Macropolyhedral Boron-containing Cluster Chemistry. Cluster Fusion to give the Novel *nido–nido* Eighteen-vertex Dithiaoctadecaborane (*anti*)-[9,9′-$S_2B_{16}H_{16}$]†

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Thermolysis of *arachno*-4-SB_8H_{12} in cyclohexane generates the eighteen-vertex dithiaborane (*anti*)-[9,9′-$S_2B_{16}H_{16}$]† *via* a simple cluster fusion previously unrealized for heteroborane species.

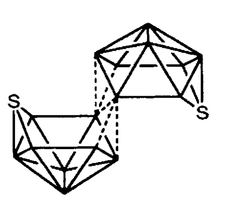
Large contiguous boron-hydride cluster structures can be generated, notionally and, in some cases, by experiment, by the fusion of smaller clusters with common edges or faces. The resulting potentially large area of binary boron-hydride 'macropolyhedral' chemistry is not extensively examined.[1] The potentially wider and possibly more useful area of heteroborane macropolyhedral chemistry, in which other types of main-group atoms are also incorporated into the large contiguous cluster, is very sparsely represented indeed.[2–4]

The few reported experimental approaches to macropolyhedral heteroboranes are limited to attempts to insert heteroatoms into the preformed macropolyhedral binary boron hydrides (*anti*)-$B_{18}H_{22}$ and (*syn*)-$B_{18}H_{22}$.[2–5] Here we report preliminary results that demonstrate the viability of the alternative experimental approach to novel contiguous macropolyhedral heteroboranes that involves a fusion reaction between smaller heteroborane single-cluster units.

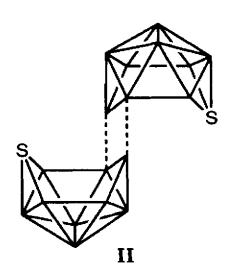
Thus we have found that the thermolysis of the *arachno* nine-vertex thiaborane *arachno*-4-SB_8H_{12} (freshly purified, prepared as in ref. 6) at 80 °C in cyclohexane solution for 2 h, followed by chromatographic separation on silica (CH_2Cl_2 liquid phase), results in the isolation of the eighteen-vertex dithiaoctadecaborane (*anti*)-[9,9′-$S_2B_{16}H_{16}$]† (Fig. 1) in 18% yield (as yet unoptimized; reaction scale *ca.* 8 mmol). It is a reasonably air-stable yellow crystalline solid. A basic stoichiometry that involves simple dihydrogen loss can be written down [eqn. (1)], although the as yet modest yield implies that alternative competing processes occur in the reaction system.

$$2\,SB_8H_{12} \rightarrow S_2B_{16}H_{16} + 4H_2 \qquad (1)$$

This novel dithiaborane, (*anti*)-[9,9′-$S_2B_{16}H_{16}$], was identified and characterised by mass spectrometry and NMR spectroscopy (Fig. 2).‡ It has a symmetric eighteen-vertex cluster constitution **I** based on the notional fusion **II** of two ten-vertex *nido* {6-SB_9} units with one common two-boron edge (formally the 6′,7′;5,6 edge in IUPAC eighteen-vertex nomenclature).† As such it is based on the *anti*-$B_{18}H_{22}$ structure, but with each of the 9- and 9′-{$B(H_{exo})(H_\mu)_2$} positions replaced by an 'isoelectronic' {S} unit. The *nido* character of the ten-vertex subclusters readily follows from comparative NMR spectroscopy (Fig. 2). The cluster fusion reaction of *arachno*-4-SB_8H_{10} has some parallels to the behaviour of two other *arachno* nine-vertex species, 4-(SMe_2)-*arachno*-B_9H_{13} and [4,4-($PMe_2Ph)_2$-*arachno*-4-PtB_8H_{12}], which respectively generate macropolyhedral bin-



I



II

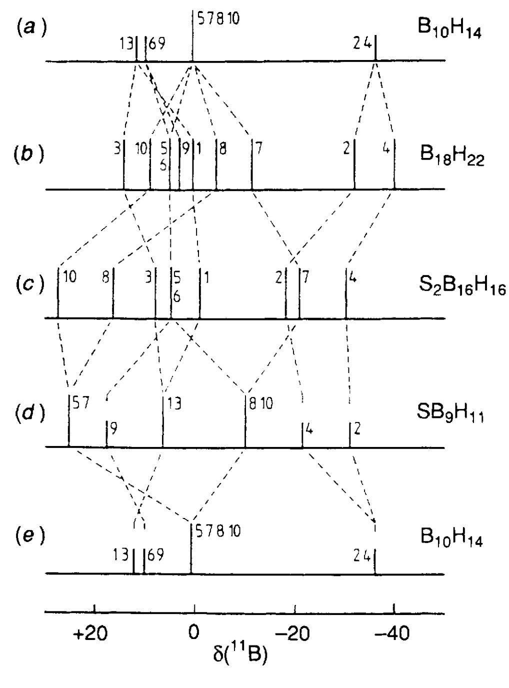


Fig. 2 Stick diagram of the chemical shifts and relative intensities in the ^{11}B NMR spectra of (*a*) *nido*-$B_{10}H_{14}$ (data from ref. 15), (*b*) (*anti*)-$B_{18}H_{22}$ (data from ref. 14, (*c*) (*anti*)-[9,9′–$S_2B_{16}H_{16}$] (*d*) *nido*-6-SB_9H_{11} (data from ref. 16), and (*e*) *nido*-$B_{10}H_{14}$ (repeated for convenience of comparison). Hatched lines join equivalent positions in the four ten-vertex *nido* units; note that IUPAC numbering conventions dictate a change in numbering between the single-cluster compound *nido*-6-SB_9H_{12} and the two double-cluster species. The constitution of (*anti*)-[9,9′–$S_2B_{16}H_{16}$] is apparent from the shielding parallels with *nido*-6-SB_9H_{11} and with (*anti*)-$B_{18}H_{22}$. Thus, firstly, comparison of (*anti*)-[9,9′–$S_2B_{16}H_{16}$] with *nido*-6-SB_9H_{11} shows deshielding at the (5) and (10) positions and shielding at the (1) and (7) positions, analogous to corresponding differences between (*anti*)-$B_{18}H_{22}$ and *nido*-$B_{10}H_{14}$. Secondly, comparison of (*anti*)-[9,9′–$S_2B_{16}H_{16}$] with (*anti*)-$B_{18}H_{22}$ shows deshielding at the (2), (4) (8), and (10) positions and shielding at the (3) and (7) positions, analogous to the corresponding differences between *nido*-6-SB_9H_{11} and *nido*-$B_{10}H_{14}$.

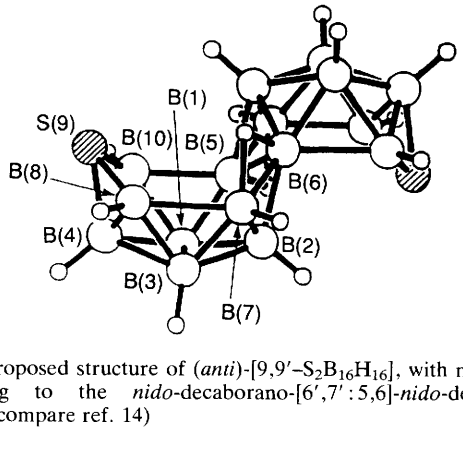


Fig. 1 Proposed structure of (*anti*)-[9,9′–$S_2B_{16}H_{16}$], with numbering according to the *nido*-decaborano-[6′,7′ : 5,6]-*nido*-decaborane system (compare ref. 14)

ary boranes[7] and metallaboranes[8] upon mild thermolysis. In the present case the disposition of the sulphur atoms in the product suggests a simple gross mechanism that involves the mutual docking at the reactive 6,7,8 positions (*arachno* nine-vertex numbering) of the two combining {*arachno*-4-SB_8} skeletons (hatched lines in **I**).

There is current interest in large macromolecular units based on assemblies of heteroborane clusters, principally dicarbaboranes of twelve vertices and fewer.[9–13] The individual clusters of these assemblies are however generally linked together with simple sigma two-electron two-centre linkages,[10,11] or by a single common atom (generally of a metallic element).[9,12,13] The results reported here now demonstrate the viability of the principle of the stepwise synthesis of macromolecular heteroborane cluster species that have more intimate subcluster fusion linkages.

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Footnotes

† The IUPAC nomenclature is *nido*-9′-thiadecaborano-[6′,7′:5,6]-*nido*-9-thiadecaborane.

‡ *NMR data* for (*anti*)-[9,9′-$S_2B_{16}H_{16}$] $\delta(^{11}B)[\delta(^{1}H)]$ ($CDCl_3$, 294–303 K): BH(1) −0.6 [+3.06], BH(2) −17.9 [+0.96], BH(3) +8.1 [+3.61], BH(4) −30.4 [+0.71], B(5)=B(6) +5.0 [common position, no directly bound H atoms], BH(7) −20.7 [$H(7)_{exo}$ +2.23 $H(6,7)_{\mu}$ −1.99], BH(8) +16.6 [+4.78], BH(10) +27.3 [+5.38]; NMR assignments by [^{11}B–^{11}B]-COSY experiments and ^{1}H-{^{11}B(selective)} spectroscopy. Mass spectrometry (70 eV EI ionisation) gave m/z_{max} 256 amu corresponding to the highest isotopomer of the proposed molecular ion.

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