

**MACROPOLYHEDRAL BORON-CONTAINING CLUSTER CHEMISTRY
[S₂B₁₆H₁₇]⁻. A NEW EIGHTEEN-VERTEX THIABORANE ANION**

Michael J. CARR^{a1,b}, William CLEGG^c, John D. KENNEDY^{a2,*},
Michael G. S. LONDESBOROUGH^{b1} and Colin A. KILNER^{a3}

^a The School of Chemistry of the University of Leeds, Leeds, UK LS2 9JT, England;
e-mail: ¹ michael.carr@bruker.co.uk, ² j.d.kennedy@leeds.ac.uk, ³ c.a.kilner@leeds.ac.uk

^b Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež near
Prague, Czech Republic; e-mail: ¹ michaell@iic.cas.cz

^c The School of Natural Sciences (Chemistry), The University of Newcastle-upon-Tyne,
UK NE1 7RU, England; e-mail: w.clegg@newcastle.ac.uk

Received May 20, 2010

Accepted May 26, 2010

Published online August 12, 2010

It is an honour and a pleasure to be able to contribute to this volume dedicated to our friend and chemical colleague Professor Bob Štíbr, not only in recognition of his 70th birthday, but also in recognition of his considerable experimental contributions and intellectual insights into polyhedral boron-containing cluster chemistry, and in recognition of many friendly discussions over many years on chemistry and on the philosophies of science and of life, and on the merits of český versus anglický pivo.

The novel eighteen-vertex macropolyhedral dithiaborane anion [S₂B₁₆H₁₇]⁻ **1** has been obtained as its [tmndH]⁺ salt from the reaction of [S₂B₁₇H₁₇] **2** and tmnd in solution in the presence of [RhCl₂(η⁵-C₅Me₅)₂]. It has two cluster skeletal electrons more than the three previously reported eighteen-vertex dithiaborane {S₂B₁₆} species *n*-[S₂B₁₆H₁₆], *n*-[S₂B₁₆H₁₅]⁻ and *iso*-[S₂B₁₆H₁₆], and the anion consists structurally of an *arachno* {SB₉} and a *nido* {B₉} cluster unit fused with two boron atoms in common, and with an *endo-to-exo* sulfur bridge that also links the two subclusters together.

Keywords: Borane cluster; Thiaborane; Macropolyhedral; Synchrotron X-ray crystal structure; Molecular structure.

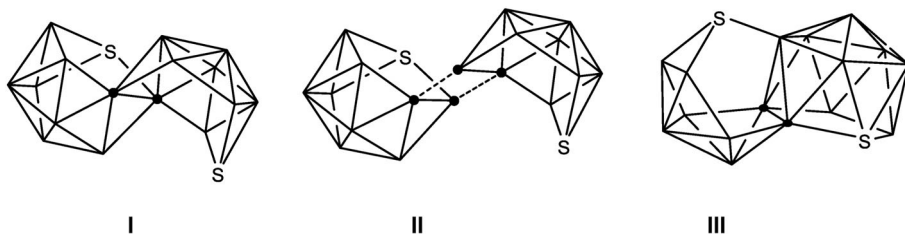
The bulk of the known chemistry of the higher boron hydrides, and of their derivatives such as the carbaboranes, heteroboranes and metallaboranes, involves polyhedral single-cluster species containing up to a synthetic barrier of twelve boron atoms. The realisation of a fused-cluster chemistry for polyhedral species considerably expands the horizons of boron-containing cluster chemistry beyond the twelve-boron barrier¹⁻⁷. Development of

this area is at present inhibited by the lack of transferable generic routes for the intimate fusion of boron-containing single clusters to give fused-cluster “macropolyhedral” species. Pending a breakthrough in finding such a generic route, the area of molecular borane and heteroborane chemistry involving clusters of more than twelve boron atoms can be developed by the investigation of reactions of known macropolyhedral species. In this regard, the macropolyhedral thiaboranes in particular exhibit a considerable flexibility and thence have a propensity readily to generate the new structural types that may ultimately define the field. Structural types established comprise (i) the eighteen-vertex neutral n -[S₂B₁₆H₁₆]^{8,9} and *iso*-[S₂B₁₆H₁₆]⁹ isomers, neutral [S₂B₁₆H₁₄(PPh₃)]¹⁰ and the n -[S₂B₁₆H₁₅]⁻⁹ and [SB₁₇H₁₉]⁻¹¹ anions¹¹, (ii) nineteen-vertex neutral [S₂B₁₇H₁₇(SMe₂)]¹², neutral [S₂B₁₇H₁₇]⁻¹³ and the [S₂B₁₇H₁₈]⁻¹⁴ and [S₂B₁₇H₁₆]⁻¹³ anions¹³, and (iii) twenty-vertex neutral [S₂B₁₈H₂₀]¹⁵ and the n -[S₂B₁₈H₁₉]⁻¹⁶ and *iso*-[S₂B₁₈H₁₉]⁻¹⁵ anions¹⁵. In this context, we now report the isolation and characterisation of a new addition to this potentially important structural library, an eighteen-vertex macropolyhedral dithiaborane species, the [S₂B₁₆H₁₇]⁻ anion.

Thus, during the course of attempts to synthesise new macropolyhedral rhodathiaboranes, we have isolated the previously undescribed [S₂B₁₆H₁₇]⁻ anion **1** in viable yield as the unexpected product from a reaction system involving [S₂B₁₇H₁₇]²⁻ **2**, [RhCl₂(η⁵-C₅Me₅)₂]₂, and *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine (tmnd). Specifically, [S₂B₁₇H₁₇]²⁻ **2** (40 mg, 150 μmol)¹³, tmnd (32 mg, 150 μmol) and [RhCl₂(η⁵-C₅Me₅)₂]₂ (46 mg, 75 μmol) were dissolved in dichloromethane (20 ml) and stirred at ambient temperature for 24 h. The reaction mixture was then filtered through flash silica and reduced in volume in vacuo. Preparative TLC (silica gel G (Fluka GF₂₅₄), 200 × 200 × 1 mm, *n*-hexane–dichloromethane 50:50 vol/vol) thence gave only one clear component, an orange compound that we have identified as the [tmndH]⁺ salt **1a** (6 mg, 13 μmol; 9 %) of the [S₂B₁₆H₁₇]⁻ anion **1** via single-crystal X-ray diffraction analysis (Fig. 1)¹⁷ and NMR spectroscopy¹⁹. The TLC analysis showed trace quantities of other coloured components, but not in viable quantities for identification.

The cluster structure of the anion **1** (Fig. 1) consists of a ten-vertex ‘*remote arachno*’ {SB₉} subcluster conjoined to a ten-vertex *arachno* {SB₉} subcluster by two common boron atoms (schematic skeletal structures I and II). An equally valid alternative description of the anion would describe the primed cluster as an eight-vertex *nido* {B₈} subcluster conjoined to the ten-vertex *arachno* {SB₉} subcluster by a sulfur-atom bridge with one common boron atom and one additional interboron linkage. The average interatomic distances are typical with a mean boron-to-boron distance of 1.797

Å and a mean sulfur-to-boron distance of 1.910 Å; selected individual interatomic distances are in the caption to Fig. 1. The cluster dimensions, as well as the NMR characteristics¹⁹, are in accord with the crystallographically determined structure and with the proposed *nido* and *arachno* characters of the two subclusters.



The type of sulfur bridge exhibited by anion 1 is closely related to that seen in *iso*-[S₂B₁₆H₁₆]⁻ 3 (schematic skeletal structure III)⁹, and seems to be becoming an increasingly-recognised structural motif as this and other

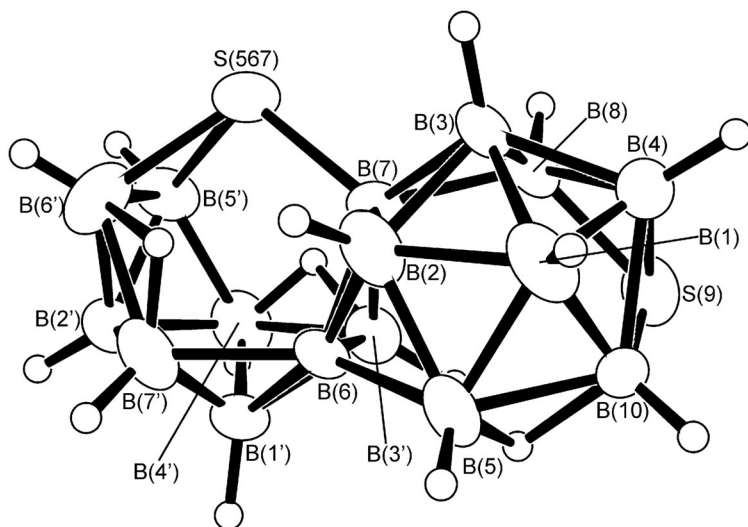
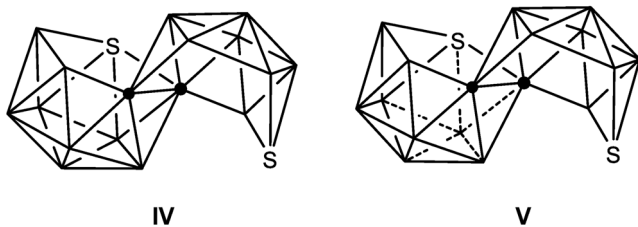


FIG. 1

ORTEP-type illustration of the crystallographically-determined molecular structure of the [S₂B₁₆H₁₇]⁻ anion 1 as determined in its [tmndH]⁺ salt 1a. Distances from the sulfur atoms are as follows: from S(9) to B(10) 1.866(9), to B(8) 1.863(6) and to B(4) 1.920(6) Å, and from S(5'6'7) to B(7) 1.915(4), to B(6') 1.996(7) and to B(5') 1.897(4) Å. Selected shorter interboron distances are: B(1')–B(6) 1.721(6), B(2)–B(6) 1.739(7) and B(3')–B(6) 1.742(8) Å, with longer ones B(5)–B(6) 1.857(7), B(5')–B(6') 1.873(8), B(5)–B(10) 1.885(10), B(4)–B(8) 1.890(8) and B(4)–B(10) 1.892(7) Å; other interboron distances are in the range of 1.750(9)–1.850(7) Å

structures emerge. Other previous examples include $[\text{S}_2\text{B}_{16}\text{H}_{14}(\text{PPh}_3)]^{10}$, $[(\text{PPh}_3)\text{NiS}_2\text{B}_{16}\text{H}_{12}(\text{PPh}_3)]^{10}$ and $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4^{\text{isoPr}})\text{RuS}_2\text{B}_{15}\text{H}_{15}]^{20}$. More generally, it seems likely that this type of *endo-to-exo* intercluster bridge, here exhibited by the sulfur atom, will be an increasingly encountered structural motif as macropolyhedral cluster chemistry develops; it is apparent, for example, that metal-atom centres can also form similar bridges, as in $[(\text{PMe}_2\text{Ph})_2\text{PtB}_{16}\text{H}_{17}\text{PtB}_{10}\text{H}_{11}(\text{PMe}_2\text{Ph})]^{21}$ and in one of the isomers of $[(\text{PMe}_2\text{Ph})_2\text{B}_{18}\text{H}_{18}]^{22,23}$.

Now that that the $[\text{S}_2\text{B}_{16}\text{H}_{17}]^-$ anion **1** is characterised as such, it is now apparent, by the retrospective inspection of NMR spectra of crude reaction mixtures, that it has also been a product in variable small quantities in several reactions of macropolyhedral dithiaboranes that we have reported, for example, most recently, in other systems involving $[\text{S}_2\text{B}_{17}\text{H}_{17}]$ **2** such as the reactions with $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]^{24}$ and $[\text{RuCl}_2(\eta^6\text{-}p\text{-MeC}_6\text{H}_4^{\text{isoPr}})_2]^{22}$. This may imply that the species may be a reasonably stable kinetic sink. In this regard, the mechanism of its formation from the starting substrate $[\text{S}_2\text{B}_{17}\text{H}_{17}]$ **2** (schematic skeletal structure **IV**) would be of interest. In gross terms (schematic skeletal structure **V**), a removal of the boron atom B(4) of **2** would give the structure of the $[\text{S}_2\text{B}_{16}\text{H}_{17}]^-$ anion **1**. It is of interest that there is an apparent abstraction of a {BH} vertex from a non-open face position, contrary to a general perception that cluster dismantling and *Aufbau* reactions generally occur on the open faces.



Contribution no. 115 from the Řež-Leeds Anglo-Czech Polyhedral Collaboration (ACPC). We thank Mr S Barrett for assistance with NMR spectroscopy. We acknowledge a contribution from the UK EPSRC towards a studentship for M. J. Carr, and thank the UK CCLRC (now STFC) for provision of synchrotron beam time at the UK National SRS Laboratory in Daresbury. Support from the Academy of Sciences of the Czech Republic, project no. M200320904, is also gratefully acknowledged.

REFERENCES

1. Kennedy J. D. in: *Advances in Boron Chemistry* (W. Siebert, Ed.), p. 451. Royal Society of Chemistry, Cambridge 1997.

2. Bould J., Clegg W., Teat S. J., Barton L., Rath N. P., Thornton-Pett M., Kennedy J. D.: *Boron Chemistry at the Millennium*, special edition of *Inorg. Chim. Acta* **1999**, 289, 95.
3. Bould J., Ormsby D. L., Yao H.-J., Hu C.-H., Sun J., Jin R.-S., Shea S. L., Clegg W., Jelínek T., Rath N. P., Thornton-Pett M., Greatrex R., Zheng P.-J., Barton L., Štíbr B., Kennedy J. D. in: *Contemporary Boron Chemistry* (M. Davidson, A. K. Hughes, T. B. Marder and K. Wade, Eds), p. 171. Royal Society of Chemistry, Cambridge 2000.
4. Jelínek T., Kennedy J. D., Barrett S. A., Thornton-Pett M., Císařová I. in: *Contemporary Boron Chemistry* (M. Davidson, A. K. Hughes, T. B. Marder and K. Wade, Eds), p. 175. Royal Society of Chemistry, Cambridge 2000.
5. Shea S. L., Bould J., Londesborough M. G. S., Perera S. D., Franken A., Ormsby D. L., Jelínek T., Štíbr B., Holub J., Kilner C. A., Thornton-Pett M., Kennedy J. D.: *Pure Appl. Chem.* **2003**, 75, 1239.
6. Londesborough M. G. S., MacLean E. J., Teat S. J., Bould J., Kilner C. A., Thornton-Pett M., Kennedy J. D.: *Boron Chemistry at the Beginning of the 21st Century* (Yu. Bubnov, Ed.), p. 248. Editorial URSS, Moscow 2003.
7. Shea S. L., Perera S. D., Bould J., Franken A., Jelínek T., Kennedy J. D., Kilner C. A., Londesborough M. G. S., Thornton-Pett M.: *Boron Chemistry at the Beginning of the 21st Century* (Yu. Bubnov, Ed.), p. 27. Editorial URSS, Moscow 2003.
8. Jelínek T., Kennedy J. D., Štíbr B.: *J. Chem. Soc., Chem. Commun.* **1994**, 1415.
9. Dosangh P. K., Bould J., Londesborough M. G. S., Jelínek T., Thornton-Pett M., Štíbr B., Kennedy J. D.: *J. Organomet. Chem.* **2003**, 680, 312.
10. Kaur P., Thornton-Pett M., Clegg W., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* **1996**, 4155.
11. Jelínek T., Kilner C., Thornton-Pett M., Kennedy J. D.: *Chem. Commun.* **1999**, 1905.
12. Kaur P., Holub J., Rath N. P., Bould J., Barton L., Štíbr B., Kennedy J. D.: *Chem. Commun.* **1996**, 273.
13. Jelínek T., Kennedy J. D., Štíbr B., Thornton-Pett M.: *Inorg. Chem. Commun.* **1998**, 1, 179.
14. Jelínek T., Kennedy J. D., Štíbr B., Thornton-Pett M.: *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1599.
15. Ormsby D. L., Greatrex R., Kennedy J. D.: *Dalton Trans. (K. Wade Special Edition)* **2008**, 1625.
16. Jelínek T., Císařová, Štíbr B., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans. (Dalton Commun.)* **1998**, 2965.
17. X-ray data. Compound **1a**: $C_{14}H_{36}B_{16}N_2S_3$; $M = 469.53$, triclinic ($0.2 \times 0.02 \times 0.01$ mm, yellow needle from $CH_3(CH_2)_3CH_3/CD_2Cl_2CH_2Cl_2$), space group $P\bar{1}$, $a = 8.9490(15)$ Å, $b = 12.665(2)$ Å, $c = 13.190(2)$ Å, $\alpha = 71.430(2)^\circ$, $\beta = 89.683(2)^\circ$, $\gamma = 69.523(2)^\circ$, $U = 1318.1(4)$ Å³, $D_{calc} = 1.183$ mg m⁻³, $Z = 2$, $\lambda = 0.6814$ Å (synchrotron, wiggler-generated, Station 9.8, UK National SRS facility, Daresbury)¹⁸, $\mu = 0.211$ mm⁻¹, $T = 150(2)$ K, $R_1 = 0.0722$ for 2805 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.2152$ for all data. Methods and programs were standard (Sheldrick G. M.: *SHELX97. Acta Crystallogr., Sect. A* **2008**, 64, 112; Sheldrick G. M.: *SHELXTL Manual*. Bruker AXS Inc., Madison (WI) 1994 and 1998; Farrugia L. J.: *ORTEP-3 J. Appl. Crystallogr.* **1997**, 30, 565). CCDC deposition number 779102.
18. Cernik R. J., Clegg W., Catlow C. R. A., Bushnell-Wye G., Flaherty J. V., Greaves G. N., Burrows I., Taylor D. J., Teat S. J., Hamichi M.: *J. Synchrotron Radiat.* **1997**, 4, 279.
19. NMR data. ¹¹B and ¹H NMR chemical shifts for the $[S_2B_{16}H_{17}]^-$ anion **1**, measured as its [tmdH]⁺ salt in CD_2Cl_2 at 300 K; ordered as assignment, $\delta(^{11}B)$ in ppm relative to

- [BF₃(OEt₂)] ($\delta(^1\text{H})$ in ppm relative to TMS of directly attached *exo*-hydrogen atoms in square brackets): BH(2) +16.7 [+4.48], B(6) +8.8 [*conjuncto* position, no *exo*-H], BH(3') +4.7 [+1.40], BH(8) +2.9 [+3.33], BH(4) +1.5 [+3.23], BH(1') -5.0 [+2.78], BH(6') -8.2 [+2.54], BH(5') -11.2 [+2.35], BH(10) -17.9 [+1.69], BH(1) -19.0 [+1.56], B(7) -25.3 [*exo*-sulfur-bound position, no *exo*-H], BH(3) -26.9 [+1.03], BH(5) -30.9 [+1.45], BH(2') -32.6 [+1.21], BH(7') -32.6 [+ 0.71] and BH(4') -34.3 [+ 0.80], with $\delta(^1\text{H})$ for $\mu\text{H}(3',4')$ -0.38, $\mu\text{H}(6',7')$ -1.08 and $\mu\text{H}(5,10)$ -1.62 ppm. Assignments by [¹¹B-¹H]-{¹H(broadband)}-COSY, [¹H-¹H]-{¹¹B(broadband)}-COSY and ¹H-¹¹B (selective) multiple resonance experiments.
20. Carr M. J., Londesborough M. G. S., Hamilton Mcleod A. R., Kennedy J. D.: *Dalton Trans. (Dalton Commun.)* **2006**, 3624.
 21. Bould J., Clegg W., Kennedy J. D., Teat S. J.: *J. Chem. Soc., Dalton Trans.* **1998**, 2777.
 22. Cheek Y. M., Greenwood N. N., Kennedy J. D., McDonald W. S.: *J. Chem. Soc., Chem. Commun.* **1982**, 80.
 23. McGrath T. D., Kennedy J. D., McInnes Y. M., Thornton-Pett M. in: *Advances in Boron Chemistry* (W. Siebert, Ed.), p. 480. Royal Society of Chemistry, Cambridge 1997.
 24. Carr M. J., Londesborough M. G. S., Bould J., Císařová I., Kennedy J. D.: *Collect. Czech. Chem. Commun.* **2005**, 70, 430.