Preparation of Large Cation Salts Containing Complex Tetrahydroborate Anions of Aluminum, Beryllium, and Uranium, and Determination of the Nature of the Hydrogen Bridging in These Salts

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Abstract: Tetramethylammonium salts of $Al(BH_4)_4^-$ and $Be(BH_4)_3^-$ have been prepared in near quantitative yield from the solvent-free reactions of $(CH_3)_4NBH_4$ with the corresponding metal tetrahydroborates. Preparation of $(CH_3)_4NAl(BD_4)_3BH_4$ and subsequent Raman study have indicated that the tetrakistetrahydroboroalanate(1−) anion may contain a "tridentate" tetrahydroborate group, suggesting a C_{3v} structure for the anion. A Raman spectrum of $(CH_3)_4NBe(BH_4)_3$ shows marked similarity to the spectrum of $Al(BH_4)_3$, indicating a likely D_{3h} structure for this anion. Cesium salts were prepared, but yield is lower, indicating the need for a larger cation. From the reaction of uranium(IV) tetrahydroborate with $(C_2H_5)_4NBH_4$ in diglyme solution, the product $((C_2H_5)_4N)_2U(BH_4)_6$ has been obtained free of solvent and in 93.9% yield. An approximately octahedral arrangement of tetrahydroborate groups is suggested by analogy with the $U(BH_4)_4$ polymeric structure. The reactions of $Al(BH_4)_3$, $Be(BH_4)_2$, and $Al(CH_3)_3$ with tetra-*n*-butylammonium iodide result in precisely 1:1 stoichiometric products. In the case of $Be(BH_4)_2$, a dramatic change in the B–H stretching region of the spectrum is noted upon formation of the iodide complex.

Structural studies of the volatile tetrahydroborates have produced some interesting results regarding the nature of the hydrogen bridging involved in the bonding of the tetrahydroborate groups to the central metal atom. Raman spectra[1] suggest that in $Al(BH_4)_3$ the BH_4^- groups in this molecule are attached by bidentate hydrogen bridging. An electron diffraction study[2] of $Be(BH_4)_2$ shows a bridging system which indicates a coordination number of four with respect to the beryllium atom. An x-ray structural determination[3] of crystalline $Be(BH_4)_2$ showed that the compound is a helical polymer in which there are six hydrogen atoms in approximately trigonal prismatic arrangement around the beryllium atom, similar to the arrangement found in $Al(BH_4)_3$. Raman and infrared studies[4] of solid $Be(BH_4)_2$, as well as the above x-ray work, suggest some ionic BH_4^- character in the solid. A single-crystal neutron diffraction study[5] of $U(BH_4)_4$ also shows a helical polymeric structure in which the uranium atom is 14 coordinate with respect to the hydrogen atoms. In this compound both tridentate and bidentate bridging is involved. Additional studies on $Hf(BH_4)_4$[6] and other neutral metal tetrahydroborates[7] deal with the nature of the hydrogen bridging in these compounds.

The structural studies on $Be(BH_4)_2$ and $U(BH_4)_4$ suggest that both of these compounds might react with additional tetrahydroborate ions to form complex tetrahydroborate anions. Complex tetrahydroborate anions of aluminum[8,9] and beryllium[10] have been reported. The beryllium compounds, however, were not isolated from ether solution.

We have prepared several new complex anions containing tetrahydroborate groups in order to ascertain similarities or differences in the nature of the bridging involved in the attachment of the BH_4^- group to the central metal atom in the anion compared to that in the neutral tetrahydroborate compounds. The method of preparation involved bringing together a large cation tetrahydroborate or halide salt and the volatile tetrahydroborate or trimethylaluminum. The volatile component was always in excess and the excess was removed upon completion of the reaction. In this manner, the following compounds were prepared: $(CH_3)_4NAl(BH_4)_4$, $(CH_3)_4NAl(BD_4)_3BH_4$, $(CH_3)_4NBe(BH_4)_3$, $((C_2H_5)_4N)_2U(BH_4)_6$, $(n\text{-}C_4H_9)_4NAl(BH_4)_3I$, $(n\text{-}C_4H_9)_4NBe(BH_4)_2I$, and $(n\text{-}C_4H_9)_4NAl(CH_3)_3I$. In all cases the yield of product was very nearly stoichiometric. We believe that all but the first of these compounds are being reported here for the first time. The nature of the hydrogen bridging in these compounds is determined by analysis of the observed Raman active terminal and bridge boron–hydrogen stretching vibrations.

Attempts to substitute $CsBH_4$ for the tetraalkylammonium tetrahydroborates resulted in only partial uptake of the volatile component. This is probably due to the relatively smaller size of the cesium ion.

Experimental Section

Materials. The nature of the volatile components in these reactions necessitated the use of well-known high-vacuum techniques. Aluminum, beryllium, and uranium tetrahydroborates were prepared by methods described previously.[11,12] Tetraalkylammonium tetrahydroborates and halides were commercial products. Raman spectra were recorded on a Cary 82 instrument using an argon laser (Coherent Radiation Labs) with a 5145 Å excitation of approximately 200 mW.

$(CH_3)_4NAl(BH_4)_4$. The preparation of this compound was carried out in a sealed tube having several side arms to provide subsequent access to the vacuum line by means of a standard "tube opener". If additional reaction time was required the reactants were returned to the tube and the side arm sealed off. The process was repeated until no further uptake of volatile component was observed. In a typical preparation the reaction tube was attached to the vacuum line and was "seasoned" with $Al(BH_4)_3$ by allowing the $Al(BH_4)_3$ to stand in the sealed tube for a few hours. The $Al(BH_4)_3$ was removed and the tube was then filled with dry nitrogen to atmospheric pressure. The tip of a special wide bore solid addition side arm was broken off and 0.4475 mmol of $(CH_3)_4NBH_4$ was added to the reaction tube. This side arm was then saled off, the tube evacuated, and 1.739 mmol of $Al(BH_4)_3$ (measured as a gas) condensed into the tube at −196 °C. The reaction tube was then sealed off and allowed to warm up to room temperature. The reaction was 60% complete after 20 h and 100% after 48 h. The volatile products obtained after the completed reaction consisted of $Al(BH_4)_3$ (1.295 mmol) and traces of H_2 and B_2H_6. The molar ratio $Al(BH_4)_3/(CH_3)_4NBH_4$ is 0.992. The white solid product was stable toward loss of volatile components to at least 100 °C. The solid was not pyrophoric, but reaction with water was extremely vigorous. The solid was insoluble in diethyl ether and hydrocarbon solvents. The reaction of the solid with HCl gas produced H_2 and B_2H_6 in the ratio 2:1 and suggests the equation

$$(CH_3)_4NAl(BH_4)_4 + 4HCl = 4H_2 + 2B_2H_6 + (CH_3)_4NAlCl_4$$

Table I. Reactions of Volatile Metal Tetrahydroborates with Large Cation Salts

$(CH_3)_4NBH_4 + Al(BH_4)_3 \xrightarrow[25\ °C]{48\ h} (CH_3)_4NAl(BH_4)_4$	(99.2%)
$(CH_3)_4NBH_4 + Al(BD_4)_3 \xrightarrow[25\ °C]{8\ days} (CH_3)_4NAl(BD_4)_3BH_4$	(74.5%)
$(CH_3)_4NBH_4 + Be(BH_4)_2 \xrightarrow[25\ °C]{20\ h} (CH_3)_4NBe(BH_4)_3$	(99.4%)
$2(C_2H_5)_4NBH_4 + U(BH_4)_4 \xrightarrow[diglyme\ 25\ °C]{48\ h} ((C_2H_5)_4N)_2U(BH_4)_6$	(93.9%)
$(n\text{-}C_4H_9)_4NI + Al(BH_4)_3 \xrightarrow[25\ °C]{24\ h} (n\text{-}C_4H_9)_4NAl(BH_4)_3I$	(98%)
$(n\text{-}C_4H_9)_4NI + Be(BH_4)_2 \xrightarrow[55\ °C]{24\ h} (n\text{-}C_4H_9)_4NBe(BH_4)_2I$	(99.8%)
$(n\text{-}C_4H_9)_4NI + Al(CH_3)_3 \xrightarrow[25\ °C]{24\ h} (n\text{-}C_4H_9)_4NAl(CH_3)_3I$	(99.9%)

$(CH_3)_4NAl(BD_4)_3BH_4$. Aluminum tetradeuterioborate was prepared from $NaBD_4$ (MS&D Isotopes) and anhydrous $AlCl_3$. This was then brought together with $(CH_3)_4NBH_4$ in the same manner as described above. The reaction is much slower than that of $Al(BH_4)_3$. $Al(BD_4)_3$ (4.374 mmol) and $(CH_3)_4NBH_4$ (3.3269 mmol) were allowed to react for 8 days at 25 °C. Volatile products recovered were $Al(BD_4)_3$ (1.894 mmol) and trace of B_2D_6, giving the ratio $Al(BD_4)_3/(CH_3)_4NBH_4 = 0.745$.

$(CH_3)_4NBe(BH_4)_3$. The low volatility of $Be(BH_4)_2$ necessitated the use of a gravimetric rather than volumetric method in its quantitative determination. The method involved the sublimation of $Be(BH_4)_2$ from its U-tube storage vessel into a weighed U-tube which could be sealed off. The weight of $Be(BH_4)_2$ was then determined by difference. This quantity of $Be(BH_4)_2$ was added to a reaction tube similar to that used in the previous preparations but modified to allow for a "pump through" transfer of $Be(BH_4)_2$. This tube contained an amount of $(CH_3)_4NBH_4$ which ensured that $Be(BH_4)_2$ was in excess. In a typical preparation $(CH_3)_4NBH_4$ (8.8292 mmol) and $Be(BH_4)_2$ (13.7512 mmol) were introduced into the reaction tube which was sealed off from the vacuum line at −196 °C and allowed to warm to room temperature. After about 15 min at room temperature a clear, viscous liquid appeared. After several hours the reaction mixture was completely liquid, and after 20 h the reaction was essentially complete. The reaction tube was attached to the vacuum line through the "tube opener" and the excess $Be(BH_4)_2$ was removed by continuous pumping while the reaction tube was kept at approximately 80 °C. The quantity of $Be(BH_4)_2$ recovered amounted to 5.228 mmol. The ratio of reactants consumed $Be(BH_4)_2/(CH_3)_4NBH_4$ is 1.006. The product was a white, finely divided solid, and was not pyrophoric.

$((C_2H_5)_4N)_2U(BH_4)_6$. The low volatility of $U(BH_4)_4$ and its decomposition in the presence of mercury vapor required additional modification of procedures used in the synthesis of the beryllium compound. Even with modifications the solvent-free reaction was not successful because it was impossible to remove the excess $U(BH_4)_4$ from the reaction mixture quantitatively at temperatures below the decomposition temperature of the $U(BH_4)_4$. It is of interest to point out, however, that the solvent-free reaction undoubtedly occurs since a dark green liquid phase appeared when the two solids were brought together. We subsequently established the stoichiometry and a successful preparation might result by using stoichiometric amounts of reactants.

In the course of our work we observed that $U(BH_4)_4$ dissolved in diglyme to produce a dark green solution. It was also found to be soluble in diethyl ether to a lesser extent. The reaction was therefore run in diglyme. Excess $U(BH_4)_4$ in this case was removed by filtration. The product is insoluble in diglyme. The stoichiometry was established by the difference in the weight of product and the initial weight of $(C_2H_5)_4NBH_4$. Using high-vacuum, mercury-free procedures, the reactants $(C_2H_5)_4NBH_4$ (9.9751 mmol) and $U(BH_4)_4$ (5.9936 mmol) were brought together in the reaction tube with 10 mL of diglyme. The mixture was stirred magnetically at 25 °C. The dark green color of the reaction mixture became distinctly lighter within a few hours. After 48 h the reaction tube was attached to the vacuum line and the reaction mixture filtered through a filter disk which was a part of the reaction tube. The solid product was washed with diethyl ether until the filtrate was colorless. The solid was grayish-white in appearance. The weight increase found was 1.3954 g, which is 93.9% of the increase in weight calculated for a compound having a ratio of 1:2 for the reactants $U(BH_4)_4/(C_2H_5)_4NBH_4$. A small amount of solid product came through the filter disk and could account for the failure to get perfect agreement with the 1:2 stoichiometry. The product obtained was not pyrophoric but rapidly changes to a bright yellow color upon contact with air.

In the following reactions tetra-*n*-butylammonium iodide was used as the nonvolatile reactant in place of the tetrahydroborate salts in the previous reactions. The procedure used was similar in each case to that previously described and the composition of the product was established on the basis of the uptake of the volatile component.

$(n\text{-}C_4H_9)_4NAl(BH_4)_3I$. The reaction mixture consisted of $Al(BH_4)_3$ (4.183 mmol) and $(n\text{-}C_4H_9)_4NI$ (0.8976 mmol). The mixture became a clear liquid as soon as the reaction tube warmed to room temperature. After 24 h at 25 °C the tube was opened and the excess $Al(BH_4)_3$ removed by pumping while the product was gradually heated to 60 °C. During this period the contents of the reaction tube remained liquid. The amount of $Al(BH_4)_3$ recovered was 3.302 mmol and the molar ratio of reactants $Al(BH_4)_3/(n\text{-}C_4H_9)_4NI$ was $0.881/0.8976 = 0.98$. The product was a white, waxy solid having a melting point of 48-50 °C.

$(n\text{-}C_4H_9)_4NBe(BH_4)_2I$. The reactants $(n\text{-}C_4H_9)_4NI$ (3.7060 mmol) and $Be(BH_4)_2$ (6.8886 mmol) were allowed to react for a period of 24 h. A liquid phase was present as soon as the tube had warmed to room temperature, but to obtain a completely liquid reaction mixture the tube had to be warmed to about 55 °C. Once the reaction mixture was completely liquid no solid phase was present, even at room temperature. After 24 h the tube was opened and the excess $Be(BH_4)_2$ was removed by pumping and heating the tube gradually to 100 °C. The $Be(BH_4)_2$ removed amounted to 3.174 mmol giving the ratio $Be(BH_4)_2/(n\text{-}C_4H_9)_4NI = 3.715/3.706 = 1.002$. This product was a white, wavy solid melting at 62-64 °C.

$(n\text{-}C_4H_9)_4NAl(CH_3)_3I$. Trimethylaluminum (6.982 mmol) and $(n\text{-}C_4H_9)_4NI$ (1.219 mmol) were introduced into the reaction tube. The mixture was entirely liquid once it had warmed to room temperature. While the mixture remained in the tube for 5 days at room temperature, the reaction was probably complete within 24 h. The tube was opened and excess $Al(CH_3)_3$ (5.764 mmol) recovered, giving the ratio $Al(CH_3)_3/(n\text{-}C_4H_9)_4NI = 1.218/1.219 = 0.999$. This product melted at about 43-45 °C and had the same white, waxy appearance of the two previous compounds.

The reactions, conditions, and respective yields are summarized in Table I. Raman spectra were recorded for solid products in sealed glass capillaries. Observed frequencies of boron hydrogen terminal and bridge stretching vibrations are reported in Table II.

Discussion

In considering boron-hydrogen stretching vibrations within a metal tetrahydroborate complex, information as to the

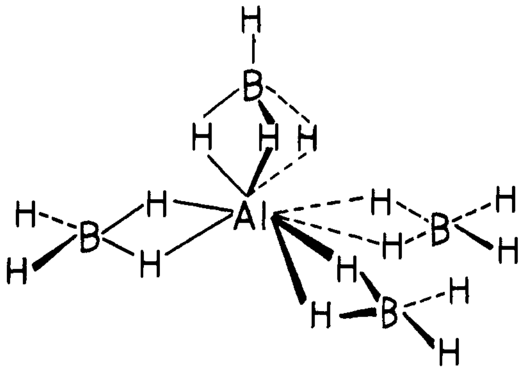

Figure 1. Proposed structure of $Al(BH_4)_4^-$.

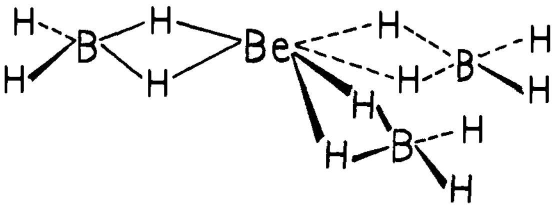

Figure 2. Proposed structure of $Be(BH_4)_3^-$.

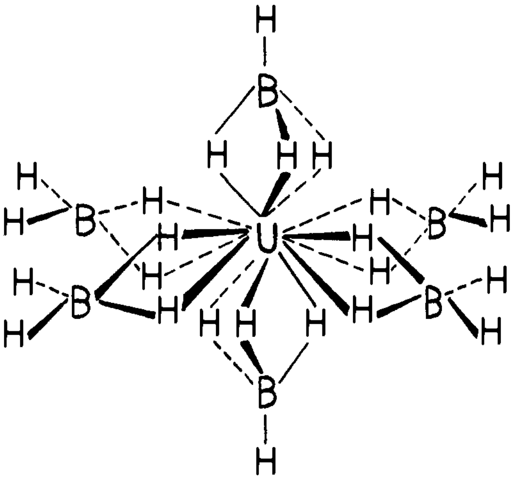

Figure 3. A possible structure of $U(BH_4)_6^{2-}$.

Table II. Frequencies of Observed Raman Active Boron-Hydrogen Stretching Vibrations

$(CH_3)_4NAl(BH_4)_4$	ν B-H$_t$:	2475 (s), 2423 cm^{-1} (vs)
	ν B-H$_b$:	2210 (s), 2195 cm^{-1} (s)
$(CH_3)_4NAl(BD_4)_3BH_4$	ν B-H$_t$:	2445 cm^{-1} (vs)
	ν B-H$_b$:	1885 (s), 1868 cm^{-1} (vs)
	ν B-D$_t$:	1825 (s), 1781 cm^{-1} (vs)
	ν B-D$_b$:	1637 (shoulder), 1599 cm^{-1} (vs, broad)
$(CH_3)_4NBe(BH_4)_3$	ν B-H$_t$:	2452 (s), 2416 cm^{-1} (vs)
	ν B-H$_b$:	2215 cm^{-1} (vs)
$(n\text{-}C_4H_9)_4NAl(BH_4)_3I$	ν B-H$_t$:	2480 (s), 2430 cm^{-1} (s)
	ν B-H$_b$:	2200 cm^{-1} (m, broad)
$(n\text{-}C_4H_9)_4NBe(BH_4)_2I$	ν B-H$_t$:	2458 (s), 2410 cm^{-1} (vs)
	ν B-H$_b$:	2200 (s), 2173 cm^{-1} (vs)

"denticity" of the BH_4^- group may be obtained. If the assumption is made that interaction between individual tetrahydroborate groups is negligible,[7] a simplified vibrational analysis becomes possible. This assumption appears to be justified with metal atoms as small as beryllium, which will be discussed later.

Group theoretical treatment of the simple MBH_4 unit for the "bidentate" (C_{2v}) and "tridentate" (C_{3v}) configurations results in a predicted number of Raman active boron-hydrogen terminal and bridge stretching vibrations which can be compared with experimental data. For the rather uncommon monodentate (C_{3v}) MBH_4 unit, two bands (A_1 + E) are predicted for ν B-H$_t$ and one (A_1) for ν B-H$_b$. In the bidentate case (C_{2v}), two bands ($A_1 + B_1$) are predicted for ν B-H$_t$ and two ($A_1 + B_2$) for ν B-H$_b$. Analysis of the tridentate MBH_4 unit (C_{3v}) results in prediction of one band (A_1) for ν B-H$_t$ and two bands (A_1 + E) for ν B-H$_b$. Vibrations of the type ν B-H$_t$ are commonly observed in the range 2400-2500 cm^{-1}, while ν B-H$_b$ is usually found at 2100-2200 cm^{-1}.[1,6,7] The symmetric stretching vibration in ionic BH_4^- is reported to occur at 2264 cm^{-1}.[13]

The Raman spectrum of $(CH_3)_4NAl(BH_4)_4$ shows two bands in the B-H$_t$ region and two in the B-H$_b$ region of the spectrum. A similar result has been reported in the infrared spectrum of the tetraethylammonium salt.[8] These results are consistent with a structure containing the "bidentate" MBH_4 unit. Two possible structures may be considered for the $Al(BH_4)_4^-$ anion with this geometry maintained throughout, i.e., a D_{4h} structure which preserves the planarity of the original $Al(BH_4)_3$ moiety, or an asymmetric C_{2v} model with tetrahedral arrangement of boron atoms about aluminum. Neither of these structures was found to be particularly satisfying, as the D_{4h} structure requires an unlikely square planar arrangement about aluminum, and the C_{2v} model is quite asymmetric, a complete analysis of which predicts Raman activity for all 57 possible vibrational modes. Such complexity is not observed in the spectrum.

These facts led us to consider the possibility of two types of Al-BH_4 bonding within the complex. If, for example, ionic BH_4^- reacts with $Al(BH_4)_3$ to produce a "tridentate", or five-centered bonding unit, it is conceivable that the single band due to ν B-H$_t$ predicted for this geometry would be masked by the doublet due to the three "bidentate" tetrahydroborate groups. A tetrahedral arrangement of boron atoms around aluminum seems most likely in light of the many known tetrahedral aluminum anions. Combination of one "tridentate" tetrahydroborate group with three "bidentate" would allow such an arrangement with a symmetric distribution of bridging hydrogen atoms, resulting in a structure of C_{3v} symmetry (Figure 1).

To examine the possibility of a "tridentate" tetrahydroborate group on aluminum, $(CH_3)_4NAl(BD_4)_3BH_4$ was prepared and its Raman spectrum recorded. Bands due to B-D vibrations are shifted to lower frequencies by approximately 600 cm^{-1} with respect to ν B-H, thus allowing clear examination of the single Al-BH_4 unit alone. This spectrum is striking in that it shows a very strong *single* band at 2445 cm^{-1}, which is the result predicted for B-H$_t$ stretching in the "tridentate" MBH_4 configuration. This observation is hence consistent with the presence of a "tridentate" tetrahydroborate group, and with the C_{3v} structure. The possibility of hydrogen-deuterium exchange has been examined but is considered unlikely in that $Al(BD_4)_3$ removed from the reaction mixture was pure, a fact inconsistent with any exchange mechanism that would require hydrogen in the volatile species. Clearly, a crystal structure determination of the substance would be most desirable at this point, but a suitable solvent from which crystals could be obtained has not been found. The diethyl ether complex of the lithium salt[10] might serve this purpose, however.

Beryllium tetrahydroborate, as mentioned previously, is a polymeric solid with an arrangement of BH_4^- groups about the metal atom which is similar to that encountered in $Al(BH_4)_3$. Formation of $Be(BH_4)_3^-$ provides three tetrahydroborate groups for each beryllium atom, so it would seem that the polymeric arrangement is no longer necessary, and molecular units could be formed having the same geometry about the metal center as is found in the polymer. Thus, one would suspect a similarity in the structures of $Be(BH_4)_3^-$ and $Al(BH_4)_3$, and hence a similarity in the vibrational spectra (neglecting frequency shifting in vibrations involving the metal atom).

It was found that Raman spectra of $(CH_3)_4NBe(BH_4)_3$ and $Al(BH_4)_3$ show remarkable similarity throughout the entire range. (A spectrum of $Al(BH_4)_3$ was obtained for the comparison.) Hence, it is not necessary in this particular case to assume noninteraction of individual BH_4^- groups in the spectral analysis. Also remarkable is the dramatic change observed in the B–H stretching region of the spectrum in going from polymeric $Be(BH_4)_2$ to $Be(BH_4)_3^-$. Beryllium tetrahydroborate exhibits a very complex Raman spectrum in this region.[4] In contrast, the $Be(BH_4)_3^-$ anion shows but three strong, well-resolved bands. The absence of a second band due to ν B–H$_b$ is a discrepancy also evident in the $Al(BH_4)_3$ spectrum.[1] However, the structure of $Al(BH_4)_3$ has been determined by other means,[14,15] and is hence still valid for comparison.

This evidence leads us to the assignment of a D_{3h} structure for $Be(BH_4)_3^-$, isostructural with $Al(BH_4)_3$ (Figure 2).

It was observed that cesium salts of $Al(BH_4)_4^-$ and $Be(BH_4)_3^-$ are difficult to prepare in good yield, as reaction temperature must be kept low enough so that decomposition of the volatile metal tetrahydroborate is minimal. The facility with which tetraalkylammonium salts react suggests a strong steric constraint in the cesium salt lattice.

The formation of the $U(BH_4)_6^{2-}$ anion from polymeric $U(BH_4)_4$ and $(C_2H_5)_4NBH_4$ can be rationalized by analogy to the formation of $Be(BH_4)_3^-$. In both cases, the metal tetrahydroborate is polymeric, and reaction most likely involves a disruption of the polymer to yield the anionic form, in which the configuration about the metal atom should not be altered to a great extent. On the basis of the known $U(BH_4)_4$ structure,[5] thus, $U(BH_4)_6^{2-}$ may contain an approximately octahedral arrangement of boron atoms about uranium, with two "tridentate" BH_4^- groups, and four "bidentate" (Figure 3). However, a satisfactory Raman spectrum of this compound has not as yet been obtained.

Reaction of tetra *n*-butylammonium iodide with aluminum tetrahydroborate and trimethylaluminum results in products in which the environment of the aluminum atom is most likely tetrahedral, giving an anion of C_{3v} symmetry in both cases. In the case of $(n\text{-}C_4H_9)_4NBe(BH_4)_2I$, the B–H stretching region of the spectrum is remarkably simplified from that shown by the $Be(BH_4)_2$ polymer.[4] It is very interesting to note, however, that in this case two bands are observed for *both* ν B–H$_t$ and ν B–H$_b$, contrary to the special case observed with the "trigonal prismatic" structures of $Be(BH_4)_3^-$ and $Al(BH_4)_3$. Hence, this anion clearly has the "bidentate" configuration and is likely to be of C_{2v} symmetry.

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