

[Et₄N][7-Me₂S-*nido*-B₁₁H₁₂]Jonathan Bould,^{a*} Raikko Kivekäs,^b Reijo Sillanpää,^c
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Tetraethylammonium 7-dimethylsulfanyl-*nido*-dodecahydro-undecaborate, [Et₄N][7-Me₂S-*nido*-B₁₁H₁₂] or C₈H₂₀N⁺·C₂H₁₈B₁₁S⁻, is a product of the deprotonation of [7-Me₂S-*nido*-B₁₁H₁₃] with KHBET₃ and precipitation with tetraethylammonium chloride. The effect of removing one *endo*-terminal H atom is to cause a general contraction of the open-face B–B distances.

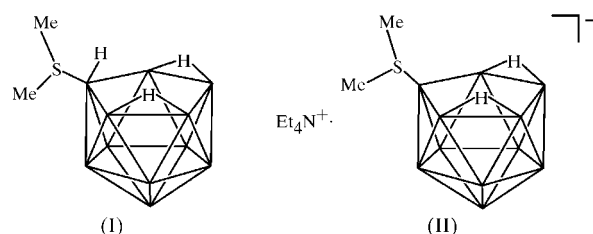
Comment

There is currently some interest in the modification of the catalytic properties of transition metals held on dicarborene clusters by the introduction of cluster substituent groups at boron or carbon cluster vertices (Teixidor *et al.*, 1996, 2000; Tutusaus *et al.*, 2002). Thus, for example, addition of an R₂S group to an open-face boron vertex in [C₂B₉H₁₁]²⁻ leads to the monoanionic dicarbollide [10-R₂S-7,8-C₂B₉H₁₀]⁻, from which metallocarborenes, such as [3-RuH(PPh₃)₂-8-R₂S-7,8-C₂B₉H₉], may be formed (Tutusaus *et al.*, 2002).

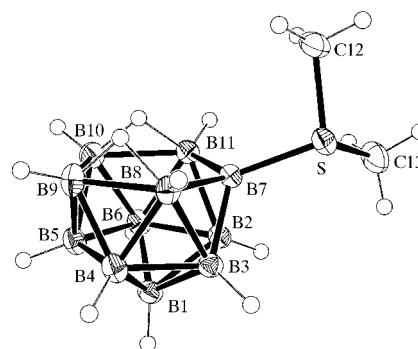
It is of interest to extend this work to binary borane compounds with substituents such as Me₂S on the five-membered open face, as in [Me₂SB₁₁H₁₃], (I) [see *Scheme* and Keller *et al.* (1993)]. Double deprotonation of this cluster, together with simultaneous Me₂S loss, is known to give K₂[*closo*-B₁₁H₁₁] in high yield (Volkov *et al.*, 1999), from which a variety of substituted *nido*-undecaborate anions may be synthesized (Volkov *et al.*, 2001). In the preparation of K₂[*closo*-B₁₁H₁₁], we obtained an occasional by-product, *viz.* K[7-Me₂S-*nido*-B₁₁H₁₂], to which the addition of aqueous [Et₄N]Cl afforded the title compound, [Et₄N][7-Me₂S-*nido*-B₁₁H₁₂], (II) (see *Scheme* and Fig. 1). ¹¹B NMR spectra of (II) feature a 2:2:2:2:1 relative intensity pattern rather than the 2:2:2:2:1:1:1 pattern expected for a *nido* 11-vertex cluster with C_s symmetry, due to coincidental overlap of the resonances due to B7 and B5, which inhibited the complete character-

ization of (II). We therefore carried out a single-crystal X-ray diffraction study of (II), which is reported here.

The clusters in (I) and its conjugate anion, (II), contain pseudo-mirror planes through atoms B1, B5 and B7, such that the interatomic B7–B2/B7–B3, B7–B8/B7–B11 and B8–B9/B10–B11 pairs of distances are equal within experimental error (Table 1). Therefore, for comparison purposes in this discussion, average values are given. The Me₂S ligand, which rotates freely in solution, lies off the pseudo-mirror plane.



The main effect of deprotonation on interatomic separations in (II) is seen for the upper-belt open-face B atoms, with the average B–B distance shrinking from 1.904 to 1.822 Å. The largest change is for distances associated with the B7 vertex, the site of the removed *endo*-terminal H atom. Thus, the B7–B8/B11 distances contract markedly by ~0.19 Å, from 1.943 (4) Å in (I) to 1.754 (3) Å in (II). There is a smaller 0.018 Å contraction of the B7–B2/B3 distance in the lower-belt vertices [from 1.762 (4) to 1.744 (3) Å]. The B9–B10 distance also exhibits a contraction of 0.046 Å, whereas the H-atom-bridged B10–B11 and B8–B9 edges slightly increase by 0.04 Å, from 1.853 (3) to 1.892 (3) Å. The shortening of the B7 vertex may be ascribed to its more intimate intracuster bonding. On deprotonation, the electron pair and the associated orbital in the *endo*-terminal B7–H bond become involved in direct cluster bonding. A similar, albeit smaller, effect may be noted in the formally isoelectronic isostructural pair [B₁₁H₁₄]⁻ and [B₁₁H₁₃]²⁻ (Getman *et al.*, 1988; Fitchie, 1967), *viz.* 1.89 to 1.80 Å for B7–B8/B11. This effect may also be reflected in the decrease of the S–B7 distance, 1.910 (3) to 1.8829 (19) Å, and in the upward tilt of the S–B7 vector towards the plane of the open-face atoms

**Figure 1**

The anion in (II), with displacement ellipsoids shown at the 50% probability level.

defined by the centroid of the B7/B8/B9/B10/B11 ring [from 164.2° in (I) to 154.0° in (II)]. There may be some additional steric relief as the Me₂S group rotates to allow a methyl group to fill the vacancy created by the loss of the H atom.

Compound (II) may be directly compared with its isostructural analogue [NBzEt₃][7-(C₅H₄N)-*nido*-B₁₁H₁₂], (III) (Volkov *et al.*, 2001), in which the ligand is a pyridine group. There are no significant differences in the cluster interatomic dimensions between the two molecules. The bridging-H-atom asymmetry that is often observed in boron hydrides (Beaudet, 1988) and has been noted for (I) and (III) is mirrored in (II), with the long B—H(bridge) distance [1.32 (2) Å] being towards the B7 vertex.

Finally, we note that the *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalenide salt of (II) may be obtained more conveniently and in high yield by deprotonation of (I) with the mild non-nucleophilic base *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalene.

Experimental

Compound (II) was obtained in an experiment to produce K₂[B₁₁H₁₁], using the method of Volkov *et al.* (1999), in which a reduced yield of the target compound was obtained. A pale-yellow residue, remaining after filtering off the solid K₂[B₁₁H₁₁] product and reducing the filtrate to dryness, was extracted with two aliquots of diethyl ether. ¹¹B NMR spectrometry of the first aliquot showed it to be predominantly one compound, together with a small amount of K₂[B₁₁H₁₁]. After removal of ether, a white powder was obtained (19% based on K[Me₂SB₁₁H₁₂]), a portion of which was dissolved in water and added to a solution of [Et₄N]Cl·xH₂O to yield compound (II). Colourless single crystals were grown by hexane diffusion into a CD₂Cl₂ solution of the compound. The second aliquot was almost pure K₂[B₁₁H₁₁]. The *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalenide salt of (II) can be produced directly by addition of *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalene (proton sponge) to (I) dissolved in a minimum of CHCl₃. Crystals of the compound drop out of solution overnight. Analysis for (II); ¹¹B NMR [p.p.m., 96.3 MHz, CD₂Cl₂, 298 K; assignment by comparison with (III) (Volkov *et al.*, 2001), for which the chemical shift values are shown in square brackets]: B7/5 -7.9 [+3.4, -11.5], B2/3 -13.3 [-12.3], B8/11 -17.7 [-18.7], B9/10 -23.3 [-24.7], B1 -29.1 [-29.1], B4/6 -30.1 [-31.6]; ¹H (with relative intensities in parentheses): δ +1.76 (1), +1.32 (4), +0.83 (1), +0.69 (1) +0.39 (3), -4.90 (2) and +2.46 (6). The measured ¹¹B and ¹H NMR spectra for both compounds show very similar chemical shift values, except for the resonance due to the B7 vertex, which is shifted to a higher field by -11.3 p.p.m. The resonance due to the antipodal B5 vertex also moves slightly to a higher field (-2.6 p.p.m.).

Crystal data

C₈H₂₀N⁺·C₂H₁₈B₁₁S⁻
M_r = 323.38
 Monoclinic, *P*2₁/*c*
a = 10.5939 (3) Å
b = 11.7359 (3) Å
c = 16.9528 (4) Å
 β = 101.666 (1)°
V = 2064.18 (9) Å³
Z = 4

D_x = 1.041 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3666 reflections
 θ = 1.0–25.0°
 μ = 0.15 mm⁻¹
T = 173 (2) K
 Needle, colourless
 0.32 × 0.22 × 0.12 mm

Table 1

Selected interatomic distances (Å).

S—C12	1.7904 (19)	B4—B8	1.793 (3)
S—C13	1.7881 (19)	B4—B9	1.782 (3)
S—B7	1.8829 (19)	B5—B9	1.760 (3)
B1—B2	1.776 (3)	B5—B6	1.775 (3)
B1—B3	1.769 (3)	B5—B10	1.757 (3)
B1—B4	1.792 (3)	B6—B10	1.786 (3)
B1—B5	1.754 (3)	B6—B11	1.794 (3)
B1—B6	1.794 (3)	B7—B8	1.750 (3)
B2—B3	1.757 (3)	B7—B11	1.758 (3)
B2—B6	1.788 (3)	B8—B9	1.888 (3)
B2—B7	1.743 (3)	B9—B10	1.884 (3)
B2—B11	1.791 (3)	B10—B11	1.895 (3)
B3—B4	1.783 (3)	B8—H9B	1.34 (2)
B3—B7	1.746 (3)	B9—H9B	1.20 (2)
B3—B8	1.815 (3)	B10—H10B	1.21 (2)
B4—B5	1.788 (3)	B11—H10B	1.30 (2)

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 6232 measured reflections
 3628 independent reflections
 2821 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.033
 θ_{max} = 25.0°
h = -12 → 12
k = -13 → 12
l = -20 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.096
S = 1.03
 3628 reflections
 256 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 0.8016P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.18 e Å⁻³
 Δρ_{min} = -0.23 e Å⁻³

Cluster H atoms were located *via* Fourier difference syntheses, with positional and isotropic displacement parameters freely refined and B—H(terminal) distances in the range 1.084 (18)–1.140 (18) Å. H atoms attached to the C atoms of the cation were treated using *SHELXL97* (Sheldrick, 1997) defaults. Methyl groups in the dimethylsulfanyl cluster substituent and the ethyl groups of the cation were included in calculated positions, with a refined rotational parameter for each methyl or ethyl group and *U*_{iso} values of 1.2–1.5 times the *U*_{eq} value of the parent C atom.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1164). Services for accessing these data are described at the back of the journal.

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