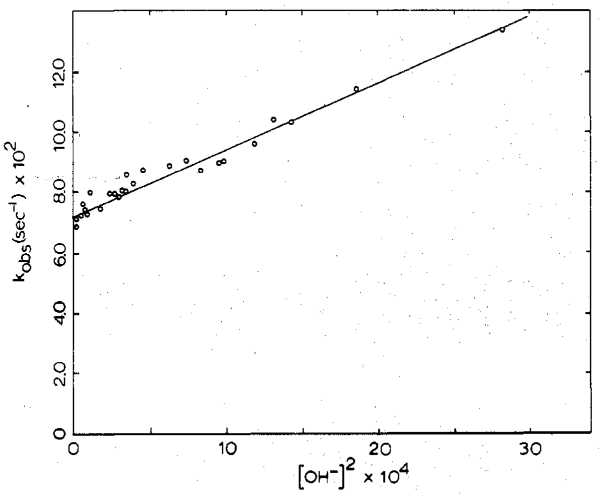

Figure 1. Plot of k_{obsd} vs. $[OH^-]^2$ for all data of pH >11.756. Above this pH, values of α_L are nearly constant. Intercept = $k_L^{PbY} = C_L = \alpha_L = 7.2 \times 10^{-} s^{-1}$. Slope = $k_{2OH}^{PbY} = 22.2\ M^{-2}\ s^{-1}$.

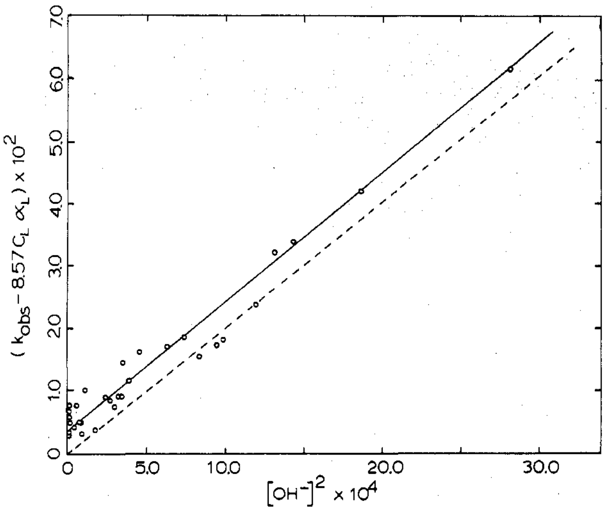

Figure 2. Plot of eq 8 rearranged with known values of k_L^{PbY}, C_L and α_L incorporated. The solid line uses $k_L^{PbY} = 8.57\ s^{-1}$ and has a slope = $k_{2OH}^{PbY} = 20.7\ M^{-2}\ s^{-1}$. The dashed line is the line for a similar plot using $k_L^{PbY} = 9.2\ M^{-1}\ s^{-1}$.

K_f is the formation constant for potassium ion complexation and equals $[KY^{3-}]/[K^+][Y^{4-}] = 8.06$ at 25 °C.[3] K_4 is the fourth ionization constant of H_4PDTA in the absence of complexing ions such as potassium but in the presence of 0.5 M ionic strength controlled with a noncomplexing ion such as Cs^+ or $(CH_3)_4N^+$. pK_4 has been measured at 25 °C to be 11.01.[3] Based upon the ΔH of ionization of EDTA, pK_4 at 20 °C is estimated to be 11.11. The pK_w at 20 °C is taken to be 14.1669. Using these numbers, α can be calculated according to eq 7 and is included in Table I. Values of α as calculated by Pearson's method (eq 7 but without the $K_f[K^+]$ term) are also included in Table I and designated "$\alpha_{L^{4-}}$ excluding K^+ complexation".

Figure 1 is a plot of k_{obsd} vs. $[OH^-]^2$ in the region where α_L is effectively constant (pH >11.756; the range of values of α_L is 0.191–0.198). The linearity of this plot suggests that the second-order dissociative reaction is reasonable and has a rate constant of 22.2 $M^{-2}\ s^{-1}$. This value is approximately 20 times greater than the corresponding value for Pb–PDTA,[2] reflecting the greater stability constant of Pb–PDTA. The intercept of Figure 1 is measured to be 7.2×10^{-2} and is equal to $k_L^{PbY} C_L \alpha_S$. Using 8.52×10^{-3} as C_L, a value of k_L^{PbY} = 43.4 $M^{-1}\ s^{-1}$ is calculated. This is in reasonable agreement with 30 $M^{-1}\ s^{-1}$, our earlier estimated value[2] of this rate constant in 0.5 M Cs^+ ionic medium.

Figure 2 is calculated utilizing pK_4 = 10.84 and ignoring K^+ complexation. In it, eq 8 is rearranged and known values of $k_L^{PbY} = 8.57$,[1] C_L, and α_L (Table I) are incorporated. The linearity of this plot demonstrates that eq 6 is sufficient to explain all the kinetic data presented in ref 1. The positive intercept can be eliminated by choosing $k_L^{PbY} = 9.2\ M^{-1}\ s^{-1}$ as is shown by the dashed line of Figure 2. The near-zero intercept of the dashed line implies that 9.2 $M^{-1}\ s^{-1}$ is a better value of k_Y^{PbY} than is 8.57 $M^{-1}\ s^{-1}$.

Registry No. *R*(–)-PDTA, 15456-17-4; PbEDTA, 11112-42-8.

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Is the Closo, Nido, or Arachno Classification for Boranes a Function of the Topological Description of the Molecule?

Sir:

Recently, Plesek, Hermanek, and Janousek[1] characterized the two interesting new heteroboranes 6,8-$S_2B_7H_9$ and 6,8-CSB_7H_{11} and also discussed the correct topological description of these molecules together with that of the isoelectronic 6,8-$C_2B_7H_{13}$ described earlier by Hawthorne.[2] It was pointed out that if a lone pair was considered to be equivalent to a substituent, the alternative topologies for these three molecules would be 2370 (corresponding to the isoelectronic $B_9H_{11}^{4-}$) and 2532 (corresponding to the isoelectronic $B_9H_{13}^{2-}$). Of particular concern were heteroatoms such as sulfur which exhibit "dual behavior" in that they can have one or two lone electron pairs. It was stated that a sulfur with one lone electron pair is formally equivalent to a BH^{2-} group and contributes three orbitals and four electrons to the skeleton but a sulfur with two lone electron pairs is equivalent to a BH_2^- group and contributes only two electrons and two orbitals to the skeleton. This latter contention raised confusion regarding the correct classification (nido or arachno) of certain "dual behavior" heteroboranes. It was argued that the nido classification corresponded to a 2370 topology and the arachno to a 2532 topology. It is the purpose of this correspondence to suggest that both BH^{2-} and BH_2^- groups formally contribute three orbitals and four electrons to framework bonding so that regardless of the topological formulation, the arachno classification is correct for 6,8-$S_2B_7H_9$ and related "dual behavior" heteroboranes.

The PERC [paradigm for the electron requirements of clusters[3]] formalism used for the closo, nido, and arachno classifications relies on electron-counting rules developed by Williams, Wade, and Rudolph.[3-5] As has been pointed out previously, bridge hydrogens and BH_2 groups formally amount to protonated framework electrons.[3] For instance, the *nido*-7,8-$C_2B_9H_{11}^{2-}$ can be singly or doubly protonated to give 7,8-$C_2B_9H_{12}^-$ or 7,8-$C_2B_9H_{13}$, respectively, without changing

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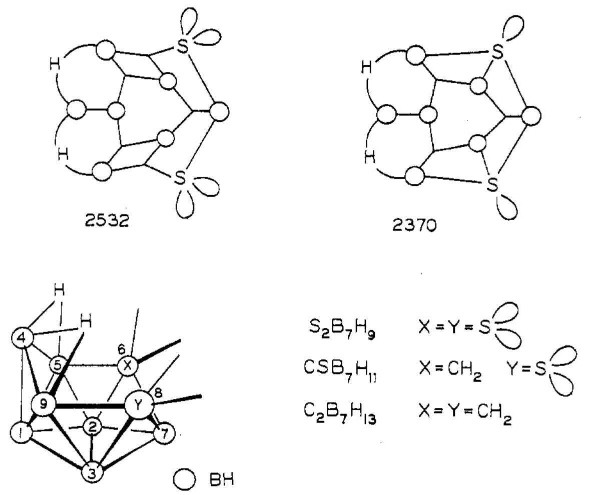

Figure 1. The topological representations, framework structure, and numbering convention for some nine-atom arachno heteroboranes.

the framework electron count. By the same token, protonation of $B_9H_{11}^{4-}$ (the borane isoelectronic with 6,8-$S_2B_7H_9$) to give $B_9H_{13}^{2-}$ does not alter the framework count.

Bridge hydrogens lie on a spheroidal extension of the borane skeleton as does one hydrogen of a BH_2 group (the endo hydrogen). Therefore, they are justifiably considered as protonated framework electrons. Extrapolating to 6,8-$S_2B_7H_9$ with a 2532 topology (Figure 1), it is apparent that both of the lone pairs are not exopolyhedral and that one of the two lone electron pairs on each sulfur is endopolyhedral; i.e., one is really a framework lone pair.

There is a simple relationship[6] between the PERC formalism and the topological *styx* number;[7] i.e., the sum of the digits in the topological *styx* number gives half of the number of framework electrons in a molecule. Therefore, in the case of the $n = 9$ cluster $S_2B_7H_9$ the *styx* numbers 2370 and 2532 give equivalent framework electron counts of $2n + 6 = 24$ for an arachno classification. Although both topologies are arachno, Hermanek, Plesek, and Janousek argued convincingly in favor of the 2532 alternative as the most reasonable valence-bond description for the molecule.[1]

Williams' original suggestion[8] for the arachno structure appropriate for nine-atom clusters was based on the known structure of n-B_9H_{15} rather than the alternative i-B_9H_{15}. Since then it has been found that all new arachno nine-atom skeletons have a structure similar to i-B_9H_{15} which is also nominally the same as that found for nido nine-atom frameworks. Couched differentially, it appears that the majority of nine-atom arachno and nido frameworks differ only in electron count and not in both electron count and framework structure.

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Registry No. 6,8-$S_2B_7H_9$, 63115-77-5; 6,8-CSB_7H_{11}, 63115-78-6; 6,8-$C_2B_7H_{13}$, 17653-38-2.

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