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Diborane(4) compounds incorporating thio- and seleno-carboranyl groups

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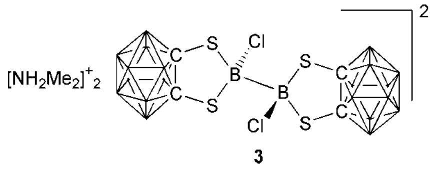
The reaction between $B_2(NMe_2)_4$ and the carborane dithiol $C_2B_{10}H_{10}(SH)_2$, followed by addition of HCl affords the $[NH_2Me_2]^+$ salt of the dianion $[B_2Cl_2(S_2C_2B_{10}H_{10})_2]^{2-}$, which has been characterised by X-ray crystallography. A similar reaction utilising the carborane diselenol $C_2B_{10}H_{10}(SeH)_2$ (generated *in situ*) afforded a compound containing the dianion $[B_2(Se_2C_2B_{10}H_{10})_3]^{2-}$.

A renewed interest in diborane(4) compounds in recent years owes much to the development of transition metal catalysed diboration chemistry.[1] Despite this interest, the chemical and structural diversity of known diborane(4) compounds remains relatively modest.[2] Key compound types include the boron(II) halides,[3] amido species[4] including $B_2(NMe_2)_4$[5] (**1**) and 1,2-$B_2Cl_2(NMe_2)_2$,[6] diolate derivatives, particularly $B_2(pin)_2$ (pin = pinacolate)[7] and $B_2(cat)_2$ (cat = 1,2-$O_2C_6H_4$),[8] and thiolate compounds such as $B_2(1,2\text{-}S_2C_6H_4)_2$ (**2**).[8] Other examples include a variety of alkyl- and aryl-substituted species,[9] phosphino and arsino compounds,[10] as well as a small number of triborane(5) and tetraborane(6) derivatives.[11] Of the many known modes of reactivity,[2] the one most relevant to this study is the Lewis acidity of many of these species, which results in mono- or bis-ligand complexes $[B_2R_4(L)_x]$ ($x = 1, 2$) with suitable donor ligands;[12] included in this class are compounds such as $[B_2Cl_6]^{2-}$[6] and $[B_2(NCS)_6]^{2-}$.[13] We note also species of the form $[R_2B–BHR_2]^-$ and $[R_2HB–BHR_2]^{2-}$ reported by Grigsby and Power, obtained from reactions involving reduction of diborane(4) compounds.[14]

The reaction between **1** and two equivalents of the carborane dithiol $C_2B_{10}H_{10}(SH)_2$ (generated *in situ* by acidification of the dianion $[C_2B_{10}H_{10}S_2]^{2-}$)[15] in Et_2O, followed by addition of HCl in Et_2O afforded, after work-up, a crystalline material identified by X-ray crystallography as $[NH_2Me_2]_2[B_2Cl_2(S_2C_2B_{10}H_{10})_2]$ (**3**)†,‡. Spectroscopic and analytical data were in accord with this formulation although the ^{11}B signal at 41.3 ppm in acetonitrile solution is more consistent with a neutral diborane(4) compound (*i.e.* $B_2(S_2C_2B_{10}H_{10})_2$) rather than a chloride adduct, indicating that some chloride dissociation may have occurred†.[8] In the solid state, compound **3** comprises $[NH_2Me_2]^+$ cations and two crystallographically independent but geometrically similar $[B_2Cl_2(S_2C_2B_{10}H_{10})_2]^{2-}$ dianions; the structure of one of the latter is shown in Fig. 1. Each diborane(4) dianion resides on a crystallographic centre of inversion and comprises a B–B unit in which each boron is bonded to a chlorine atom and a chelating (*i.e.* 1,1-) *ortho*-$C_2B_{10}H_{10}S_2$ carborane dithiolate group. All angles around each boron centre are close to ideal tetrahedral values and an *anti* conformation about the B–B bond is observed as required for the crystallographic inversion centre. The B–B [B(1)–B(1′) 1.72(2), B(2)–B(2′) 1.765(12) Å] and B–S [B(1)–S(1) 1.956(8), B(1)–S(2) 1.919(8), B(2)–S(3), 1.926(10), B(2)–S(4), 1.937(11) Å] distances are all similar to those found in the adducts of **2**, *viz.* $[B_2(1,2\text{-}S_2C_6H_4)_2(L)_2]$[12] [L = 4-picoline: B–B 1.715(10), B–S 1.910(5) 1.913(5) Å; L = PMe_2Ph: B–B 1.750(4), B–S 1.928(2) 1.930(2) Å]. The B–Cl lengths [B(1)–Cl(1) 1.972(9), B(2)–Cl(2) 1.986(6) Å] are long but fall within the range observed for $[BCl_4]^-$ structures [1.790–1.986 Å].



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The formation of **3** most likely proceeds *via* formation of the intermediate amine adduct $[B_2(S_2C_2B_{10}H_{10})_2(NHMe_2)_2]$ (**4**) in the initial reaction between **1** and the carborane dithiol according to eqn. (1),†

$$B_2(NMe_2)_4 + 2C_2B_{10}H_{10}(SH)_2 \rightarrow [B_2(S_2C_2B_{10}H_{10})_2(NHMe_2)_2]\ (\mathbf{4}) + 2NHMe_2 \quad (1)$$

such amine adducts having been observed previously in reactions between **1** and diols and dithiols.[8,17] Subsequent addition of HCl is sufficient to remove any amine (whether coordinated or not to the boron centre) as the ammonium chloride $[NH_2Me_2]Cl$ but the Lewis acidity of the boron centres in the parent diborane(4) species $[B_2(S_2C_2B_{10}H_{10})_2]$ is presumably sufficient to scavenge chloride, affording the dianionic dichloride adduct observed in solid **3**. However, ^{11}B NMR data indicate (see above†) that uncomplexed $[B_2(S_2C_2B_{10}H_{10})_2]$ may be present in solution. The Lewis acidity of the thiocatecholate species **2** is well documented[12] although chloride retention in the manner seen here was not observed for **2**.§

An analogous reaction between **1** and the carborane selanol $C_2B_{10}H_{10}(SeH)_2$ was also carried out although spectroscopic

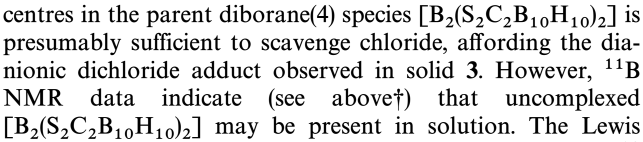

Fig. 1 A view of the structure of one of the $[B_2Cl_2(S_2C_2B_{10}H_{10})_2]^{2-}$ diborane(4) dianions in **3**. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°) include: B(1)–B(1′) 1.72(2), B(2)–B(2′) 1.765(12), B(1)–S(1) 1.956(8), B(1)–S(2) 1.919(8), B(2)–S(3) 1.926(10), B(2)–S(4) 1.937(11), B(1)–Cl(1) 1.972(9), B(2)–Cl(2) 1.986(6); B(1a)–B(1)–Cl(1) 106.4(6), B(1′)–B(1)–S(1) 110.7(7), B(1′)–B(1)–S(2) 113.7(7), Cl(1)–B(1)–S(1) 107.9(4), Cl(1)–B(1)–S(2) 110.1(4), S(1)–B(1)–S(2) 108.0(4), B(2′)–B(2)–Cl(2) 107.1(5), B(2′)–B(2)–S(3) 111.8(8), B(2′)–B(2)–S(4) 112.5(8), Cl(2)–B(2)–S(3) 109.4(4), Cl(2)–B(2)–S(4) 108.1(5), S(3)–B(2)–S(4) 107.9(3).

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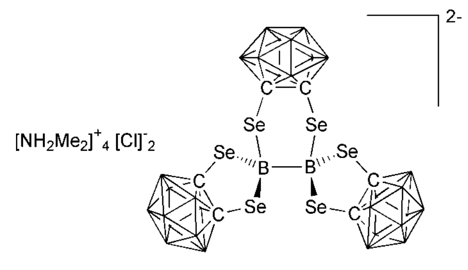

5

and analytical data indicated that more than one species had been formed. Crystals of one compound were isolated, however¶ which were identified by X-ray crystallography|| as the complex salt $[NH_2Me_2]_4[Cl]_2[B_2(Se_2C_2B_{10}H_{10})_3]$ (**5**) comprising $[NH_2Me_2]^+$ cations, chloride anions and the diborane(4) dianion $[B_2(Se_2C_2B_{10}H_{10})_3]^{2-}$. The diborane(4) dianion in **5** is shown in Fig. 2 and consists of a diboron unit in which each boron is bonded to a carborane diselenide group in a 1,1-fashion with the B–B bond bridged by a third carborane diselenide group (*i.e.* 1,2-). The B–B distance is 1.55(2) Å and the B–Se bond lengths range from 2.063(13) to 2.19(2) Å. The B–B distance is shorter than those observed in other structures containing linked tetrahedral boron centres[12] and is probably an artefact of libration/disorder as indicated by elongated displacement ellipsoids of the central atoms, particularly B(1) and B(2). Few B–Se distances are available for comparison but with the exception of carborane cages incorporating Se atoms, distances range from 1.965–2.079 Å.[18] The conformation about the B–B bond is close to staggered [for example, torsion angles Se(1)–B(1)–B(2)–Se(3) 174.1(7), Se(1)–B(1)–B(2)–Se(4) 53.3(14), Se(1)–B(1)–B(2)–Se(6) −56.3(11)°]. The boron atoms are tetrahedral with no angles deviating substantially from ideal values.

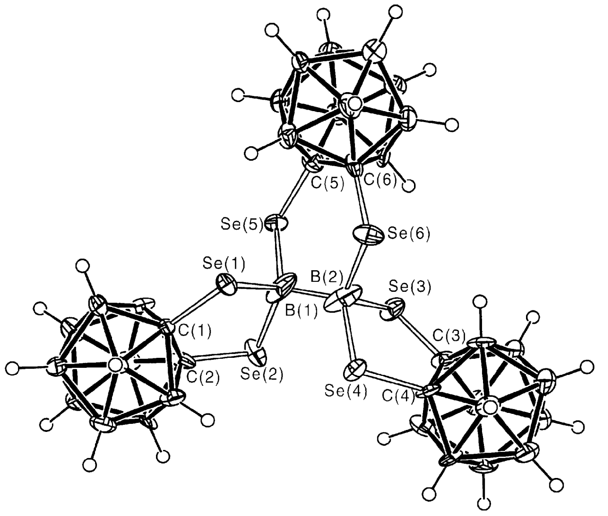

Fig. 2 A view of the structure of the $[B_2(Se_2C_2B_{10}H_{10})_3]^{2-}$ dianion in **5**. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°) include: B(1)–B(2) 1.55(2), B(1)–Se(1) 2.063(13), B(1)–Se(2) 2.19(2), B(1)–Se(5) 2.112(12), B(2)–Se(3) 2.092(15), B(2)–Se(4) 2.134(13), B(2)–Se(6) 2.13(2); B(2)–B(1)–Se(1) 113.0(10), B(2)–B(1)–Se(2) 107.7(10), B(2)–B(1)–Se(5) 110.2(9), Se(1)–B(1)–Se(2) 108.6(7), Se(1)–B(1)–Se(5) 114.5(6), Se(2)–B(1)–Se(5) 102.1(6), B(1)–B(2)–Se(3) 113.4(10), B(1)–B(2)–Se(4) 113.1(10), B(1)–B(2)–Se(6) 107.2(10), Se(3)–B(2)–Se(4) 106.0(6), Se(3)–B(2)–Se(6) 116.2(8), Se(4)–B(2)–Se(6) 100.3(6).

In conclusion, we note the following points: (i) a thiocarborane substituted diborane(4) compound is sufficiently Lewis acidic to scavenge chloride (a feature not hitherto observed in related thiolate systems) and the resulting salt can be isolated in reasonable yield and (ii) diborane(4) dianions incorporating selenocarboranyl groups have been isolated, albeit only in low yield, for the first time.

Acknowledgements

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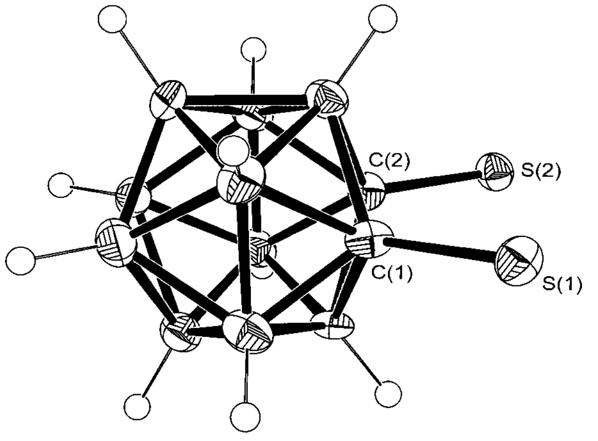
Notes and references

† The dilithium salt of the thiocarboranyl dianion $Li_2[S_2C_2B_{10}H_{10}]$ was prepared as described in ref. 15 although the dithiol, $[(C_2B_{10}H_{10}(SH)_2]$, was generated *in situ* by addition of a solution of HCl in Et_2O rather than by simple hydrolysis with H_2O as detailed in ref. 15. To a solution of $[(C_2B_{10}H_{10}(SH)_2]$ (0.30 g, 1.45 mmol) in Et_2O (10 cm^3), a solution of **1** (0.14 g, 0.725 mmol) in Et_2O (10 cm^3) was added and the resulting mixture stirred for 15 h during which time a white precipitate formed of the bis-amine adduct $[B_2(S_2C_2B_{10}H_{10})_2(NHMe_2)_2]$ (**4**).[8] After allowing the precipitate to settle, the solvent was removed by syringe and the solid washed with Et_2O (3 × 5 cm^3) and hexanes (3 × 10 cm^3), after which it was suspended in Et_2O (20 cm^3). A solution of HCl (1.44 cm^3 of a 1 M solution in Et_2O) was then added and the mixture stirred for 2 h. Filtration afforded a colourless filtrate, which was reduced in volume to *ca.* 7 cm^3 to which a small volume of CH_2Cl_2 was added. Addition of an overlayer of hexanes (10 cm^3) and subsequent solvent diffusion at room temperature over a period of days afforded colourless crystals of **3** (recrystallised yield 50%).

Spectroscopic data for **4** (unrecrystallised) ^{11}B NMR chemical shifts are reference to $BF_3 \cdot OEt_2$; positive values to high frequency: NMR (CD_3CN): ^{1}H δ 6.91 (br s, 2H, NH), 2.60 (br s, 12H, Me_2NH), 3.10–1.68 (br m, 20H, BH); ^{11}B-{^{1}H} δ 7.2 (B_2 unit), −4.5, −11.3, −13.9 (B_{10} units). $C_8H_{34}B_{22}N_2S_4$ requires C, 18.3; H, 6.5; N, 5.3. Found C, 20.4; H, 6.9; N, 7.1%.

Spectroscopic data for **3**: NMR (CD_3CN): ^{1}H δ 7.51 (br m, 4H, NH_2), 2.54 (t, 12H, Me_2NH_2), 2.6–1.9 (br m, 20H, BH); ^{11}B-{^{1}H} δ 41.3 (B_2 unit), −.6, −10.3, −11.8 (B_{10} units). $C_8H_{36}B_{22}Cl_2N_2S_4$ requires C, 16.1; H, 6.1; N, 4.7. Found C, 15.1; H, 6.1; N, 4.1%.

During the course of this reaction, a few crystals of the salt $[NH_2Me_2]_2[S_2C_2B_{10}H_{10}]$ as a MeCN solvate containing the thiocarboranyl dianion[15] were isolated and characterised by X-ray crystallography. This compound is not discussed in the text but selected crystal data are reported here and full data have been deposited. Crystal data for $[NH_2Me_2]_2[S_2C_2B_{10}H_{10}]$: $M = 339.56$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.209(4)$, $b = 8.974(4)$, $c = 19.784(9)$ Å, $\beta = 94.14(4)°$, $U = 1984.8(14)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.262 mm^{-1}, 11 867 reflections measured, 4503 unique ($R_{int} = 0.168$), final $R_1 = 0.0931$. A comparison of the C–S and C–C distances for the $[S_2C_2B_{10}H_{10}]^{2-}$ anion [S–C 1.753(5), 1.766(5) and C–C 1.844(7) Å] and **3** [S–C 1.800(8)–1.809(8) and C–C 1.680(8), 1.628(10) Å] reveals that the S–C distances are slightly shorter in the free thiocarborane dianion whereas the C–C distance is correspondingly longer. The structure of $[S_2C_2B_{10}H_{10}]^{2-}$ is shown below.



‡ Crystal data for $[NH_2Me_2]_2[B_2Cl_2(S_2C_2B_{10}H_{10})_2]$ (**3**): $M = 597.35$, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.683(3)$ $b = 22.229(5)$, $c = 10.367(4)$ Å, $\beta = 90.485(14)°$, $U = 3153.0(15)$ Å^3 $T = 173(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.480 mm^{-1}, 19667 reflections measured, 7015 unique ($R_{int} = 0.118$), final $R_1 = 0.079$. Data for **3** (and **5** and $[NH_2Me_2]_2[S_2C_2B_{10}H_{10}]$) were collected on a Bruker SMART-CCD detector and the structure was solved and refined against F^2 using SHELXL97.[16] Hydrogen atoms were attached in idealised positions. CCDC reference number 440/210. See http://www.rsc.org/suppdata/nj/b0/b004942p/ for crystallographic files in .cif format.

§ All diborane(4) B_2R_4 compounds contain three-coordinate boron centres that are Lewis acidic to some degree, the acidity depending on the nature of the substituents. In the examples we have previously studied, thiolate derivatives are always more Lewis acidic than diolate examples, presumably due to the reduced efficiency of B–S *vs.* B–O π-bonding and resulting population of the formally vacant B 2p orbital.[12]

¶ The reaction from which crystals of **5** were obtained was performed in the same manner as described for **3** with the following differences. The diselanol $[(C_2B_{10}H_{10}(SeH)_2]$ used here was generated *in situ* from the diselanide salt $Li_2[Se_2C_2B_{10}H_{10}]$ itself prepared as described in ref. 15 for the dithiolate but using elemental selenium rather than sulfur and a THF–Et_2O solvent mixture. Spectroscopic and elemental analysis of the final solid product(s) indicated impure material; ^{11}B NMR data were consistent with the presence of diborane(4) species whilst mass spectrometric analysis indicated the presence of the oxidatively coupled selenocarborane product $\{Se_2C_2B_{10}H_{10}\}_2$ (*m*/*z* 600 with correct isotope pattern).

‖ Crystal data for $[NH_2Me_2]_4[Cl]_2[B_2(Se_2C_2B_{10}H_{10})_3]$ (**5**): $M = 1177.26$, monoclinic, space group $P2_1/c$ (No. 14), $a = 19.521(6)$, $b = 21.945(5)$, $c = 11.965(2)$ Å, $\beta = 103.803(14)°$, $U = 4977.5(21)$ Å^3, $T = 173(2)$ K, $Z = 4$, μ(Mo-Kα) = 4.451 mm^{-1}, 25 918 reflections measured, 8697 unique ($R_{int} = 0.088$), final $R_1 = 0.0674$.

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