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Macropolyhedral boron-containing cluster chemistry. The $[S_2B_{18}H_{19}]^-$ anion, and the reversible dismantling and regeneration of an apical boron cluster site with cluster connectivity six

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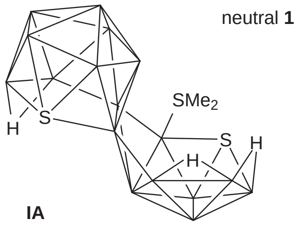
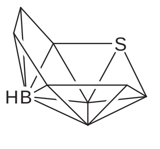
The double-cluster $[S_2B_{18}H_{19}]^-$ anion, from the [*syn*-$B_{18}H_{21}]^-$ anion and elemental sulfur, has an eleven-vertex *arachno*-type subcluster with a $\{B_7\}$ hexagonal planar-based pyramidal feature that reversibly disassembles and reassembles upon protonation followed by deprotonation.

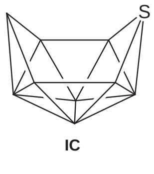
There is contemporary continuing interest in the generation of new geometries in boron-containing cluster chemistry.[1] In the development of this context we have described the nineteen-vertex macropolyhedral thiaborane cluster compound $[S_2B_{17}H_{17}(SMe_2)]$ (compound **1**, schematic **IA**), obtained from the heat-induced autofusion of $[SB_8H_{10}(SMe_2)]$.[2] Compound **1** has an unusual cluster structure in that one of its subclusters, formally *arachno* ten-vertex (**IB**), has an apical boron atom with the high cluster connectivity of six (vertex BH in **IB**). This open *arachno*-type subcluster geometry **IB** is quite different from the conventional[3] *arachno* ten-vertex geometry as exhibited, for example, by the *arachno* $[6\text{-}SB_9H_{12}]^-$ anion (**IC**).[4] From this isolated result it has not been clear whether the six-connectivity {BH} component of this new cluster shape **IB** is *(a)* inherently stable, and has not yet been seen in an isolated single-cluster compound because the necessary synthetic route is not yet discovered, or *(b)* it is a kinetic artefact trapped by the constraints of the reaction coordinate that generates the intercluster linkage.[2] Of relevance here, we have found now a second example of this type of high cluster connectivity. It occurs in an *eleven*-vertex *arachno*-type subcluster in the twenty-vertex $[S_2B_{18}H_{19}]^-$ macropolyhedral thiaborane monoanion (compound **2**, $[N(PPh_3)_2]^+$ salt). The route to anion **2** involves a completely different synthetic strategy to that for compound **1**, and, furthermore, it appears that the observed six-connectivity feature can reversibly disassemble and reassemble *via* a simple protonation–deprotonation sequence.



IA



IB



IC

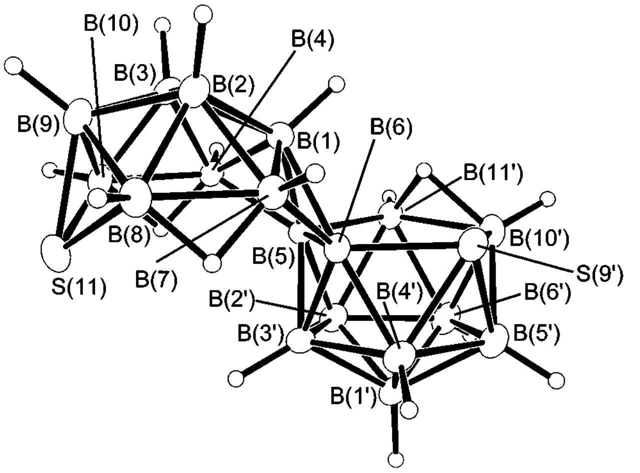
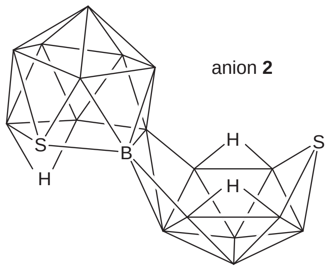
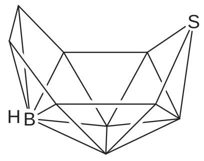


Fig. 1 Crystallographically determined molecular structure of the $[S_2B_{18}H_{19}]^-$ anion **2**. Selected interatomic distances (pm) are: from B(1) to B(2) 185.2(11), to B(3) 1.851(11), to B(4) 1.952(12), to B(5) 1.869(11), to B(6) 1.883(11), and to B(7) 1.913(11); B(2)–B(3) is 1.770(12), B(3)–B(4) 1.781(11), B(4)–B(5) 1.735(10), B(5)–B(6) 1.709(11), B(6)–B(7) 1.734(11) and B(7)–B(2) is 1.787(12); from S(11) to B(8) 1.964(10), to B(9) 1.945(10), and to B(10) 1.940(9). There was 50:50 {S(9′)}:{BH(11′)H(10′,11′)} crystallographic disorder within the conventionally structured (primed numbering) subcluster.

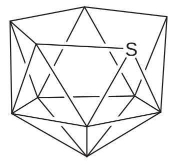
syn-$B_{18}H_{22}$ (360 mg, 1.64 mmol) in thf (25 ml) was deprotonated with excess NaH, elemental sulfur (400 mg) was added, the mixture stirred for 12 h, and then heated at reflux for 3 h. Water was added, the thf was evaporated (water pump), and the solution was filtered and then precipitated with a slight excess of $[N(PPh_3)_2]Cl$. The pale yellow precipitate, the $[N(PPh_3)_2]^+$ salt of the yellow anion $[S_2B_{18}H_{19}]^-$ (compound **2**), was purified by column chromatography (silica gel, $CHCl_3$) (R_F 0.25 by analytical TLC on silufol with CH_2Cl_2 as liquid phase), yield 48%. The other principal product was the well recognised [*nido*-7-$SB_{10}H_{11}]^-$ anion. Compound **2** is characterised by single-crystal X-ray diffraction analysis (Fig. 1 and schematic **IIA**)* and NMR spectroscopy.† It is seen to consist of a conventionally shaped[3] *nido* eleven-vertex $\{B_{10}S\}$ subcluster that is fused, with two boron atoms in common, with a $\{B_{10}S\}$ unit of a previously unrecognised eleven-vertex *arachno*-type. The shape of this latter unit (**IIB**), formally based on an (as yet hypothetical) $[SB_{10}H_{13}]^-$ anion, resembles a conventional ten-vertex *arachno* cluster (*e.g.* **IC**) except that an additional boron atom is incorporated in the open face, thus generating an eleven-vertex cluster and a cluster connectivity of six for the adjacent apical boron atom (vertex BH in **IIB**). This geometry of type **IIB** is previously unobserved. It is quite different from the more conventional[5] eleven-vertex *arachno* geometries of structures **IIC** and **IID**. The essential planar-based hexagonal pyramidal $\{B_7\}$ unit is an unprecedented feature of both **1** and **2**, and does not figure in classical[3] borane building-block philosophies.



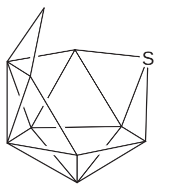
IIA



IIB



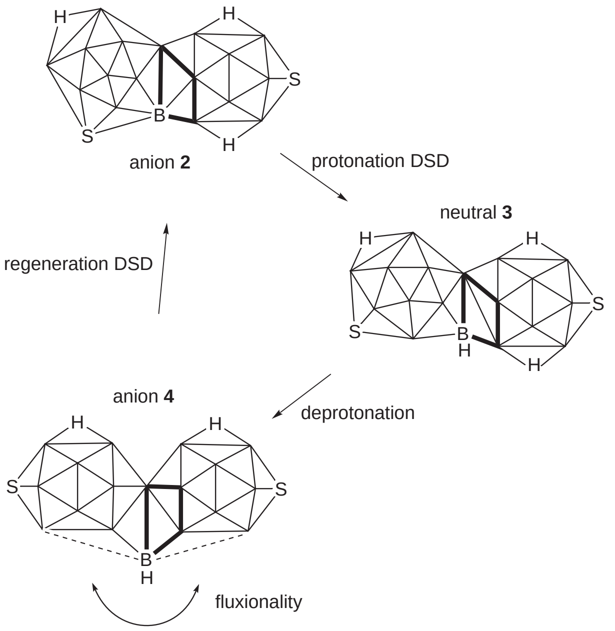
IIC



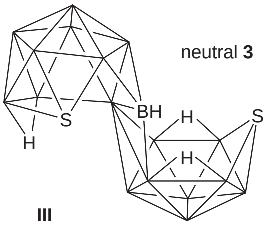
IID

The ^{11}B and ^{1}H NMR chemical shifts † of species **2** are tentatively but reasonably assigned and are consistent with the molecular formulation. The two common boron atoms B(5) and B(6) do not have BH(*exo*) bondings, and, in accord with this, two singlets are discernible in the ^{11}B spectrum, at $\delta(^{11}\text{B}) = -3.9$ and -14.8. An interesting feature of the ^{11}B spectrum consists of four unusually high-field resonances between $\delta(^{11}\text{B})$ -47 and -50 which arise from the hexagonal basal B(2), B(3), B(4) and B(7) positions of the novel eleven-vertex subcluster of geometrical type **IIB**. Upon reprotonation with concentrated H_2SO_4, monitoring by ^{11}B NMR spectroscopy shows that *(a)* these four very high-field resonances are lost, *(b)* a completely new, more compact, spectrum is obtained,‡ and *(c)* there is now only one singlet in the ^{11}B NMR spectrum, at $\delta(^{11}\text{B}) = -13.1$. We propose that these features result from the loss of the hexagonal pyramidal feature and the generation of a neutral conjugate acid $[S_2B_{18}H_{20}]$ (compound **3**) which consists of two more conventional (though mutually different) eleven-vertex *arachno* subclusters **IIC** and **IID** joined as in schematic **III**. There is a precedent for both cluster types in thiaborane cluster chemistry,[5] and the NMR assignments ‡ are not inconsistent with this formulation. In this scheme, the common vertex, designated B in **IIA** and BH in **III** (see also Scheme 1), is protonated on conversion of anion **2** to neutral **3**. Concomitant with this, there is a diamond–square–diamond (DSD) intra-cluster flexing (bold lines in Scheme 1), and the twenty-vertex macropolyhedral unit thereby acquires a somewhat reduced inter-subcluster intimacy.

Interestingly, deprotonation of neutral **3** with tmnda (*N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine) does not immediately regenerate the starting anion **2**, but immediately and quantitatively generates a species **4** which exhibits a 1 : 2 : 2 : 2 : 2 : 2 : 1 : 2 : 2 : 2 relative intensity pattern in its ^{11}B NMR spectrum.§ This may result from the conversion of neutral **3** to a fluxional anion **4**. Such a fluxionality could for example arise from an *arachno*(**IIC**)/*arachno*(**IID**)↔*arachno*(**IID**)/*arachno*(**IIC**) interconversion as in Scheme 1: clusters of types **IIC** and **IID** are very closely related, and deprotonation of the right-hand subcluster of structure **III** and adjustment of the two open-face connectivities to the vertex designated BH would readily achieve interconversion of the two subcluster types. Over 3 h at 294–297 K in CDCl$_3$ solution, this fluxional species **4** reverts quantitatively to the original anion **2** with its unusual hexagonal pyramidal feature. This reversion entails an unusual movement of hydrogen (presumably as a proton) from an open-face bridging position to an apical site, and a reversal of the original DSD process (Scheme 1). In sum, the overall protonation–deprotonation sequence appears to result in the deconstruction and the reconstruction of the very unusual hexagonal pyramidal feature.



Scheme 1



III

This second incidence of a {BH} vertex with a cluster connectivity to six other boron atoms in the context of an open cluster, but now one which can apparently be readily disassembled and reassembled, reinforces ideas[2] that the hexagonal pyramidal $\{B_7\}$ unit may be of fundamental significance and can therefore be used as a building block in future borane-based architecture. We are currently attempting to elucidate further the two intermediates **3** and **4** associated with this fundamental cluster disassembly–reassembly sequence, as well as attempting to devise entries into other systems that may exhibit this type of feature.

Acknowledgements

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Notes and references

* Crystals of $[N(PPh_3)_2][S_2B_{18}H_{19}]$, $C_{36}H_{49}B_{18}NP_2S_2$, $M = 816.40$, from $CHCl_3$–OEt_2, triclinic, space group $P\bar{1}$, $a = 1092.28(8)$, $b = 1421.90(12)$, $c = 1532.04(10)$ pm, $\alpha = 70.977(6)$, $\beta = 88.202(6)$, $\gamma = 80.321(6)°$, $U = 2216.8(3)$ Å^3, $Z = 2$, $T = 200(2)$ K, 5851 independent reflections collected on a Stoe STADI4 diffractometer in the range $3.05 < \theta < 60°$ were used in calculations after Lorentz-polarisation and absorption corrections ($\mu = 1.97$ mm^{-1}, based on azimuthal ψ-scans). The borane anion possesses a pseudo-mirror plane [passing through atoms B(1), B(9), S(11), B(1′), B(3′) and B(10′)] which causes a 50:50 disorder {S(9′)}:{B(11′)H(10′,11′)} within the eleven-vertex subcluster. Thus the 9- and 10-positions of this subcluster were refined as 50:50 B:S atoms. Final $wR2 = 0.1232$ for all unique data, conventional $R = 0.0446$ for F values of 4941 reflections with $F_o^2 > 2\sigma(F_o^2)$. CCDC reference number 186/1101. See http://www.rsc.org/suppdata/dt/1998/2965/ for crystallographic files in .cif format.

† ^{11}B and ^{1}H NMR data for anion **2** [formally the *nido*-9′-thiaundecaborano-(7′,8′:5,6)-*iso*-($11_{6kc}\langle VII\rangle$)-*arachno*-11-thiaundecaboranate-(1−) anion]; CD_3CN, 294–297 K (Note: $[PPh_4]^+$ salt, not $[N(PPh_3)_2]^+$ salt) {ordered as: tentative assignment $\delta(^{11}B)$ relative to Ξ 32.083971 MHz [$\delta(^1H)$ of directly attached hydrogen]}: BH(2′) +16.5 [+3.81], BH(4′) +3.0 [+3.43], BH(10′) +1.9 [+2.83], BH(1) +0.9 [+3.91], B(5) *ca.* −3.9 [*conjuncto* position], BH(5′) *ca.* −3.9 [+2.74], BH(9) −8.6 [+3.13], B(6) −14.8 [*conjuncto* position], BH(8) −15.3 [+2.33], BH(10) −15.8 [+2.28], BH(11′) −17.6 [+1.13], BH(6′) −21.1 [+1.51], BH(3′) −23.2 [−0.38], BH(1′) −23.6 [+1.805], BH(7) *ca.* −47.4 [+0.52], BH(4) −47.4 [+0.11], BH(2) −48.7 [+0.37], BH(3) −49.7 [+0.15], with μ-H(7,8), (4,10) and (10′,11′) at $\delta(^1H)$ −1.45, −1.70 and −1.79 respectively; assignments by homo- and hetero-nuclear ^{11}B and ^{1}H NMR experiments.

‡ ^{11}B and ^{1}H NMR data for neutral **3** [formally μ-(7′,8)-*arachno*-9′-thiadecaborano-(6′:7)-*nido*-10-thiaundecaborane], $CDCl_3$, 294–297 K {ordered, assigned and referenced as above}: BH(3) +15.9 [+3.69], BH(2′) +15.3 [+4.55], BH(5) +11.1 [+3.57], BH(4′) + 9.1 [+3.65], BH(11) +7.3 [+3.39], BH(8) +5.6 [+3.13], BH(6) −1.9 [+3.09], BH(5′) −5.1 [+2.58], BH(8) −5.95 [+2.60], BH(10′) −8.5 [+2.41], BH(1) and BH(6′) both *ca.* −11.6 [+2.98 and +2.79], B(6′) −13.1 [*conjuncto* position], BH(2) and BH(3′) both *ca.* −19.5 [+2.47 and +1.61], BH(7) −22.2 [+1.08], BH(4) −24.2 [+1.54], BH(1′) −34.9 [+1.52], and μ-H(7′,8′), (8,9) and (5′,10′) at $\delta(^1H)$ +1.00, −0.88 and −1.14 respectively.

§ $\delta(^{11}B)$ NMR values (and relative intensities) for the fluxional anion **4**, which exhibits time-average two-fold symmetry (see Scheme 1): $CDCl_3$, 294–297 K: *ca.* +4.8 (2BH), *ca.* +4.8 (1B), +2.3 (2BH), −5.3 (2BH), −6.8 (2BH), −7.9 (2BH), −10.0 (1BH), −11.1 (2BH), −38.0 (2BH) and −41.6 (2BH); all had doublet structures arising from couplings $^1J(^{11}B–^1H)$ in the range *ca.* 135 to *ca.* 165 Hz, except for the resonance of relative intensity 1B at $\delta(^{11}B)$ *ca.* +4.8; ^1H-{^{11}B} NMR work was precluded because of the relatively rapid reversion of **4** to regenerate **2**.

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