8. If one counts the close M–H contacts without M–B interactions, then the coordination number is 12 and rises to 14 if the boron atoms are included in the coordination shell. It is evident that the μ_3 bonding of BH_4^- allows the closest contact of this group with the metal centers to be realized. Thus, the bonding in the four compounds could be considered as resulting primarily from polar forces, and the structures would then represent contact ion pairs and ion-dipole interactions between the metal center and the ether ligands. However, the ^{11}B -NMR data as well as the IR spectra would not be fully in accord with this kind of model because there are clearly covalent contributions. This is also indicated by the behaviour of these compounds in DMSO. If the compounds were built from ion pairs, one would expect replacement of the BH_4^- ions by DMSO molecules, a behavior that is observed for diglyme solvates of Mg halides^[21].

Following Edelstein's reasoning^[22] for the estimation of the effective radius of a $\mu_3\text{-BH}_4^-$ group and taking into account the ionic radii of Sr and Ba atom in a coordination site of 8^[23] then we arrive at values of 1.66, 1.64, 1.57, and 1.56 \AA for **3** to **6**, respectively. The average value then is 1.61 \AA . This corresponds closely to a value of 1.67 \AA for $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{ThBH}_4$ ^[24] while Edelstein forecasted an effective radius of 1.36 \AA ^[22]. Typical values are 1.44 \AA for Cp_2UBH_4 ^[25], 1.36 \AA for $\text{Np}(\text{BH}_4)_4$ ^[26], or 1.37 \AA for $\text{Zr}(\text{BH}_4)_4$ ^[27]. The larger values found for **3–6** are, therefore, a strong indication of a high bond polarity. However, if we take into account the effective ionic radii for coordination number 12, as suggested by Shannon^[23], then we arrive at effective radii for the BH_4^- group in **3–6** with values of 1.39, 1.37, 1.48, and 1.45 \AA . These are much closer to Edelstein's estimates. This would also be in harmony with the expected increase in ionic character as one moves from tetrahydridoborates of beryllium to those of barium.

The crown ether complexes are to the best of our knowledge the first examples in which the crown features perfect D_{3d} symmetry with the metal atom being at the center of

the crown. All other crystal structures of complexes $\text{MX}_2 \cdot 18\text{-crown-6}$ have the composition $\text{BaX}_2 \cdot 18\text{-crown-6} \cdot \text{OH}_2$ ($\text{X} = \text{O}_2\text{PBu}_2^{[28]}$, $\text{NCS}^{[29]}$) in which the barium ion is placed outside of the mean plane of the crown ligand [e.g. 0.59 Å in $\text{Ba}(\text{NCS})_2 \cdot 18\text{-crown-6} \cdot \text{OH}_2$]. Although one might therefore expect some distortion of the crown ether in **5** and **6**, the differences in torsion angles (see Table 1) and bond angles are rather small (0.7° for the C–O–C bond angles) and compare well with those found for the free ligand^[30]. The differences reflect the somewhat shorter Sr–O bond length (2.713 Å) as compared to the Ba–O atom distance (2.772 Å). However, the metal–boron distance differs by 0.142 Å between the two crown complexes. This may be an indication of the increased polar character in **6**. Moreover, the high thermal stability of **5** and **6** demonstrates that hydrogen bonding^[28] is not a necessary prerequisite for thermal stability.

Experimental

In all experiments the Schlenk technique was used. All glassware was flame-dried and then filled with dinitrogen gas (99.999 purity). – NMR: Jeol 400 MHz for ^1H and ^{13}C , Bruker AC 200 for ^{11}B (internal TMS and external $\text{BF}_3 \cdot \text{OEt}_2$ as standards, positive sign at lower field than the standard). – IR: Nicolet 520 FT-IR instrument, range 200 to 4000 cm^{-1} . – X-ray structure determinations: Nicolet R3, Siemens P4, Mo- K_α radiation, graphite monochromator, SHELX Plus programs for structure solution and refinement (SHELX 93 for compounds **1** and **2**).

Strontium Bis(tetrahydridoborate)–Bis(tetrahydrofuran) (1): A suspension of $\text{Sr}(\text{OEt})_2$ (8.34 g, 32 mmol) in THF (80 ml) was heated to reflux with stirring. While stirring was continued a solution of diborane in THF (180 ml of a 1.9 M solution of BH_3 in THF) was added for a period of 5 h. During this time most of the

solid $\text{Sr}(\text{OEt})_2$ went into solution. Insoluble material was removed by centrifugation, and the $\text{Sr}(\text{BH}_4)_2$ solution was reduced at 10 Torr to a volume of 200 ml. This solution was then cooled to -25°C . After 14 h clear colorless needles had separated which were isolated by filtration. Yield: 7.36 g of $\text{Sr}(\text{BH}_4)_2 \cdot 2 \text{ THF}$ (88%), m.p. $>360^\circ\text{C}$. – NMR: $\delta^1\text{H}$ ($[\text{D}_8]\text{THF}$): 0.2 [BH, q, $^1J(^{11}\text{B}^1\text{H}) = 79.5 \text{ Hz}$], 1.6 (m), 3.6 (m). – $\delta^{13}\text{C}$: 25.1, 66.9. – $\delta^{11}\text{B}$ (THF): -36.4 [quint, $^1J(^{11}\text{B}^1\text{H}) = 80.5 \text{ Hz}$]. – IR (Nujol, cm^{-1}): $\tilde{\nu} = 2371.8$ (m), 2313.2 (st). – $\text{C}_8\text{H}_{24}\text{B}_2\text{O}_2\text{Sr}$ (261.5): calcd. C 36.74, H 9.25, B 8.27, Sr 33.50; found C 38.51, H 8.90, B 7.91, Sr 32.85.

Barium Bis(tetrahydridoborate)–Bis(tetrahydrofuran) (2): To a boiling suspension of $\text{Ba}(\text{OEt})_2$ (10.41 g, 45 mmol) in 100 ml of THF was added within a period of 6 h a diborane solution (195 ml of a 1.9 M BH_3 solution in THF). During this time the insoluble ethoxide reacted to afford the insoluble $\text{Ba}(\text{BH}_4)_2$. All volatile components were then removed in vacuo leaving behind $\text{Ba}(\text{BH}_4)_2 \cdot n \text{ THF}$ (n between 0 and 2, depending on the time and reduced pressure applied). Yield: not determined, m.p. $>360^\circ\text{C}$. – NMR: $\delta^1\text{H}$ ($[\text{D}_8]\text{THF}$): -0.3 [BH, q, $^1J(^{11}\text{B}^1\text{H}) = 83 \text{ Hz}$]; 1.5 (m), 3.5 (m). – $\delta^{13}\text{C}$: 25.3, 66.8. – $\delta^{11}\text{B}$ (THF): -31.4 [quint, $^1J(^{11}\text{B}^1\text{H}) = 82 \text{ Hz}$]. – IR (nujol, cm^{-1}): $\tilde{\nu} = 2353.5$ (st), 2308.2 (st), 2241.2 (st), 2215.9 (sh), 2186.4 (m), 2169.4 (m). – Analysis, Ba:B:H: calcd. 1:2:8; found 1:1.98:7.94.

Strontium Bis(tetrahydridoborate)–Bis(diglyme) (3): $\text{Sr}(\text{BH}_4)_2 \cdot 2 \text{ THF}$ (**1**) (2.52 g, 0.5 mmol) was dissolved in diglyme (50 ml). Small amounts of insoluble material were removed by centrifugation. The solution was then kept at -25°C for 12 h and the rhombohedrally shaped crystals that had formed during this period were isolated by filtration. Yield 2.43 g of **3** (66%), m.p. $88\text{--}90^\circ\text{C}$. – NMR: $\delta^1\text{H}$ (DMSO): -0.3 [BH, q, $^1J(^{11}\text{B}^1\text{H}) = 81.6 \text{ Hz}$]; 3.1 (s, CH_3O), 3.3 (m, MeOCH_2), 3.4 (m, $\text{CH}_2\text{CH}_2\text{O}$). – $\delta^{13}\text{C}$: 58.0, 69.6, 71.3. – $\delta^{11}\text{B}$ (diglyme): -35.2 , [quint, $^1J(^{11}\text{B}^1\text{H}) = 82.4 \text{ Hz}$]. – IR (nujol, cm^{-1}): $\tilde{\nu} = 2346.9$ (st), 2247.4 (st), 2166.9 (m). – $\text{C}_{12}\text{H}_{36}\text{B}_2\text{O}_6\text{Sr}$ (385.7): calcd. C 37.37, H 9.41, B 5.61, Sr 22.72; found C 37.13, H 8.91, B 5.75, Sr 22.34.

Table 2. Summary of crystallographic details, data collection and refinement

	1	2	3	4	5	6
Formula	$\text{C}_8\text{H}_{24}\text{B}_2\text{O}_2\text{Sr}$	$\text{C}_8\text{H}_{24}\text{B}_2\text{O}_2\text{Ba}$	$\text{C}_{12}\text{H}_{36}\text{B}_2\text{O}_6\text{Sr}$	$\text{C}_{12}\text{H}_{36}\text{B}_2\text{O}_6\text{Ba}$	$\text{C}_{12}\text{H}_{32}\text{B}_2\text{O}_6\text{Sr}$	$\text{C}_{12}\text{H}_{32}\text{B}_2\text{O}_6$
Form. wght.	261.51	311.28	385.6	435.3	381.6	431.3
Cryst.size(mm)	.12x.2x.25	.25x.4x.5	.28x.35x.4	.2x.36x.5	.3x.3x.35	.3x.3x.3
Cryst. system	monoclinic	monoclinic	monoclinic	monoclinic	rhomboedric	rhomboedric
Space group	$\text{P}2_1/n$	$\text{P}2_1/n$	$\text{P}2_1/n$	$\text{P}2_1/n$	R-3	R-3
a [Å]	4.405(1)	4.613(1)	8.799(2)	8.839(4)	11.850(3)	11.951(10)
b [Å]	7.997(2)	8.091(2)	9.789(2)	9.879(3)	11.850(3)	11.951(10)
c [Å]	18.826(5)	19.056(3)	12.247(3)	12.490(6)	11.969(4)	12.056(11)
α (°)	90	90	90	90	90	90
β (°)	90.00(2)	90.04(1)	102.56(2)	103.54(4)	90	90
γ (°)	90	90	90	90	120	120
V (Å ³)	663.2(3)	711.2(3)	1029.6(4)	1060.3(8)	1457.6(8)	1491(2)
Z	2	2	2	2	3	3
d_c (Mg/m ³)	1.310	1.453	1.244	1.364	1.304	1.441
μ (mm ⁻¹)	4.037	2.766	2.555	1.888	2.707	2.013
F(000)	272	308	408	444	600	654
T(K)	193	193	293	298	298	298
2θ (°)	4 - 52	4 - 53	3 - 50	3 - 48	3 - 48	2 - 48
Refl.collected	1764	2304	2046	1918	1596	564
Refl.independent	1303	1473	1835	1677	516	1652
R_{int}	0.0385	0.0715	0.0288	0.0369	0.068	0.080
max/min transm.	.455/.300	.31/.234	.70/.578	.549/.450	.681/.593	.697/.554
scan range	1.6	1.85	0.8	0.8	1.5	0.8
speed (°/min)	3.7 - 60	3 - 60	1.8 - 29	2 - 29	2 - 29	2 - 29
R1 (4 σ (F))	0.0318	0.0286	0.0422	0.0271	0.030	0.0247
R1 (all data)	0.0707	0.0417	0.0729	0.0362	0.031	0.0247
wR2 (all data)	0.889*	0.0792*				
GOOF	1.025*	1.117*	1.21	1.01	1.01	1.74

* Data for calculation on F^2 basis (SHELX 93).

Barium Bis(tetrahydridoborate)–Bis(diglyme) (4): A suspension of $\text{Ba}(\text{BH}_4)_2 \cdot n \text{ THF}$ in 100 ml of diglyme was stirred for 12 h. Then the solid material was removed by centrifugation. The flask containing the saturated $\text{Ba}(\text{BH}_4)_2$ solution in diglyme was then connected with another flask which contained pentane. During a period of 3 weeks crystals (up to 0.5 mm) grew in the diglyme solution. These were isolated by filtration. Yield: 0.19 g of **4** (37%), m.p. 120°C (dec.). – NMR: $\delta^1\text{H}$ (DMSO): -0.3 [BH, q, $^1J(^{11}\text{B}^1\text{H}) = 81.3$ Hz], 3.1 (s), 3.3 (m), 3.4 (m). – $\delta^{13}\text{C}$ (DMSO): 58.2, 70.0, 71.2. – $\delta^{11}\text{B}$ (diglyme) = -31.2 [quint, $^1J(^{11}\text{B}^1\text{H}) = 82.5$ Hz]. – IR (nujol, cm^{-1}): $\tilde{\nu} = 2339.7$ (st), 2273.8 (m), 2232.6 (st), 2203.5 (m), 2153.3 (w). – $\text{C}_{12}\text{H}_{36}\text{B}_2\text{BaO}_6$ (435.4): calcd. C 33.11, H 8.33, B 4.96, Ba 31.54; found C 28.63, H 6.83, B 4.85, Ba 30.91 (C:H = 12:34.3).

Strontium Bis(tetrahydridoborate)–18-Crown-6 (5): A solution of 18-crown-6 (0.281 g, 1.2 mmol) in THF (20 ml) was added with stirring to a solution of $\text{Sr}(\text{BH}_4)_2 \cdot 2 \text{ THF}$ (**1**) (0.330 g, 1.2 mmol) in THF (30 ml). A precipitate formed almost immediately. It was isolated and dried in vacuo. Yield: 0.472 g of **5**, (93%), m.p. $>360^\circ\text{C}$. Single crystals were obtained by dissolving **5** in DMSO to form a saturated solution, then diethyl ether vapor was allowed to diffuse into the latter during a period of 6 d. Clear crystals of **5** had then formed. – NMR: $\delta^1\text{H}$ (DMSO): -0.3 [BH, q, $^1J(^{11}\text{B}^1\text{H}) = 81.7$ Hz], 3.5 (s). – $\delta^{13}\text{C}$ (DMSO): 69.7. – $\delta^{11}\text{B}$ (DMSO) = -34.9 [quint, $^1J(^{11}\text{B}^1\text{H}) = 82.1$ Hz]. – IR (nujol, cm^{-1}): $\tilde{\nu} = 2351.3$ (st), 2297.4 (m), 2254.2 (st), 2220.8 (st), 2163.5 (m). – $\text{C}_{12}\text{H}_{32}\text{B}_2\text{O}_6\text{Sr}$ (381.6): calcd. C 37.77, H 8.45, B 5.67; found C 38.47, H 8.07, B 5.51.

Barium Bis(tetrahydridoborate)–18-Crown-6 (6): 100 ml of THF was saturated with $\text{Ba}(\text{BH}_4)_2 \cdot n \text{ THF}$. Then a solution of 18-crown-6 in THF was added dropwise with stirring until no more precipitate formed. This precipitate was isolated by filtration and dried in vacuo. Yield: 0.578 g of **6** (92%), m.p. $>340^\circ\text{C}$ (dec.). Single crystals were obtained by letting THF vapor diffuse into a saturated solution of **6** in DMSO. Cube-shaped crystals separated within 7 d. – NMR (DMSO): $\delta^1\text{H}$: -0.2 [BH, q, $^1J(^{11}\text{B}^1\text{H}) = 81.4$ Hz], 3.5 (s). – $\delta^{13}\text{C}$ (DMSO): 69.6. – $\delta^{11}\text{B} = -35.1$ [quint, $^1J(^{11}\text{B}^1\text{H}) = 81.6$ Hz]. – IR (nujol, cm^{-1}): $\tilde{\nu} = 2339.8$ (st), 2285.1 (m), 2237.0 (st), 2205.6 (st), 2154.2 (m). – $\text{C}_{12}\text{H}_{32}\text{B}_2\text{BaO}_6$ (431.4): calcd. C 33.41, H 7.48, B 5.01; found C 33.52, H 6.70, B 4.92.

X-Ray Structure Determinations: Samples were sealed in glass capillaries under argon and protected against hydrolysis with perfluoroether oil (compounds **1** and **2**). In this case the measurements were conducted at -100°C by using the Siemens LT device. Lorentz and polarization correction as well as empirical absorption corrections (psi scans) were applied, but no correction was made for anomalous dispersion. The structures were solved by Patterson methods and completed by difference Fourier synthesis. All hydrogen atoms could be located, but only those at the boron atoms were refined freely with fixed, adapted isotropic U_i values while all other hydrogen atoms were put into calculated positions and included in

the final refinement as a riding model with isotropic U_i . More details are summarized in Table 2^[31].

- * Dedicated to Prof. Dr. Nils Wiberg on the occasion of his 60th birthday.
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