Macropolyhedral boron-containing cluster chemistry. The $[SB_{17}H_{19}]^-$ anion: a *nido*-ten-vertex : *arachno*-ten-vertex cluster architecture and the first single-sulfur macropolyhedral thiaborane

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Reaction of *syn*-$B_{18}H_{22}$ with metabisulfite gives a good yield of the first single-sulfur macropolyhedral thiaborane, the $[SB_{17}H_{19}]^-$ anion, which exhibits the unusual *arachno–nido* two-borons-in-common cluster fusion mode.

In the development of boron-containing cluster chemistry, the inhibiting cluster-size limit of about twelve to fourteen vertices that is a characteristic of single-cluster chemistry can be exceeded by the intimate fusion of smaller clusters to generate fused-cluster 'macropolyhedral' species. Of the known macropolyhedral species, the thiaboranes constitute very malleable molecular matrices with which to examine and extend the variety of structure available in this macropolyhedral boron-containing cluster chemistry.[1,2] However, all previously reported species have been dithiaboranes, and macropolyhedral monothiaboranes have, surprisingly, previously been lacking. Here we now report the first macropolyhedral monothiaborane, the $[SB_{17}H_{20}]^-$ anion, of *nido*-decaborano-(8′,7′:5,10)-*arachno*-6-thiadecaboranate constitution, obtained in good yield from the reaction of *anti*-$B_{18}H_{22}$ with potassium metabisulfite, $K_2S_2O_5$. Although metabisulfite and sulfite reactions have previously been used for sulfur-atom incorporation into single-cluster heteroboranes,[3] they have not previously been applied to binary boranes or to macropolyhedral species.

Four portions of $K_2S_2O_5$ (4 × 0.5 g, total 2.0 g) were added at 6 h intervals to a stirred solution of *anti*-$B_{18}H_{22}$ (0.2 g, 910 μmol) in a mixture of thf (40 cm^3) and dilute HCl (*ca.* 4 M, 30 cm^3). Stirring was continued for 2 days at ambient temperature, the mixture was filtered from the solid residue, and a solution of $[PPh_4]Cl$ (0.4 g, 1.07 mmol) in H_2O (20 cm^3) added to the filtrate. After evaporation *in vacuo*, the solid residue was extracted with CH_2Cl_2 (2 × 20 cm^3), the extract dried, filtered, and then subjected to column chromatography (silica gel, 2 cm × 20 cm) using CH_2Cl_2 as eluent. The fraction with R_F 0.22 [analytical TLC, silica G on aluminium (silufol, Kavalier, Prague), 100% CH_2Cl_2] was collected, filtered, evaporated and recrystallised from chloroform–hexane to give $[PPh_4][SB_{17}H_{20}]$ (380 mg, 656 μmol, 72%). No other chromatographically mobile products were found in significant amounts. The preparation is reproducible at the 70% level.

This product was characterised by an all-atom single-crystal X-ray diffraction analysis (Fig. 1)† allied with corroborative NMR spectroscopy.‡ The cluster architecture of the $[SB_{17}H_{20}]^-$ anion is seen to derive formally from the fusion of the structure of an [*arachno*-6-SB_9H_{12}]$^-$ anion [4] with a *nido*-$B_{10}H_{14}$ structure, with two boron atoms held in common [schematic connectivity structures **I** and **II**, unlettered vertices are BH(*exo*) units]. In accord with this, the NMR data for the two subclusters trace to the respective shielding patterns of the [*arachno*-6-SB_9H_{12}]$^-$ anion[5] and *nido*-$B_{10}H_{14}$, which have mutually distinct shielding patterns, there being a typical inversion of shielding sequence when otherwise equivalent positions in *nido* and *arachno* ten-vertex clusters are compared.[5] There are only three significant deviations from these shielding parallels: (a) for the *conjuncto* B(10) position the shielding, at $\delta(^{11}B)$ −3.0 differs substantially from either single cluster model, but is nevertheless between the positions observed for the two models (δ +10.2 and −33.8), which is expected; (b) the *nido*-decaboranyl B(8′) and B(10′) resonances at $\delta(^{11}B)$ +12.5 and −8.6, respectively, differentiate considerably from the value of +0.5 for *nido*-$B_{10}H_{14}$ itself; (c) the *nido*-decaboranyl B(5′) position adjacent to the B(10) fusion site is much more highly shielded at δ −27.8 than the equivalent position in *nido*-$B_{10}H_{14}$ itself at δ +0.5. For (b) and (c) it is probably significant here that the *nido*-decaboranyl long 'gunwale' distance, B(5)–B(8′), at 2.032(5) Å, is much longer than the other gunwale distance B(10′)–B(5′) of 1.914(7) Å at the opposite side of this sub-cluster, demonstrating markedly differential bonding induced by the constraints of the fusion to the other, *arachno*, subcluster. In *nido*-$B_{10}H_{14}$ itself this distance is 1.973(5) Å (by neutron diffraction).[6] Mechanist-

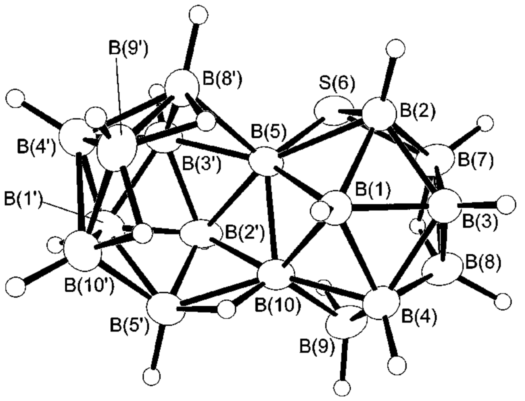
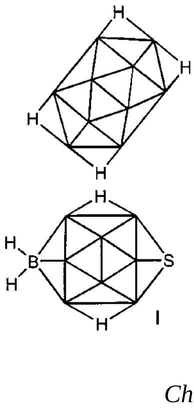


Fig. 1 Crystallographically determined molecular structure of the $[SB_{17}H_{20}]^-$ anion in $[PPh_4][SB_{17}H_{20}]$. Selected interatomic distances (in Å) are as follows: from S(6) to B(2) 1.953(3), B(5) 1.937(4) and B(7) 1.948(4), B(7)–B(8) 1.852(3), B(8)–B(9) 1.882(6), B(9)–B(10) 1.922(6), B(5)–B(10) 1.839(4), B(5)–B(8′) 2.032(5), B(8′)–B(9′) 1.778(5), B(9′)–B(10′) 1.830(7), B(10′)–B(5′) 1.914(7) and B(5′)–B(10) 1.843(5). These dimensions are for one of two independent $[SB_{17}H_{20}]^-$ anions in the unit cell; the dimensions for the other anion are within experimental deviation of these.



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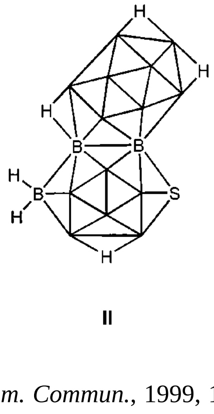
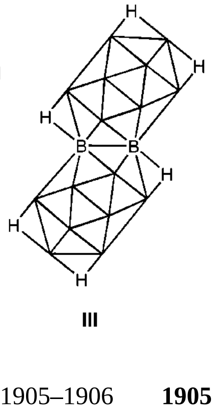


II



III

ically the conversion of *anti*-$B_{18}H_{22}$ (schematic **III**) to the $[SB_{17}H_{20}]^-$ anion (schematic **II**) has involved a net reductive replacement of $\{BH + H\}^-$ by $\{S\}^{2-}$, associated with a skeletal rearrangement. With no labelling we cannot speculate as to which of the original boron atoms of the *anti*-$B_{18}H_{22}$ skeleton is lost. In view of the great variety already exhibited by thiaborane macropolyhedral chemistry when sulfur atoms are incorporated in the cluster assemblies,[1,2] and in view of this high yield route from *anti*-$B_{18}H_{22}$, for which a variety of routes have long been known,[7] and which is also currently available commercially, the synthesis of this new $[SB_{17}H_{20}]^-$ species will constitute a very useful starting point for continued explorative investigation in macropolyhedral boron-containing cluster chemistry.

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Notes and references

† *X-Ray data*: crystallisation was from dichloromethane–hexane. *Crystal data* for $[PPh_4][SB_{17}H_{20}]$; $C_{24}H_{40}B_{17}PS$: M = 575.36, monoclinic, space group $P2_1/a$, a = 13.7139(2), b = 21.8452(4), c = 22.0843(4) (7) Å, β = 98.3210(11)°, U = 6546.43(19) Å^3, Z = 8, Mo-Kα radiation, λ = 0.71073 Å, μ = 0.166 mm^{-1}, T = 100(2) K, $R1$ = 0.0594 for 9943 observed reflections with $I > 2.0\sigma(I)$ and $wR2$ = 0.1557 for all 12855 unique reflections. Methods and programs were standard;[8] CCDC 182/1367. See http://www.rsc.org/suppdata/cc/1999/1905/ for crystallographic files in .cif format.

‡ *NMR data*: $CDCl_3$ solution of $[PPh_4][SB_{17}H_{20}]$ at 294–300 K, ordered as assignment $\delta(^{11}B)$ [$\delta(^1H)$] $^1J(^{11}B–^1H)$/Hz: BH(1) −38.1 [−0.94] 144; BH(2) *ca.* −10.2 [+3.36] *J* obscured; BH(3) −32.8 [+1.22] 145; BH(4) +0.6 [+2.95] 142; B(5){≡B(7′)} *ca.* −10.2 [*conjuncto* position, no bound H]; BH(7) −11.1 [+2.40] *ca.* 148; BH(8) −42.7 [−0.10] 146 (*exo*) and 37 (bridge); BH(9) *ca.* −8.6 [+2.06 (*exo*) and +1.02 (*endo*)] *J* obscured; B(10) {≡(B(6′)} −3.0 [*conjuncto* position, no bound H]; BH(1′) +10.0 [+3.58] 143; BH(2′) −24.5 [+1.71] 159; BH(3′) −9.3 [+2.07] *J* obscured; BH(4′) −41.6 [−0.03] 152; BH(5′) −27.8 [+1.71] 150 (*exo*) and 29 (bridge); BH(8′) +12.5 [+3.75] 151; BH(9′) −1.3 [+3.06] 165 and BH(10′) *ca.* −8.6 [+1.89] *J* obscured; additional $\delta(^1H)$ values for H(7,8) *ca.* −2.02, H(5′,10) *ca.* −2.02, H(8′,9′) −0.73 and H(9′,10′) −3.36, and for $[PPh_4]^+$ at *ca.* +7.5 to +7.8 (20H, complex multiplet); assignments by [$^{11}B–^{11}B$], [$^1H–^1H$] and $^1H–\{^{11}B\}$ correlation experiments.

1 T. Jelínek, J. D. Kennedy and B. Stíbr, *J. Chem. Soc., Chem. Commun.*, 1994, 1415; T. Jelínek, J. D. Kennedy, B. Stíbr and M. Thornton-Pett, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1599; P. Kaur, J. Holub, N. P. Rath, J. Bould, L. Barton, B. Stíbr and J. D. Kennedy, *Chem. Commun.*, 1996, 273; T. Jelínek, B. Stíbr, J. D. Kennedy and M. Thornton-Pett, in *Advances in Boron Chemistry*, ed. W. Siebert, Royal Society of Chemistry, Cambridge, 1997, pp. 426–429; T. Jelínek, J. D. Kennedy, B. Stíbr and M. Thornton-Pett. *Inorg. Chem. Commun.*, 1998, **1**, 179; T. Jelínek, I. Cisarová, B. Stíbr, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1998, 2965.

2 P. Kaur, J. D. Kennedy, M. Thornton-Pett, T. Jelínek and B. Stíbr, *J. Chem. Soc., Dalton Trans.*, 1996, 1775; P. Kaur, M. Thornton-Pett, W. Clegg and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1996, 4155; P. Kaur, A. Brownless, S. D. Perera, P. A. Cooke, T. Jelínek, J. D. Kennedy, M. Thornton-Pett and B. Stíbr, *J. Organomet. Chem.*, 1998, **557**, 181.

3 J. Plesek, S. Heřmánek and Z. Janousek, *Collect. Czech. Chem. Commun.*, 1977, **42**, 785; V. A. Brattsev, S. P. Knyazev, G. N. Danilova and V. I. Stanko, *Zh. Obsch. Khim.*, 1975, **45**, 1393; K. Base, S. Heřmánek and F. Hanousek. *J. Chem. Soc., Chem. Commun.*, 1984, 299.

4 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 2657.

5 M. Bown, X. L. R. Fontaine, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1988, 1467.

6 A. Tippe and W. C. Hamilton, *Inorg. Chem.*, 1969, **8**, 464.

7 A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1962, **84**, 3218; J. Dobson, P. C. Keller and R. Schaeffer, *Inorg. Chem.*, 1968, **7**, 399; D. F. Gaines, C. K. Nelson and G. A. Steehler, *J. Am. Chem. Soc.*, 1984, **196**, 7266; G. B. Jacobsen, D. G. Meina, J. H. Morris, C. Thompson, S. J. Andrews, D. Reed, A. J. Welch and D. F. Gaines, *J. Chem. Soc., Dalton Trans.*, 1985, 1645.

8 COLLECT, Data Collection Strategy Program, Nonius, 1999; DENZO-SMN, Z. Otwinowski and W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, *Methods Enzymol.*, 1997, **276**, 307.

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