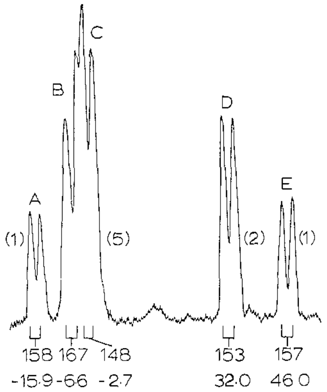

Figure 1.—The ^{11}B nmr spectrum of n-B_9H_{15} at 64.16 MHz. Coupling constants (top line) are in Hz; chemical shifts (bottom line) are in ppm relative to $(C_2H_5)_2O\cdot BF$·.

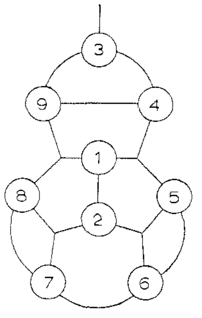

Figure 2.—The boron arrangement in n-B_9H_{15}.

a 12.8-MHz[3] spectrum of n-B_9H_{15} and 19.3-MHz[4] spectra of partially deuterated n-B_9H_{15}, we felt it worthwhile to examine the high-resolution spectrum of this material.

The spectrum in Figure 1 represents a fivefold improvement in resolution over the 12.8-MHz spectrum published by Burg and Kratzer.[3] Five of the six magnetically distinguishable boron environments are clearly represented. The signal from the sixth boron is obscured by the two overlapping doublets B and C, since the integrated area of this set of peaks is five-ninths that of the total spectrum.

Although it is still not possible to interpret the spectrum of n-B_9H_{15} unambiguously, it seems reasonable to make a tentative assignment using a suggestion by Lipscomb[5] based on the similarity of environment between many of the boron atoms in n-B_9H_{15} and those in B_4H_{10} and B_5H_{11}. Figures 2 and 3 illustrate the boron arrangement in n-B_9H_{15} and in B_4H_{10} and B_5H_{11}, respectively. The configuration of the 3-, 4-, and 9-boron atoms in n-B_9H_{15} bears a strong resemblance to the arrangement of the 1-, 2-, and 3-boron atoms in B_4H_{10}, while the 2-, 5-, 6-, 7-, and 8-boron atoms in n-B_9H_{15} are similar to the apical and basal borons in B_5H_{11}.

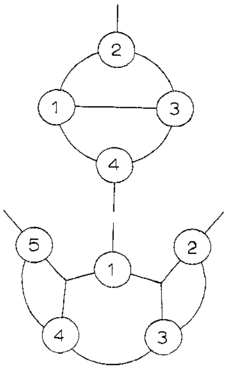

Figure 3.—The boron arrangement in B_4H_{10} and B_5H_{11}.

The doublet E of unit intensity at highest field may be assigned to the B(2) atom on the basis of its similarity to the apical position in B_5H_{11}. Proceeding to lower field, one might assign doublet D to the 4- and 9-boron atoms, corresponding to the BH groups in B_4H_{10}. The overlapping set of peaks, B and C, of intensity 5 may be correlated with the 5-, 6-, 7-, and 8-boron atoms, which resemble the basal atoms in B_5H_{11}, and the B(3) atom, obscured by the other peaks, which resembles the BH_2 groups in B_4H_{10}. By process of elimination the extreme low-field signal A may be assigned to the boron atom in position 1.

Acknowledgment.—We gratefully acknowledge the support of the National Science Foundation through Grant GP4944.

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A Proton Magnetic Resonance Hydration Study of Scandium, Yttrium, and Thorium Perchlorates in Water–Acetone Mixtures

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The value of the direct proton magnetic resonance (pmr) method for measuring cation hydration numbers has been demonstrated for a variety of systems.[1-14] In a pmr investigation of the nitrate solutions of diamagnetic Sc^{3+}, Y^{3+}, and Th^{4+} in water–acetone mixtures, hydration numbers of about 3.9, 2.4, and 2.9, respectively, were obtained for these ions, and the results

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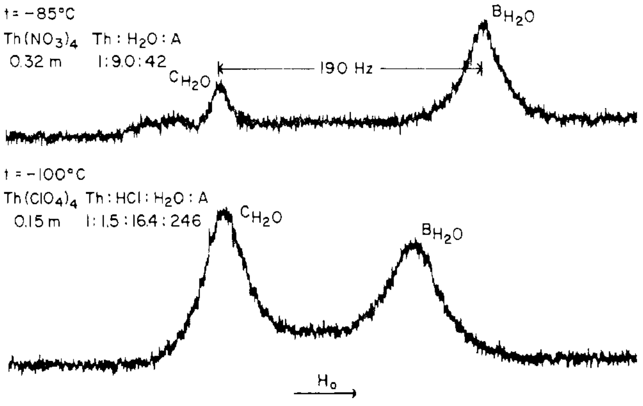

Figure 1.—The water pmr spectra of $Th(NO_3)_4$ and $Th(ClO_4)_4$ solutions in water–acetone mixtures, recorded on a Varian A-60 nmr spectrometer. The salt molalities, the mole ratios of all components, and the signals arising from bulk (B_{H_2O}) and complexed (C_{H_2O}) water molecules are shown in the diagram.

were attributed to complex formation and hydrolysis.[11] Since complex formation of these cations with perchlorate ion does not occur to any appreciable extent,[15,16] the present study was undertaken to obtain an estimate of their maximum hydration numbers.

The pmr measurements were carried out on a Varian A-60 and a Varian HA-100 nmr spectrometer, each equipped with a variable-temperature device for studies between −150 and +200°. The experimental method has been described in more detail elsewhere[3,6,7,11] and it involves cooling the example in the spectrometer probe until proton exchange has been slowed sufficiently to permit the observation of resonance signals for water molecules in the primary coordination shell of the cation and in bulk medium.

To assess the contribution of hydrolysis to the low hydration numbers found for the nitrate solutions of these cations, the same systems were studied in the presence of perchloric acid. Although the Y^{3+} and Th^{4+} hydration numbers remained unchanged in these experiments, the Sc^{3+} value increased from 3.9 to 5.1, a clear indication that a hydrolysis process was important in this solution. Since the mole ratio of H^+ to Sc^{3+} was varied from 0.7:1 to 1.1:1 in these experiments, it may be assumed that hydrolysis was completely repressed. The hydration number of 5.1 probably is still low, as a result of complex formation with nitrate ion.

Unacidified perchlorate solutions of these cations did not exhibit separate resonance signals for bound and bulk water molecules, since proton exchange was rapid even at −100°. This situation also prevailed for acidified $Sc(ClO_4)_3$ solutions and only broad, nonmeasurable signals were found for acidified $Y(ClO_4)_3$ solutions. However, as shown in Figure 1, acidified solutions of $Th(ClO_4)_4$ gave well-defined signals for bulk water and the cation solvation shell. The reason for this phenomenon cannot be stated without a knowledge of the proton-exchange mechanism.

From Figure 1, the spectra for solutions of $Th(NO_3)_4$ and $Th(ClO_4)_4$ in water–acetone can be compared. In contrast to the Th^{4+} hydration number of 2.9 previously found for the nitrate solution of Figure 1,[11] area measurements indicate that each Th^{4+} is hydrated by about 9.1 water molecules on the average in the perchlorate solution shown. This value was reproduced over an HCl to $Th(ClO_4)_4$ mole ratio range of about 0.8:1 to 1.5:1. These hydration numbers reflect the different complexing tendencies of nitrate and perchlorate ions. In the absence of appreciable complexing in the perchlorate solutions, each Th^{4+} can bind an average of nine water molecules in the first coordination shell, a value which must be close to the maximum for this ion.[17-22] Although the exact structure of the ionic species in the perchlorate solutions cannot be deduced solely from the pmr results, any future postulate must be consistent with this relatively large hydration number. Displacement of water molecules by nitrate ions reduces the average hydration number to about 3 in this system. This sharp reduction may indicate that a bidentate-type linkage between Th^{4+} and NO_3^- is occurring.

At the present time, studies of hydration and complex formation in solutions of Sn^{4+}, UO_2^{2+}, and Zn^{2+} are under way by this direct pmr method, and preliminary results indicate maximum solvation numbers of 6, 4, and 6, respectively, for these species.

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The Protonation of Zerovalent Nickel Complexes

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The formation of metal hydrides by the protonation of phosphine complexes of zerovalent platinum has been reported by Cariati, Ugo, and Bonati.[1] These authors

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