An Interesting *arachno* Eight-vertex Tungstaborane: Isolation and Characterisation of the Fluxional Anion $[3,3,3,3\text{-(CO)}_4\text{-}arachno\text{-WB}_7\text{H}_{12}]^-$

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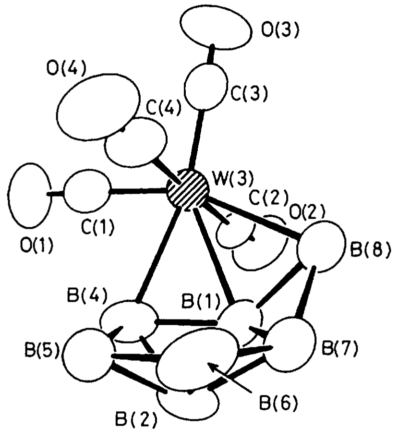
The anion $[(CO)_4WB_7H_{12}]^-$ is the first characterised open eight-vertex contiguous metallaborane cluster, and it exhibits an interesting hydrogen fluxionality; its structure has been determined by *X*-ray crystallography.

We report here preliminary results on the isolation, and characterisation by single-crystal diffraction analysis[†] and n.m.r. spectroscopy, of the new eight-vertex metallaborane species $[NBu^n_4][(CO)_4WB_7H_{12}]$, a yellow air-stable crystalline solid. The molecular structure is as shown in Figure 1. Hydrogen atoms were not locatable from the *X*-ray work, but n.m.r. spectroscopy established the presence of an *exo*-terminal hydrogen on each boron atom, an *endo*-terminal hydrogen on each of B(5), B(6), and B(8), together with a bridging hydrogen at each of the W(3)–B(8) and B(5)–B(6) positions.[‡]

The tungstaborane anion is seen to be an analogue of the neutral *arachno*-B_8H_{14} (itself not yet structurally characterised),[1] in which, formally, a $\{BH_2\}^+$ unit at the open-face 3-position has been replaced by a neutral d^6 $\{W(CO)_4\}$ moiety (structure I). As such it is the first open eight-vertex contiguous metallaborane to be characterized; other examples of eight-vertex metallaboranes are limited to two ferraborane species which consist of *nido* six-boron units with mono-iron and mono-boron units pendant from them (structure II),[2] and to polymetallic *closo* species based on the dodecahedral geometry III.[3] The tungstaborane anion exhibits an interesting fluxionality; the three hydrogen atoms on B(8), *viz* H(8)(*exo*), H(8)(*endo*), and H(3,8)(bridge) mutually exchange ($\Delta G^\ddagger$ *ca.* 48 kJ mol^{-1} at 263 K), and it is of interest in this context that the B(1)–B(8) linkage appears somewhat longer than the other interboron distances.

The salt $[NBu^n_4][(CO)_4WB_7H_{12}]$ was isolated in *ca.* 10% yield from the reaction in air between $[W(CO)_3(MeCN)_3]$ and $[NBu^n_4][arachno\text{-}B_9H_{14}]$ in dichloromethane solution, the only other stable metallaborane product being the $[NBu^n_4]^+$ salt of the known[4] anion $[(CO)_4WB_3H_8]^-$ (*ca.* 4%). Interest-



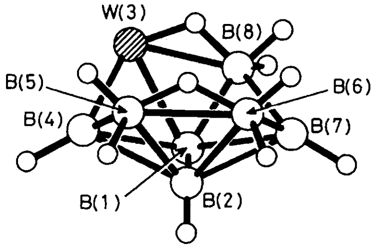
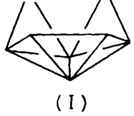
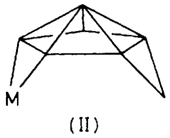


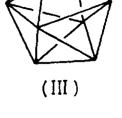
Figure 1. Crystallographically determined molecular structure[†] (upper diagram) of the anion of $[NBu^n_4][(CO)_4WB_7H_{12}]$, and (lower diagram) a schematic representation of the hydrogen-atom positions [note that the *exo*-bound hydrogen atom on B(1) is obscured in this projection]. Hydrogen atoms were not located in the diffraction analysis, but n.m.r. spectroscopy[‡] shows that each boron atom has an *exo*-terminal hydrogen atom bound to it, that each of B(5), B(6), and B(8) has additionally an *endo*-terminal hydrogen atom, and that there are bridging hydrogen atoms at W(3)–B(8) [probably approximately *trans* to CO(1)] and at B(5)–B(6). Interatomic distances from W(3) are as follows: to B(1) 249.2(15), to B(4) 251.5(18), to B 256.1(17), and to C(carbonyl) 191.6(16)—205.8(15) pm. Interboron distances are in the range 175.6(21)—185.7(22) pm except for B(1)—B(8) which is 187.9(24) pm.



(I)



(II)



(III)

[†] *Crystal Data:* $C_{20}H_{48}B_7NO_4W$, $M = 626.13$, orthorhombic, space group $Pna2_1$, $a = 1993.2(6)$, $b = 1129.2(2)$, $c = 1343.2(3)$ pm, $U = 3.023$ nm^3, $Z = 4$, $\mu = 36.69$ cm^{-1}, $F(000) = 1264$. Scans running from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speeds 2.0—29.3 ° min^{-1}, and $4.0 < 2\theta < 45.0°$, $T = 290$ K. All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the $\omega/2\theta$ scan mode using graphite monochromated Mo-K_α radiation following a procedure described elsewhere.[5] The data set was corrected for absorption empirically.[6] The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares using SHELX76.[7] All atoms were refined anisotropically, but no hydrogen atoms were located. The weighting scheme $w = [\sigma^2(F_o) + 0.0004(F_o)^2]^{-1}$ was used at the end of refinement. Final R and R_w values are 0.0378 and 0.0372 (297 parameters, 2189 observed data). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] $\delta(^{11}B)$ values [with $\delta(^1H)$ values in brackets] are as follows: B(1) *ca.* +6 [+3.74 or +3.89], B(2) −55.3 [−1.19], B(4) +20.2 [+4.88], B(5) −7.9 [+2.72, −1.16], B(6) *ca.* +6 [+3.89 or +3.74], B(7) −4.6 [+1.72], and B(8) −34.3 [+2.50, +0.83, −9.44]; in addition ^{1}H(bridge) resonates at δ −2.08 p.p.m. Tentative assignments are based on [^{11}B–^{11}B]COSY spectroscopy, $\delta(^1H)$ values being for CD_2Cl_2 solution at 243 K. At higher temperatures $\delta(^1H)$ resonances at +2.50, +0.83, and −9.44 mutually coalesce with $\Delta G^\ddagger$ *ca.* 48 kJ mol^{-1} at 263 K.

ingly, when the reaction was carried out in the absence of air, the sole identifiable metallaborane product (*ca.* 12%) was the new anion $[(CO)_3WB_9H_9]^{2-}$ of ten-vertex C_{3v} '*isocloso*' cluster geometry.

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