Macropolyhedral boron-containing cluster chemistry. Nineteen-vertex $[S_2B_{17}H_{17}(SMe_2)]$. An unusual apical boron atom of cluster connectivity six that introduces a new polyhedral borane building block

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Mild thermolysis of $[SB_8H_{10}(SMe_2)]$ results in the formation of a small amount of macropolyhedral $[S_2B_{17}H_{17}(SMe_2)]$ of which the structure is based on the fusion, with two boron atoms in common, of a conventional *nido*-type eleven-vertex $\{SB_{10}H_9\}$ subcluster with an unprecedented *arachno*-type ten-vertex $\{SB_9H_8(SMe_2)\}$ subcluster that exhibits an apical boron atom of cluster connectivity six.

Polyhedral boron-containing cluster chemistry is currently typified predominantly, but perhaps restrictively, by carbaboranes and carbametallaboranes that form relatively simple clusters of up to a maximum of about fourteen atoms[1] that may generally be described in terms of the Williams–Wade cluster-geometry/electron-counting formalism,[2] commonly known as 'Wade's Rules'. It is of interest to extend the horizons of this chemistry. Ways in which this can be attempted include (*a*) the incorporation of heteroatoms other than carbon to extend the range of heteroatom chemistry beyond the carbaboranes,[3] (*b*) the generation of new structure types that challenge and extend the Williams–Wade formalism,[4,5] and (*c*) the intimate fusion of simple clusters to generate larger, more complex 'macropolyhedral' boron-containing cluster compounds.[6,7] We here report preliminary results on an interesting new compound that involves elements of all these three progressive aspects of cluster chemistry.

A solution of the nine-vertex eight-boron thiaborane $[SB_8H_{10}(SMe_2)]$[8] (500 mg, 2.63 mmol) in toluene (40 cm^3) was heated at reflux for 18 h. Repeated chromatography on silica using CH_2Cl_2–hexane resulted in the isolation of a pale-yellow air-stable crystalline species of formulation $[S_2B_{17}H_{17}(SMe_2)]$† **1** as an identifiable macropolyhedral product. Ultimately 3 mg (9 μmol, < 1%) was obtained in a pure state, although the product proportion by integrated NMR spectroscopy was some two to three times higher than this in the initial reaction products. In analytical TLC on foil-backed 250 μm silica gel G the compound had R_F 0.40 using CH_2Cl_2–hexane (1 : 3) as eluting medium. The constitution of compound **1** (Fig. 1) was determined by single-crystal X-ray diffraction analysis on a crystal grown from dichloromethane–hexane solution.‡ The compound was additionally characterised by NMR spectroscopy.§ It is seen to be based upon the fusion, with two boron atoms in common, of a conventional *nido*-shaped $\{SB_{10}H_9\}$ unit with a very unusual *arachno*-type $\{SB_9H_9(SMe_2)\}$ unit (schematic structures **I** and **II**). The subclusters are based on the well known[9] neutral compound [*nido*-7-$SB_{10}H_{12}$] (structure **IIA**) and an unknown neutral [*arachno*-$SB_9H_{11}(SMe_2)$] species of novel type (structure **IIB**).

Of the remainder of the reaction yield, some 60% was insoluble in common organic solvents. A large proportion of the chromatographically mobile products have so far proved to be mutually inseparable, although ^{11}B NMR spectroscopy suggests mixtures of macropolyhedral borane cluster compounds along with some new single-cluster species. Four other species were however separable in a state pure enough for better characterisation in yields of *ca.* 6% (**2**) and 1–3% (**3**, **4** and **5**). Compounds **2** and **3** were identified as the known $S_2B_7H_9$ and $S_2B_{16}H_{16}$,[7] respectively, compound **4** as an asymmetric thiaborane of tentative *nido* eleven-vertex formulation $SB_{10}H_{10}(SMe_2)$,¶ and compound **5** as a second macropolyhedral seventeen-boron species of tentative formulation $[S_2B_{17}H_{15}(SMe_2)]$,‖ *i.e.* with two hydrogen atoms less than the $[S_2B_{17}H_{17}(SMe_2)]$ formulation of compound **1**. Compounds **4** and **5** are very soluble in organic solvents, and have so far defied crystallisation in a form suitable for single-crystal work.

The formation of seventeen-boron species from an eight-boron starting monomer is of interest, and contrasts to the thermolysis[7] of the simplest eight-boron *arachno*-thianonaborane $[SB_8H_{12}]$ which yields a more stoichiometric sixteen-boron species, $[S_2B_{16}H_{16}]$, as the predominant macropolyhedral product. However, thermolysis of $[SB_8H_{10}(\text{ligand})]$ species in the absence of solvent under other conditions is known to yield isolatable amounts of $[BH_3(\text{ligand})]$ compounds,[10] and so in the present instance it seems likely that $[BH_3(SMe_2)]$ could act as a one-boron transfer agent; this has more general synthetic implications.

Irrespective of the mechanism of formation, the predominant interest resides in the very unusual structure of the $\{SB_9H_8(SMe_2)\}$ subcluster of compound **1**, which is based on an as yet hypothetical *arachno*-$[SB_9H_{11}(SMe_2)]$ species of schematic cluster **IIB**. This clearly differs from conventionally structured[11] [*arachno*-$SB_9H_{11}(SMe_2)$] (schematic cluster structure **III**). Its ten-vertex cluster structure resembles that of the nine-vertex '*iso*' *arachno* skeleton, as typified,[8] for example, by $[SB_8H_{10}(\text{ligand})]$ species, except that, unusually, an additional {BH} vertex is now accommodated in such a way as to generate a seven-membered open face. This has the effect of creating an apical cluster boron atom of cluster connectivity six (overall coordination number 7) at the apical B(1) position. As far as we are aware, this latter feature is quite novel in an open boron-containing cluster compound, although six-connectivity does exist in awkward *closo* species, for example (*a*) in the $[B_{11}H_{11}]^{2-}$ and $[CH_{10}H_{11}]^-$ anions where it is unstable with respect to fluxional reversion to cluster connectivity five,[5,12] and (*b*) in the comparatively few thirteen- and fourteen-vertex 'supraicosahedral' species that are known.[13] Higher connectivity numbers also of course exist in macropolyhedral species[14] at the points of cluster fusion [as typified by B(6) and B(7) in the present compound] but in these cases the connectivities are divided between the two subclusters.

The high connectivity and consequent generation of a hexagonal-pyramidal building block in a stable open cluster have fundamental consequences for boron cluster-pattern recognition theory,[2,15] which is currently generally based upon deltahedral skeletons with a maximum cluster connectivity of

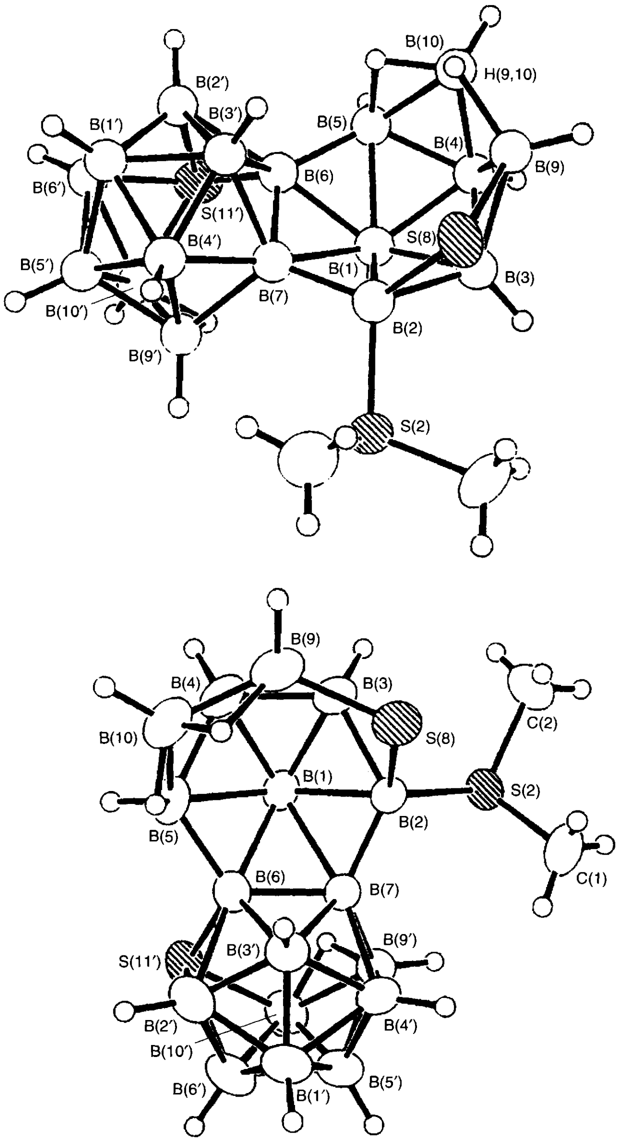
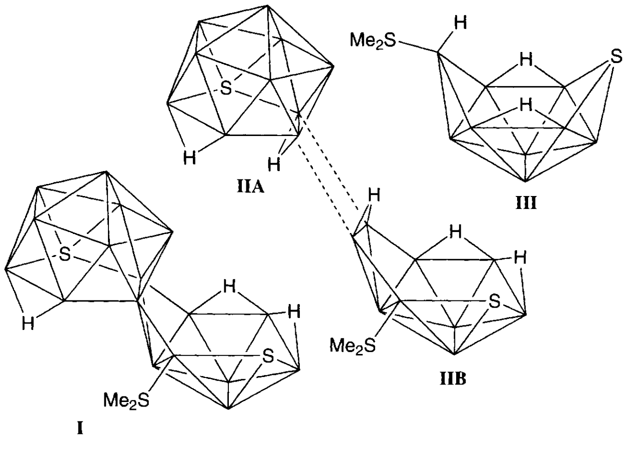


Fig. 1 ORTEP[18] drawings of the crystallographically determined molecular structure of $[S_2B_{17}H_{17}(SMe_2)]$ **1**: (top) a general view, and (bottom) a perspective to demonstrate the seven-coordinate boron atom B(1) of cluster connectivity six. Selected interatomic distances (in pm) are as follows: B(2)–S(8) 190.6(2), S(8)–B(3) 197.9(2), S(8)–B(9) 194.0(2), B(9)–B(10) 178.6(4), B(10)–B(5) 181.6(3), B(5)–B(6) 170.6(3), B(6)–B(7) [= B(7′)–B(8′)] 173.2(2), B(7)–B(9′) 184.8(3), B(6)–S(11′) 196.2(2), B(10′)–S(11′) 195.2(2), B(9′)–B(10′) 182.3(3). Interboron distances (in pm) to B(1) are as follows: to B(2) 186.6(3), B(3) 183.3(3), B(4) 189.4(3), B(5) 191.9(3), B(6) 187.5(3) and to B(7) 197.1(2), and angles (in °) between interatomic vectors at B(1) are in the ranges 51.80(9)–56.94(10), 100.35(11)–107.37(13) and 126.36(12)–136.65(13).

five and which thereby generates square and pentagonal pyramids (principally the latter) as the fundamental polyhedral building blocks. The present results now suggest that the hexagonal-pyramidal building block should also be accommodated in general boron-containing cluster bonding theory and not be limited to awkward closed cluster shapes. The experimental demonstration of a hexagonal pyramid also has relevance to theoretical work that attempts to predict fullerene-related higher borane clusters in which the hexagonal pyramidal motif figures largely,[16,17] but in which BH units joined to six other boron atoms have hitherto been perceived to be a problem.[17] It is not clear in the present case whether (*a*) this unusual subcluster is inherently unstable and is stabilized by the constraints of the intercluster fusion linkage, and would otherwise revert to a more conventional geometry, or whether



(*b*) it is inherently stable and the reaction coordinate for its synthesis happens to take a course not yet established for a synthesis of a stable single-cluster analogue. Whatever the reasons for the stabilisation of the hexagonal pyramidal unit in the present compound, it nevertheless constitutes a new seven-boron architectural unit in boron-containing cluster chemistry, and suggests substantial new families of new closed and open structural types if and when its designed general incorporation can be achieved.

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Footnotes

† A full nomenclature would be *nido*-11′-thiaundecaborano-[7′,8′:6,7]-2-dimethylsulfido-*iso*-(-10_{6kc}-< *VII* >-)-*arachno*-8-thiadecaborane.

‡ *Crystallography*: All measurements were made at 295 K on a Siemens P4RA diffractometer operating in the ω–2θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were reduced using XSCANS,[19] the structure was determined by direct methods using SHELXTL-PLUS (5.03),[20] and, using the same program, refined by full-matrix least squares by the minimization of $\Sigma w(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located from a Fourier difference map and were freely refined with isotropic thermal parameters.

Crystal data: $C_2H_{23}B_{17}S_3$, $M_r = 327.15$, monoclinic, space group *C2/c*, $a = 27.432(2)$, $b = 7.2482(4)$, $c = 20.047(2)$ Å, $\beta = 112.966(11)°$, $U = 3670.0(5)$ Å^3, $Z = 8$, $D_c = 1.184$ Mg m^{-3}, $\mu = 0.381$ mm^{-1}, $F(000) = 1344$. $R_1 = 0.0375$ for 3215 observed reflections $[I > 2\sigma(I)]$, $wR_2 = 0.1123$, and $S = 1.055$ for all data. Atomic coordinates, interatomic distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *NMR data* for compound **1** ordered as: δ(^{11}B) [δ(^{1}H)] {tentative assignment where possible} for $CDCl_3$ solution at 294–303 K: ten-vertex *isoarachno* subcluster: +11.3 [+4.34] {BH(5) or BH(9); resonances A}, −11.0 [+3.14], −20.0 [—]{SMe_2-substituted site, SMe_2 at +2.83 and +2.58}, −20.7 [+1.66] {BH(5) or BH(9); resonances B}, *ca.* −28.0 [+2.01] and *ca.* −28.0 [+1.83] {one of these is BH(10), resonances C}, −58.2 [+0.19] {probably BH(1) or BH(4)}; additional δ(^{1}H) values are μ-(5,10) and μ-(9,10) at −1.40 {associated with resonances A and C} and −1.69 {associated with resonances B and C]; eleven-vertex *nido* subcluster: +17.9 [+3.99], +4.3 [+3.80], +1.7 [+3.00], −0.4 [+2.97] {one of BH(9′) and BH(10′)}, −19.0 [+1.76], −20.0 [+1.25] {one of BH(9′) and BH(10′)}, −20.7 [−0.88], −24.0 [+2.03]; additionally δ(^{1}H) for μ-H(9′,10′) at −1.69, δ(^{11}B) for common atoms B(6/7′) and B(7/8′) at −3.2 [—] and −14.9 [—]; NMR assignments by [^{11}B–^{11}B]-COSY and [^{1}H–^{1}H]-COSY–{^{11}B} experiments and ^{1}H–{^{11}B(selective)} spectroscopy; insufficient correlation data were obtainable for a complete assignment, although interproton correlations permit the tentative assignments to individual subclusters and proton-boron correlations assign bridging positions.

¶ *NMR data* for compound **4** {possible formulation [*nido*-$SB_{10}H_{10}(SMe_2)$]}, ordered as: δ(^{11}B) [δ(^{1}H)], for $CDCl_3$ solution at 294–303 K: −3.9 [SMe_2 site; SMe_2 at +2.70 and +2.66], −5.8 [+2.39], −9.4 [+2.20], −14.5 [+1.93], −17.2 [+1.78], −17.5 [+1.46], −17.8 [+2.05], −18.7 [+1.66], −18.7 [+1.38], −36.9 [+1.21]; additionally δ(^{1}H), μ-H at −3.36.

∥ *NMR data* for compound **5** {possible formulation [$S_2B_{17}H_{15}(SMe_2)$]}, ordered as: δ(^{11}B) [δ(^{1}H)], for $CDCl_3$ solution at 294–303 K: +19.9 [+4.99] +19.0 [+4.21], +14.8 [*conjuncto* or SMe_2 site], +12.0 [*conjuncto* or SMe_2 site], +1.5 [+2.63], −1.1 [+3.00], −5.0 [+2.14], −6.3 [+3.48], −7.6 [+2.57], −11.1 [+0.77], −14.2 [+1.98], −15.9 [+1.52], −17.5 [+2.14], −18.9 [+2.28], −21.6 [+2.08], −24.7 [*conjuncto* or SMe_2 site], −33.1 [+0.75 and *endo*-H or μ-H at −0.67]; additionally δ(^{1}H), SMe_2 at +2.79 and +2.80.

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