Macropolyhedral Boron-containing Cluster Chemistry—The Nineteen-vertex Oxaborane Anion, $[OB_{18}H_{21}]^-$†

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The first structurally characterised polyhedral oxaborane species, the macropolyhedral anion $[OB_{18}H_{21}]^-$, has been isolated (30–35%) from the reaction of water with the products of the reaction between *anti*-$B_{18}H_{22}$ and either Na or $Na[BH_4]$ in THF; the structure is based on the *anti*-$B_{18}H_{22}$ type of macropolyhedral cluster, with an oxygen atom between the B(8) and B(9) positions.

Of the pure first-row heteroboranes, the carbaboranes, particularly the dicarbaboranes, are very well examined.[1] Other first-row heteroboranes are much rarer, although some beryllaboranes are known,[2] and azaborane chemistry is now becoming established.[3,4] For oxygen as heteroatom, only one oxaborane, the twelve-vertex $[OB_{11}H_{12}]^-$ anion, has been reasonably claimed,[5] but not yet substantiated by structural work. There are three known oxametallaboranes, all established by single-crystal X-ray work.[6–8] In only one of these, twelve-vertex $[(C_5Me_5)RhOB_{10}H_9Cl(PMe_2Ph)]$,[7] is the oxygen atom contiguously bound to boron atoms only. We now report the isolation and structural characterization of the contiguous oxaborane anion $[OB_{18}H_{21}]^-$.

Reaction of *anti*-$B_{18}H_{22}$ with excess sodium metal and a small quantity of naphthalene in THF at reflux for 48 h was followed by filtration and addition of water. The THF was evaporated and the resultant aqueous solution treated with aqueous $[PPh_4]Cl$ to yield a yellow precipitate. This was filtered and dried, and subjected to column chromatography on silica in air using CH_2Cl_2–MeCN 6 : 1 as liquid phase, to yield orange $[PPh_4]^+[$*anti*-$B_{18}H_{21}]^-$ (62%; identified[11] by NMR spectroscopy) and yellow $[PPh_4]^+[OB_{18}H_{21}]^-$ (35%). In an alternative procedure, the reaction of *anti*-$B_{18}H_{22}$ with $Na[BH_4]$ in THF at reflux for 3 d, followed by evaporation of the THF, dissolution in 5% aqueous $K_2[CO_3]$, filtration, and addition of aqueous $[PPh_4]Cl$ to the filtrate, yielded a yellow precipitate as above; chromatography thence yielded $[PPh_4]^+[$*anti*-$B_{18}H_{21}]^-$ (47%) and $[PPh_4]^+[OB_{18}H_{21}]^-$ (30%). The yellow oxaborane salt $[PPh_4]^+[OB_{18}H_{21}]^-$ was characterised by NMR spectroscopy‡ and identified by single-crystal X-ray diffraction analysis (Fig. 1).§

These reactions were carried out with the idea of generating $[B_{18}H_{22}]^{2-}$ in analogy to the classical[12] *nido* → *arachno* reduction of $B_{10}H_{14}$ that gives the $[B_{10}H_{14}]^{2-}$ anion. A simple stoichiometry, [Eqn. (1)] could thence be written down for the generation of the $[OB_{18}H_{21}]^-$ anion from $[B_{18}H_{22}]^{2-}$ and H_2O.

$$[B_{18}H_{22}]^{2-} + 2H_2O \rightarrow [OB_{18}H_{21}]^- + OH^- + 2H_2 \quad (1)$$

The structure of the $[OB_{18}H_{21}]^-$ anion (Fig. 1 and cluster schematic **I**) is seen to be based on neutral *anti*-$B_{18}H_{22}$ (cluster schematic **II**),[13] with, in one subcluster, an oxygen atom in a position approximating to that occupied by the μ-8,9 bridging hydrogen atom in the neutral boron hydride model: geometrically this oxaborane subcluster could be regarded either as a *nido* ten-vertex subcluster with an oxygen bridge, or as an *arachno*-type eleven-vertex $\{OB_{10}\}$ subcluster. The compound crystallises in space group *P*2/*c* so that the cation and the anionic cluster species possess crystallographic C_2 and 1 symmetry respectively. Since the oxaborane cluster must be asymmetric, the crystallographic centre of symmetry mutually disorders the cluster oxygen atom with a bridging hydrogen atom over two positions that are related by the centre of symmetry [bridging B(8)B(9) and B(8′)B(9′), see Fig. 1]. Any cluster asymmetry brought about by the presence of the cluster oxygen atom is therefore averaged over the two ten-vertex subclusters and detailed structural comparisons are thus precluded. It is however reasonably apparent that the oxygen-bridged interboron distance B(8)–B(9) is not markedly different from a conventionally hydrogen-bridged interboron distance. It is therefore clearly much shorter than the otherwise corresponding non-bonding B(5)–B(6) distance of 269(2) pm[14] in, for example, the phosphorus-bridged species μ-5,6-$(PPh_2)B_{10}H_{13}$. This shorter distance suggests a three-centre two-electron bond joining the B(8), B(9) and oxygen atoms, rather than two two-electron two centre bonds, one from each of B(8) and B(9) to oxygen. These considerations suggest that the $\{OB_{10}\}$ subcluster may perhaps therefore be better regarded as a contiguous eleven-vertex *arachno*-type oxaborane unit rather than a ten-vertex *nido* decaboranyl entity that is bridged.

It has often been surmised that contiguous oxaborane species might, in the general case, be inherently unstable, and that otherwise reasonable entries into the area might be fraught with

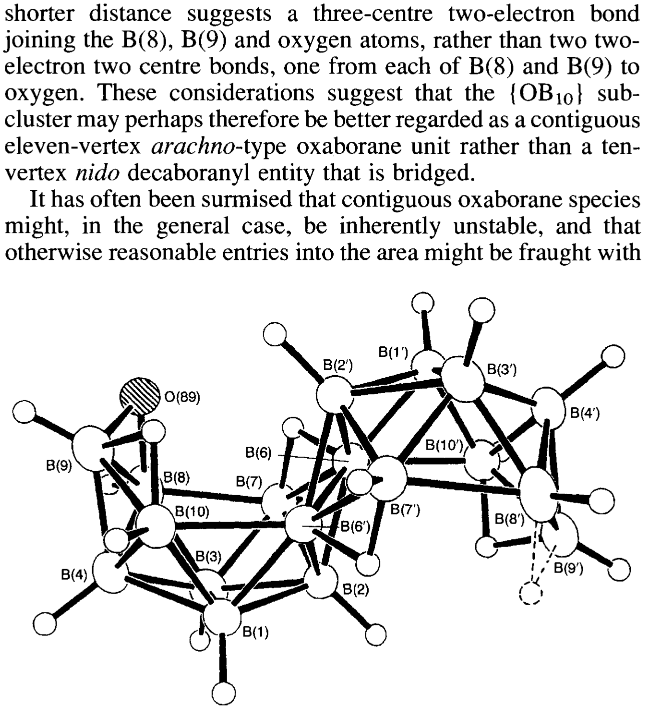
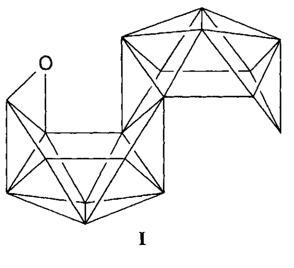


Fig. 1 ORTEP[17] drawing of the crystallographically determined structure of the $[\mu$-8,9-O-(*Anti*)-$B_{18}H_{21}]^-$ anion. The crystallographic inversion centre mutually disorders the oxygen cluster atom and H(8′,9′) bridge (shown here by hatched lines, but not located crystallographically). Ellipses are at the 50% probability level. Selected distances are as follows (although these have to be interpreted with due regard to the crystallographic disorder): B(7)–B(8) 201.9(4), B(8)–B(9) 186.4(4), B(9)–B(10) 182.4(5), B(10)–B(6′) 197.4(4), B(8)–O(8,9) 152.0(4), and B(9)–O(8,9) 135.0(4) pm. Note that the diagram is numbered in a crystallographic sense so that atoms with primed and unprimed numbers are related across the inversion centre. For the systematic IUPAC cage nubmering† B(6′) becomes B(5), B(7′) becomes B(5′), B(8′) and B(10′) are interchanged, and B(1′) and B(3′) are interchanged.



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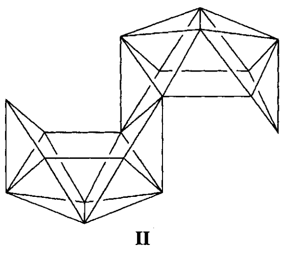

II

problems of destructive degradation to borate residues. The present compound and the recently reported[5] twelve-vertex anion $[OB_{11}H_{12}]^-$, together with the previously known[7] metallaborane $[(C_5Me_5)RhOB_{10}H_9Cl(PMe_2Ph)]$, are all stable cluster compounds in which oxygen is bound contiguously to boron atoms only. They therefore confirm a stable and examinable oxaborane cluster chemistry. The essentially direct addition of oxygen to the eighteen-boron residue to give $[OB_{18}H_{21}]^-$, and to the eleven-boron residue[5] to give $[OB_{11}H_{12}]^-$, suggest that mild one-oxygen Aufbau reactions that do not trigger cluster degradations, long a target for borane cluster chemists,[8] are indeed feasible, and we are presently devising experiments that might result in other directed and stoichiometric entries into these types of systems.

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Footnotes

† A full IUPAC structural nomenclature would most conveniently be 8,9-μ-oxo-*nido*-decarborano-[6′,7′:5,6]-*nido*-decaborane(1−). The anion is enantiomeric, the other enantiomer being 9,10-μ-oxo-*nido*-decaborano-[5′,6′:6,7]-*nido*-decaborane(1−). Note both enantiomers are contained in the unit cell of the crystals of the $[PPh_4]^+$ salt examined in this work (space-group $P2/c$). An alternative nomenclature involving the description of the oxaborane subcluster as an *arachno* type of eleven-vertex unit is more unwieldy and less helpful at present.

‡ *NMR data* for [μ-8,9-O-(*anti*)-$B_{18}H_{21}]^-$ {ordered as: assignment $\delta(^{11}B)$ [$\delta(^1H)$ in square brackets]} for $[PPh_4]^+$ salt in CD_3CN solution at 294–303 K: oxaborane subcluster: BH(1) +2.7 [+3.17], BH(2) −40.0 [−1.24], BH(3) +1.5 [+2.33], BH(4) *ca.* −40.0 [+0.45], BH(7) *ca.* +2.2 [+3.64 or +3.50], BH(8) *ca.* +2.2 [+3.64 or +3.50], BH(9) +11.6 [+3.68], BH(10) −4.6 [+2.99 or +2.62]; unoxygenated subcluster: BH(1′) + 13.0 [+3.76], BH(2′) −31.9 [−0.61], BH(3′) −4.8 [+2.99 or +2.68], BH(4′) −42.3 [+0.12], BH(5′) −15.7 [+2.64], BH(8′) +9.1 [+3.82], BH(9′) −1.0 [*ca.* +2.90], BH(10′) −7.7 [+2.49]: common atoms: B(5/6′) +7.6 [-], B(6/7′) +4.3 [-]; bridging H atoms: μH(6,7) −0.45, μH(9,10) (tentatively) +1.08, μH(5′,5/6′) −1.84, μH(8′,9′) −0.55, μH(9′,10′) −2.74; NMR assignments by [^{11}B-^{11}B]-COSY experiments and ^1H-{^{11}B(selective)} spectroscopy. It is interesting that the μH(9,10) hydrogen atom adjacent to the oxygenated site appears to have a low shielding, $\delta(^1H)$ + 1.08, perhaps suggesting some BH(10) *endo* character.

§ *Crystal data* for $C_{24}H_{41}B_{18}OP$, M_r = 571.12, monoclinic, a = 11.1044(11), b = 7.7474(8), c = 18.835(2) Å, β = 97.910(7)°, V = 1607.1(3) Å^3, space group $P2/c$, Z = 2, D_c = 1.180 g cm^{-3}, μ = 0.886 mm^{-1}, $F(000)$ = 596. All 2648 unique data, collected in the range $4.0 < 2\theta < 130°$, were used in refinement which converged with $R_1 = \{\Sigma||F_o| - |F_c||/\Sigma|F_o|\} = 0.0496$ and $wR_2 \{= (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{\frac{1}{2}}\} = 0.1342$.

Crystals were obtained from CH_2Cl_2–hexane. All measurements were made at 200 K on a Stoe STADI4 diffractometer operating in the ω-θ scan mode using graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å). The structure was determined by direct methods using SHELXS-86[15] and was refined by full-matrix least-squares (based on F^2) using SHELXL-93.[16] The oxygen atom was refined with an occupancy factor of $\frac{1}{2}$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Restraints were applied to phenyl groups such that they were flat with overall C_{2v} symmetry and phenyl hydrogen atoms were constrained to calculated positions (C–H = 0.95 Å) and refined with a fixed isotropic displacement parameter of $1.5U_{eq}$ of the parent carbon atom: cluster hydrogen atoms were located on a Fourier difference map and were freely refined. The weighting scheme $w = [\sigma^2(F_o^2) + 0.0349(P)^2 + 1.2630P]^{-1}$ was used, where $P = (F_o^2 + 2F_c^2)/3$.

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