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Electrospray Mass Spectrometry of Borane Salts: Observation of High Molecular Weight Ion Clusters

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Electron impact (EI) in the positive ion mode is the most frequently used ionization method for mass spectrometric analysis of boranes.[1] However, interpretation of the EI mass spectra of boranes is complicated by (1) thermal decomposition of the boranes prior to ionization, (2) extensive fragmentation of the boranes after ionization, and (3) the existence of two boron isotopes, ^{10}B and ^{11}B. More to the point, however, borane salts cannot be analyzed via EI. Liquid secondary ion mass spectrometry is not very successful for analysis of borane salts either, as the signals corresponding to the borane anions appear in the low-mass region of the spectrum, which is dominated by intense matrix signals, and the borane salts often react with the matrix. Electrospray ionization[2] (ESI) revolutionized mass spectrometry in the late 1980s, in part because it is a very mild, solvent-based ionization technique, which does not produce solvent signals. As a result, compounds with a molecular weight in excess of 10 000 were amenable to mass spectrometry. Owing to a parallel surge in biotechnology, molecular biology, and related fields, the primary focus of ESI has been analysis of large biopolymers. Much less attention has been paid to inorganic compounds.[3] Herein, we report preliminary results to show that ESI mass spectrometry is very useful for analysis of borane salts,[4] avoiding many of the problems associated with other mass spectral analysis techniques.

A VG AutoSpec triple-sector (EBE) mass spectrometer equipped with the mark II ESI source was operated in the negative ion mode.[5] The ESI source has larger orifices for the skimmer cones, increased pumping capacity, and a hexapole focusing unit to improve sensitivity and ease of use. The samples were dissolved in CH_3CN or CH_3OH (200 $ng{\cdot}\mu L^{-1}$) and the flow rate was 15 $\mu L{\cdot}min^{-1}$. All experiments were performed with a resolution of 1250 (to obtain maximum signal strength) and a scan speed of 10 s per decade. Nitrogen was used as both the nebulizer gas (16 $L{\cdot}h^{-1}$) and the bath gas (60 °C; 400 $L{\cdot}h^{-1}$). The five borane salts examined, $[(Me)_4N][B_3H_8]$ (**I**), $Cs[B_3H_8]$ (**II**), $[(n\text{-}Bu)_4N][B_3H_8]$ (**III**), $Na_2[B_{12}H_{12}]$ (**IV**), and $Cs_2[B_{10}H_{10}]$ (**V**), were from laboratory stocks. The high-resolution ^1H, ^{11}B, and $^{11}B\{H\}$ NMR spectra of these compounds showed only resonances attributable to the cations and/or anions.

Figure 1 shows the ESI mass spectrum of $[(Me)_4N][B_3H_8]$, **I**, in CH_3CN. The most remarkable feature of this spectrum is the extensive clustering displayed by **I** under ESI conditions. Up to *m/z* 1000 all signals correspond to anionic clusters of ions (henceforth called cluster ions) having the formula $\{[(Me)_4N]_{x-1}[B_3H_8]_x\}^-$. Indeed, the observed isotope patterns of these signals (inset, Figure 1) match the calculated patterns. The $[B_3H_8]^-$ anion was not observed. The variation in intensity among the signals is noteworthy; the signal due to $\{[(Me)_4N]_2[B_3H_8]_3\}^-$, *m/z* 270,[6] is rather weak, while the $\{[(Me)_4N]_9[B_3H_8]_{10}\}^-$ signal, *m/z* 1073, is remarkably intense. Above *m/z* 1000, doubly charged cluster ions $\{[(Me)_4N]_{x-2}[B_3H_8]_x\}^{2-}$ are visible; *m/z* 1015, for example, corresponds to $\{[(Me)_4N]_{17}[B_3H_8]_{19}\}^{2-}$.[7,8] The first triply charged cluster ion, $\{[(Me)_4N]_{37}[B_3H_8]_{40}\}^{3-}$,[8,10] is observed at *m/z* 1454, while the first quadruply charged cluster ion, $\{[(Me)_4N]_{65}[B_3H_8]_{69}\}^{4-}$,[8,11] is observed at *m/z* 1903. The series of cluster ions having an overall 5− charge commences at ca. *m/z* 2425, $\{[(Me)_4N]_{104}[B_3H_8]_{109}\}^{5-}$.[8,12] Thus, to go from a charge of 2− to 3− requires at least 21 additional $[B_3H_8]^-$ units, to go from 3− to 4− requires at least 29 additional $[B_3H_8]^-$ units, and to go from 4− to 5− requires about 40 more $[B_3H_8]^-$ units. By comparison with ESI data for peptides of similar size, the charge per unit mass of borane salt is relatively small.[2] These results may suggest a globular structure for the borane salt cluster ions. The ESI mass spectrum of **I** in CH_3OH contains the same signals up to *m/z* 2000 as that of **I** in CH_3CN.[13] However, above *m/z* 1000, the spectrum is dominated by a broad, ill-defined hump that continues up to at least *m/z* 4500.

The ESI mass spectrum of $Cs[B_3H_8]$, **II**, in CH_3CN shows predominantly $\{Cs_{x-1}[B_3H_8]_x\}^-$ and $\{Cs_{x-2}[B_3H_8]_x\}^{2-}$ species. The first of the doubly charged cluster ions, $\{[Cs]_{19}[B_3H_8]_{21}\}^{2-}$,[8,14]

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(6) All the cluster ions are identified by their average *m/z* values, instead of their *m/z* distribution.

(7) $\{[(Me)_4N]_{16}[B_3H_8]_{18}\}^{2-}$, *m/z* 958, could be the first doubly charged cluster ion, but its signal coincides with that of $\{[(Me)_4N]_8[B_3H_8]_9\}^-$.

(8) These experiments were performed with a low sampling cone voltage. At a high voltage the onset of multiply charged ions shifts to higher mass. Higher voltages are known[9] to cause fragmentation of relatively weakly bound species, such as our cluster ions, by energetic collisions with background gas.

(9) See e.g.: Hamdan, M.; Curcuruto, O. *Rapid Commun. Mass Spectrom.* **1994**, *8*, 274.

(10) $\{[(Me)_4N]_{36}[B_3H_8]_{39}\}^{3-}$, *m/z* 1416, could be the first triply charged ion, but its signal coincides with those of $\{[(Me)_4N]_{12}[B_3H_8]_{13}\}^-$ and $\{[(Me)_4N]_{24}[B_3H_8]_{26}\}^{2-}$.

(11) $\{[(Me)_4N]_{64}[B_3H_8]_{68}\}^{4-}$, *m/z* 1875, could be the first cluster ion with four charges, but its signal coincides with those of $\{[(Me)_4N]_{16}[B_3H_8]_{17}\}^-$, $\{[(Me)_4N]_{32}[B_3H_8]_{34}\}^{2-}$, and $\{[(Me)_4N]_{48}[B_3H_8]_{51}\}^{3-}$.

(12) The uncertainty is due to the low intensity of signals above *m/z* 2000 and to the fact that the cluster ions with a 5− charge appear close to those with a 4− charge.

(13) The low signal-to-noise ratio prevents unambiguous assignments above *m/z* 2000.

(14) $\{[Cs]_{18}[B_3H_8]_{20}\}^{2-}$, *m/z* 1601, could be the first doubly charged cluster ion, but its signal coincides with that of $\{[Cs]_9[B_3H_8]_{10}\}^-$.

(15) The tetra-*n*-butylammonium salt of $[B_3H_8]^-$ was prepared by cation exchange of $Na[B_3H_8]$ with $[(n\text{-}Bu)_4N]I$.

(16) The unit cells of $Rb_2[B_{12}H_{12}]$ and $Cs[B_3H_8]$ each contain four anions, but the former cell is 2.2 times larger than the latter.[17] No data are available for $Na_2[B_{12}H_{12}]$.

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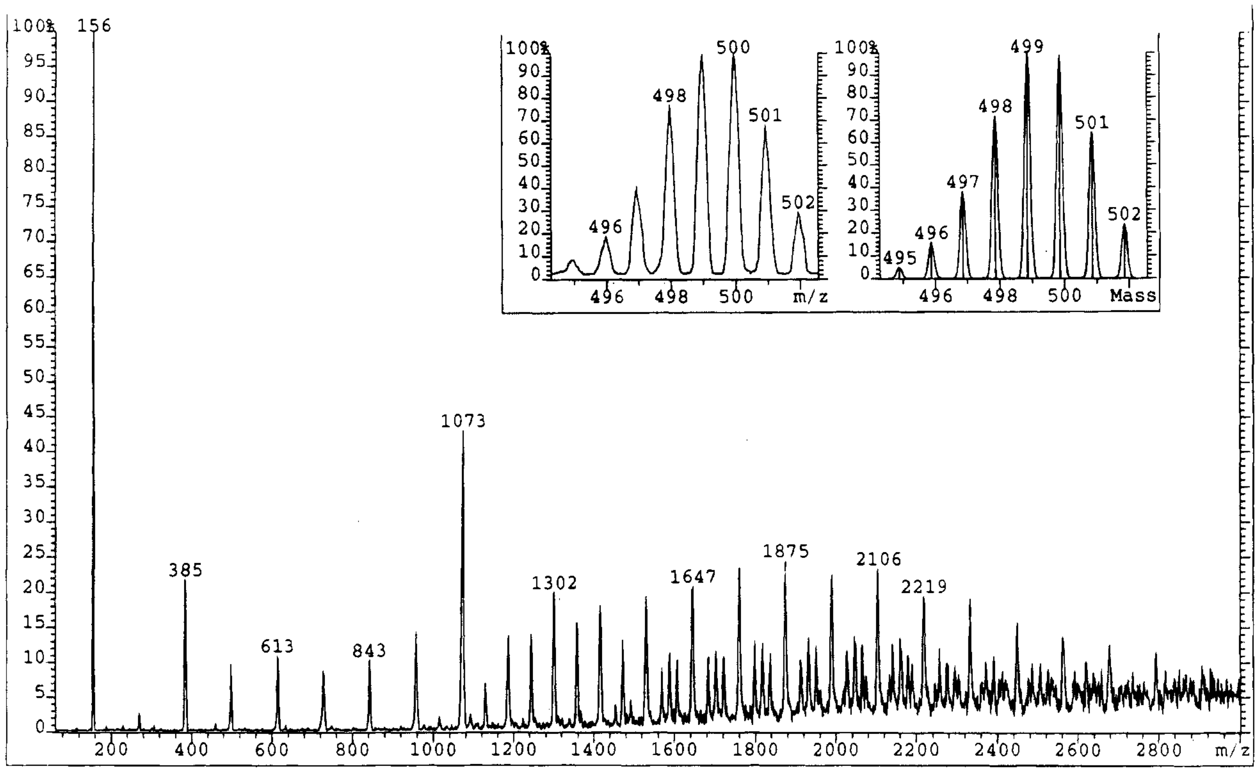

Figure 1. ESI mass spectrum of **I** in CH_3CN. Inset: experimental vs theoretical isotope pattern of $\{[(Me)_4N]_4[B_3H_8]_5\}^-$.

is observed at *m/z* 1688. Thus the onsets of the doubly charged cluster ions in terms of $[B_3H_8]^-$ units are similar for **I** and **II**. Triply charged clusters ions could not be unambiguously detected for **II**.

The ESI mass spectrum of $[(n\text{-}Bu)_4N][B_3H_8]$, **III**, is augmented by the presence of I^- anions in the sample.[15] Consequently, mixed cluster ions, $\{[(n\text{-}Bu)_4N]_{x-1}[B_3H_8]_{x-y}[I]_y\}^-$, are observed in addition to the expected $\{[(n\text{-}Bu)_4N]_{x-1}[B_3H_8]_x\}^-$. The data show that I^- is preferentially incorporated into the larger cluster ions. For example, the signal corresponding to $\{[(n\text{-}Bu)_4N][B_3H_8]_2\}^-$ is more intense than that due to $\{[(n\text{-}Bu)_4N][I]_2\}^-$, whereas the intensity of the signal associated with $\{[(n\text{-}Bu)_4N]_2[B_3H_8]_3\}^-$ is less than 25% of that due to $\{[(n\text{-}Bu)_4N]_2[I]_3\}^-$. The first doubly charged cluster ion in the spectrum of **III** is $\{[(n\text{-}Bu)_4N]_{13}[I]_{15}\}^{2-}$, *m/z* 2528. The analysis of **III** illustrates the value of ESI for the identification of ionic impurities that may escape detection by NMR.

Signals due to $[B_{12}H_{12}]^{2-}$ and $\{Na[B_{12}H_{12}]\}^-$ are the most intense in the ESI mass spectrum of $Na_2[B_{12}H_{12}]$, **IV**, in CH_3CN. Signals corresponding to adducts of these ions with one or two CH_3CN molecules are present as well, illustrating the gentle nature of the ionization process. A small signal corresponding to $[B_{12}H_{11}]^-$ was also observed. In contrast to the spectrum of **I** in CH_3CN, no clearly discernible signals from **IV** are observed above *m/z* 1500. On the other hand, **IV** exhibits a lower *m/z* onset for multiply charged cluster ions, as well as cluster ions of greater overall charge than **I** and **II**.[8] For example, around *m/z* 259 a number of small signals are present, separated by 0.5 mass unit, which can be ascribed to doubly charged cluster ions $\{Na_4[B_{12}H_{12}]_3\}^{2-}$, while the first doubly charged cluster ion for **I** was observed at *m/z* 1015, $\{[(Me)_4N]_{17}[B_3H_8]_{19}\}^{2-}$. Cluster ions from **IV** with a charges up to 7− (!) are clearly visible; the first 6− cluster ion is $\{[Na]_{64}[B_{12}H_{12}]_{35}\}^{6-}$, *m/z* 1073, and the first 7− cluster ion is $\{[Na]_{87}[B_{12}H_{12}]_{47}\}^{7-}$, *m/z* 1238 ($m = 8666$; $z = 7$). The enhanced ability of cluster ions from **IV** to support negative charges correlates with the larger size of the closo $[B_{12}H_{12}]^{2-}$ anions in **IV** compared to the arachno $[B_3H_8]^-$ anions in **I** and **II**.[16]

The ESI mass spectrum of $Cs_2[B_{10}H_{10}]$, **V**, displays features similar to those of **IV**, although the onset for multiply charged ions is somewhat higher.

In conclusion, we have shown that ESI mass spectrometry in the negative ion mode is a valuable technique for identification of borane salts. For the salts investigated here, acetonitrile solutions provided the most informative spectra; virtually all signals correspond to anionic clusters ions, having the general formula $\{[\text{cation}^{m+}]_x[\text{anion}^{n-}]_y\}^{(ny-mx)-}$. Neat methanol and acetonitrile/methanol and acetonitrile/water solutions yielded less readily interpretable spectra of lower quality. The degree of clustering and the charge density of the cluster ions depend on the nature of both the cation and the anion present. For example, **I** yields up to quintuply charged cluster ions, whereas doubly charged cluster ions are the most highly charged species observed for **II**, under identical conditions. The closo **IV** exhibits a single parent molecular anion, $[B_{12}H_{12}]^{2-}$, as well as a species corresponding to hydride loss, $[B_{12}H_{11}]^-$. The arachno $[B_3H_8]^-$ salts **I**−**III** do not exhibit a single parent molecular anion or ionic fragments thereof. The ESI mass spectra of acetonitrile solutions of these borane salts were also recorded in the positive ion mode. Cationic cluster ions, either singly or multiply charged, were observed, and details of this study as well as a systematic effort to clarify the influence of solvent, cation, and anion on the cluster ion chemistry observed under ESI conditions will be presented elsewhere.[4]

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Supplementary Material Available: A figure showing the ESI mass spectrum of $Na_2[B_{12}H_{12}]$ in CH_3CN (1 page). Ordering information is given on any current masthead page.

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